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CHEMICAL KINETICS

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BY

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NEW YORK TORONTO LONDON
McGRAW-HILL BOOK COMPANY, INC
1950

CHEMICAL KINETICS

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To

M. A. L.

M. C. L. AND A. A. L.

PREFACE

The object of this book is the presentation, within a reasonably small compass, of the more important facts and theories relating to the rates with which chemical reactions occur. The book is primarily intended as an introductory text for university students, but it is hoped that it may prove useful to those already acquainted with the field.

The subject matter of chemical kinetics falls conveniently into two parts: the first is concerned with elementary reactions, the second with how the over-all rates of complex reactions are related to the rates of the individual steps. This distinction is here preserved, the first part being represented by Chapters 1 to 6 and 13, the second by Chapters 7 to 12. In the first part reactions in the gas phase, in solution, on surfaces, and in the solid state, are treated separately, but in the second part they are treated together. This procedure may help to emphasize the very important similarities that exist between reactions in different phases.

Attention is drawn to the problems included at the end of some of the chapters. These have been designed in such a manner as to cover the main points made in the various chapters, and a student who works all or many of the problems will achieve a sound understanding of most of the fundamental principles of chemical kinetics. Some of the problems require a considerable amount of time for their solution, and these have been marked with an asterisk.

The author's very best thanks are due to Dr. S. Glasstone, who made valuable suggestions as to the general arrangement of the book and read and commented on early drafts of much of the material. He is also grateful to the following who have read the whole or parts of the manuscript and have contributed to its improvement by their constructive suggestions: Dr. E. J. Casey, John Coleman, Professor H. M. Hulburt, Professor W. J. Moore, Dr. K. E. Shuler, Sister Irene Marie Socquet, and Dr. E. W. R. Steacie. He is also indebted to his wife for her help in the preparation of the indexes and in many other ways.

KEITH J. LAIDLER

WASHINGTON, D.C.
July, 1950

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CHAPTER 1

THE MEASUREMENT OF REACTION RATES

The quantitative study of the rates of chemical reactions and of the factors upon which they depend is a comparatively recent one. In a few investigations carried out at the beginning of the last century, rates of reactions were determined, but little attempt was made to interpret them in terms of exact laws. Among these early studies may be mentioned the experiments of Kirchhoff[1] on the hydrolysis of starch by dilute acids and Thénard's investigation[2] of the rate of decomposition of hydrogen peroxide in the presence of alkalis.

The first kinetic measurements may, however, be said to have been those of Wilhelmy,[3] who in 1850 measured the rate of inversion of sucrose and investigated the influence of concentration upon the rate. The important result at which he arrived was that the rate of reaction at any instant was proportional to the concentration of sucrose remaining at that time. A similar conclusion was reached in 1862 by Berthelot and St. Gilles;[4] their investigations mainly concerned the equilibrium between ethanol, acetic acid, ethyl acetate, and water, but they obtained some data on the rate of combination of the acid and alcohol and concluded that the rate in this case was proportional to the product of the two concentrations.

In the years 1865 to 1867 Harcourt and Esson[5] published the results of their investigations on the reaction between potassium permanganate and oxalic acid. Very detailed experimental studies of the rate of this reaction and of its variation with the concentrations of the reacting substances were carried out by Harcourt, and the results were analyzed mathematically by Esson in the manner in which this is still frequently done today. Expressions for the amount of reaction as a function of time were worked out for the case of a "first-order" reaction, in which the rate is proportional to the concentration of only one reacting substance, and of a "second-order" reaction, in which the rate is proportional to the product of two concentra-

[1] J. Kirchhoff, *Schweigger's Journal*, **4**, 108 (1812).

[2] J. Thénard, *Ann. chim. et phys.* (2), **9**, 314 (1818).

[3] L. Wilhelmy, *Pogg. Ann.*, **81**, 413, 499 (1850).

[4] M. Berthelot and L. P. St. Gilles, *Ann. chim. et phys.* (3), **63**, 385 (1862); Berthelot, *ibid.* **66**, 110 (1862), and several later papers.

[5] A. V. Harcourt and W. Esson, *Proc. Roy. Soc.* (London), **14**, 470 (1865); *Phil. Trans.* **156**, 193 (1866); **157**, 117 (1867).

tions. The theory of successive first-order reactions, in which the product of one reaction undergoes a second reaction, was also developed.

At about the same time it was pointed out by Guldberg and Waage[1] that the laws of chemical equilibrium can be derived from the kinetic laws by assuming that at equilibrium the rates of forward and reverse reactions are the same. This concept has been of great value, although it should be noted that the kinetic laws employed in the derivations of the equilibrium laws frequently do not correspond to reality; for a rigorous treatment of equilibrium it is better to avoid the use of kinetic laws and to use thermodynamics or statistical mechanics.

In 1889 an important advance was made by Arrhenius,[2] who explained the large increases in velocity that are very often brought about by a rise in temperature. This development will be discussed in some detail in Chap. 3; the remainder of the present chapter will be devoted to a study of the laws expressing the influence of concentration on the rate, and to showing how reaction rates are obtained from the experimental data.

Kinetic laws[3]

Rate of a Reaction. The rate of a reaction, which may also be called its velocity or speed, may be expressed in terms of the concentration of any one of the substances which are reacting or of any product of the reaction. It may be expressed as the rate of decrease of the concentration of a reactant, or as the rate of increase of a product of the reaction. Thus if the substance chosen is a reactant which has a concentration c at any time t, the rate is $-dc/dt$, while the rate with reference to a product having a concentration x at time t is dx/dt. In some cases it makes a difference which reactant or product species is chosen, so that this should be specified, at least when there is any possibility of ambiguity; this point will be discussed in more detail later.

According to this formulation the rate must have the units of concentration divided by time. The time is almost invariably expressed in seconds, while concentrations are frequently given as moles per liter; in such a case the units for the rate are moles per liter per second. For gas reactions pressure units are sometimes used in place of concentrations, so that the rate could be expressed as atmospheres per second.

Order of a Reaction. The manner in which the rate of a reaction varies with the concentrations of the reacting substances can sometimes be indicated by stating the order of the reaction; thus a reaction whose rate de-

[1] C. M. Guldberg and P. Waage, "Etudes sur les affinités chimiques," Brøgger and Christie, *Christiania* (Oslo), 1867.

[2] S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[3] *Cf.* K. J. Laidler and S. Glasstone, *J. Chem. Education*, **25**, 383 (1948).

pends upon the first power of the concentration of one reactant is said to be of the first order, while if the rate is proportional to the product of two reactant concentrations it is of the second order. In general, if it is found experimentally that the rate of a reaction is proportional to the αth power of the concentration of one of the reactants A, to the βth power of the concentration of B, etc.,

$$\text{Rate} = kc_A^{\alpha}c_B^{\beta} \cdots \tag{1}$$

the over-all order of the reaction is simply

$$n = \alpha + \beta + \cdots \tag{2}$$

Such a reaction would be said to be of the αth order with respect to A, the βth order with respect to B, etc.

Some simple examples may be noted briefly. If only one chemical substance is concerned in the reaction (*e.g.*, in a thermal decomposition or an isomerization), the rate equation may take the form

$$-\frac{dc}{dt} = kc^n \tag{3}$$

the order being n. Reactions of this class having $n > 2$ probably do not exist, but many examples of $n \leqslant 2$ are known, and both integral and nonintegral orders are possible. Thus for the decomposition of nitrogen pentoxide $n = 1$, for the decomposition of hydrogen iodide into hydrogen and iodine $n = 2$, while for the para-ortho hydrogen conversion $n = 1.5$. An order of zero ($n = 0$) is frequently found in surface reactions involving a high degree of surface adsorption, an example being the decomposition of ammonia on tungsten. Nonintegral values are common, and it is sometimes found that the order varies with the total concentration.

The simplest examples of reaction rates which depend upon the concentrations of two substances obey the law

$$\text{Rate} = kc_Ac_B \tag{4}$$

This corresponds to a second-order process which is of the first order with respect to both A and B; an example is the reaction between hydrogen and iodine. Reactions having a total order of three are also known, but it is doubtful whether there are any gas-phase reactions of a higher order.

Specific Reaction Rate. The specific reaction rate, which is also known as the *rate constant* and also as the *rate coefficient*, is the value of the constant k appearing in the above equations; it is numerically equal to the reaction rate when the reactants are present at unit concentrations. In general, its units depend upon those employed for the concentration; thus, if moles per liter are used, the specific rate has the units (moles per liter)/(sec)

(moles per liter)^n, where n, equal to $\alpha + \beta + \cdots$, is the over-all order; this reduces to moles^{1-n} liters^{n-1} sec^{-1}. For a second-order reaction ($n = 2$) this becomes liters mole^{-1} sec^{-1}, while for a reaction of the first order ($n = 1$) the units are sec^{-1}, *i.e.*, the concentration units are irrelevant. For a reaction of the three halves order the units are liters^{½} mole$^{-½}$ sec^{-1}.

Determination of reaction rates[1]

Change of Concentration with Time. In a kinetic study of a reaction there is no way of measuring the rate directly in a simple manner; normally the concentration of a reactant or product is determined at various times. If this concentration is plotted against the time, a smooth curve should be

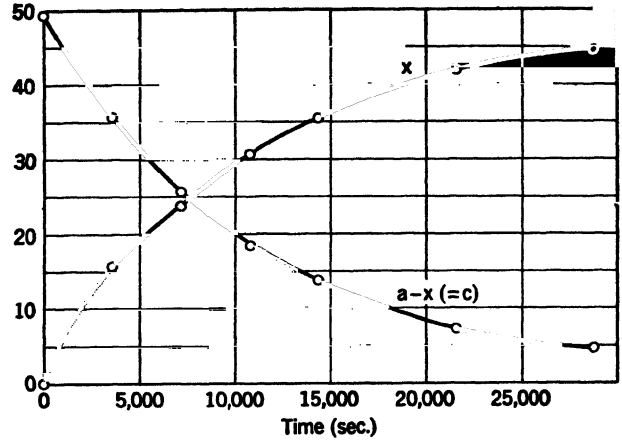


FIG. 1. The conversion of *N*-chloroacetanilide into *p*-chloroacetanilide; plots of the concentrations of reactant ($a - x$) and product (x) against time (for data see Table 1, p. 6).

obtained as is seen in the example given in Fig. 1, and the slope of the curve at any time, $-dc/dt$ or dx/dt, is the rate of the reaction at that time. In particular, the initial slope, at $t = 0$, gives the rate of the reaction corresponding to the concentrations with which the experiment was started. This method of determining the initial slope has in fact been employed in certain investigations and is sometimes the only reliable procedure (*cf.* p. 17). Another method which is very commonly employed involves using expressions relating the concentration to the time for reactions of various orders, and fitting the appropriate expression to the experimental data. Some of the more important of these expressions will now be derived.

First-order Kinetics. A reaction of the first order may be represented as

$$A \rightarrow P$$

[1] *Cf.* J. W. Mellor, "Chemical Statics and Dynamics," Longmans, Roberts and Green, London, 1904; A. Skrabal, "Homogenkinetik," T. Steinkopf, Leipzig, 1941.

A being the reactant and P the product; the rate expression is

$$-\frac{dc}{dt} = kc \tag{5}$$

where c is the concentration of the reacting substance. This equation can be rearranged to

$$-\frac{dc}{c} = k\,dt \tag{6}$$

which integrates to

$$-\ln c = kt + k' \tag{7}$$

where k' is the constant of integration. If the initial concentration at time $t = 0$ is denoted by a, k' is equal to $-\ln a$, so that

$$-\ln \frac{c}{a} = kt \tag{8}$$

which may be written as

$$c = ae^{-kt} \tag{9}$$

The concentration c therefore falls exponentially with the time, and theoretically becomes zero only at infinite time. An equation of this form was used by Wilhelmy to interpret his results on the hydrolysis of cane sugar.

A somewhat different, but equivalent, treatment may be carried out when the rate is expressed in terms of a product of the reaction, *i.e.*, as dx/dt; in this case

$$\frac{dx}{dt} = kc \tag{10}$$

After x moles per liter of the product have been formed, the concentration of the reactant is $a - x$, *i.e.*, $c = a - x$, so that

$$\frac{dx}{dt} = k(a - x) \tag{11}$$

This rearranges to

$$\frac{dx}{a - x} = k\,dt \tag{12}$$

which on integration gives

$$-\ln (a - x) = kt + k' \tag{13}$$

The constant of integration is evaluated using the condition that $x = 0$ when $t = 0$; hence $k' = -\ln a$, so that

$$\ln \frac{a}{a - x} = kt \tag{14}$$

or

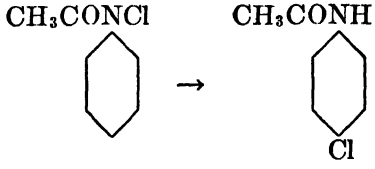
$$k = \frac{1}{t} \ln \frac{a}{a - x} \tag{15}$$

This result can also be written as

$$x = a(1 - e^{-kt}) \tag{16}$$

These equations could, of course, have been derived directly from Eqs. (8) and (9) by putting c equal to $a - x$.

As an example of the use of Eq. (15) for obtaining the specific rate of a reaction may be taken the work of Blanksma[1] on the conversion of *N*-chloroacetanilide into *p*-chloroacetanilide:



The rate was followed by removing a sample of the solution after various periods of time, adding excess of a solution of potassium iodide, and titrating the iodine liberated with standard thiosulfate solution. *N*-Chloroacetanilide liberates iodine from potassium iodide solution while *p*-chloroacetanilide does not; the titer is therefore a measure of the number of moles, $a - x$, of the reactant remaining in the solution, and the initial titer represents a. The constant k can therefore be calculated at each time using Eq. (15), and some of the results are shown in Table 1. The fact that k is constant

TABLE 1. CONVERSION OF *N*-CHLOROACETANILIDE INTO *p*-CHLOROACETANILIDE

t, sec	$a - x$	$k \times 10^5$, sec^{-1}
0	49.3	
3,600	35.6	9.03
7,200	25.75	9.03
10,800	18.5	9.07
14,400	13.8	10.55
21,600	7.3	8.84
28,800	4.8	8.09

within the experimental error is an indication that the reaction is really of the first order.

A great many other reactions of the first order are known. Some, but

[1] J. J. Blanksma, *Rec. trav. chim.*, **21**, 366 (1902); **22**, 290 (1903).

not all, of these are reactions in which there is only one reacting substance; examples are the decomposition of nitrogen pentoxide both in the gas phase and in solution, the decomposition of hydrocarbons, a number of isomerizations, and many other reactions. There are also a number of reactions of the first order in which the over-all change involves more than one chemical substance. An example of this is the inversion of cane sugar, which occurs according to the equation

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$$

both the sucrose and water entering into the reaction. However, the rate of the reaction apparently depends only on the concentration of the sucrose, since a constant is obtained by use of the first-order equation [Eq. (15)]; this is shown by the figures in Table 2. The reason for this

TABLE 2. INVERSION OF SUCROSE

$a = 10.023$

t, sec	$a - x$	x	$k \times 10^5$, sec^{-1}
0	0	10.023	
1,800	1.001	9.022	1.03
3,600	1.946	8 077	1.31
5,400	2.770	7.253	1.13
7,800	3.726	6.297	1.12
10,800	4.676	5.347	1.10

result is that the water is in such great excess that its concentration hardly changes during the course of the reaction, the slight change which does occur being inadequate to affect the value of the first-order constant. The rate is, however, proportional to the concentration of the water, as may be shown by experiments in nonaqueous solvents containing small quantities of water (the concentration of which therefore shows more variation during the course of reaction); the rate is then found to be proportional to the first power of the water concentration, and the reaction is consequently of the second order. Many other hydrolyses in aqueous solution, such as those of the alkyl halides, are of the first order when the water is in excess.

The same type of behavior may also be shown when a reacting substance other than the solvent is in excess; thus Harcourt and Esson[1] showed that the reduction of potassium permanganate by a great excess of oxalic acid obeys Eq. (15) with respect to the permanganate.

Another situation in which a reaction may obey the first-order law, in spite of the fact that more than one substance enters into the chemical

[1] A. V. Harcourt and W. Esson, *Phil. Trans.*, **156**, 193 (1866); *Proc. Roy. Soc.* (London), **14**, 470 (1865).

change, arises when one of the reacting substances, although not necessarily in excess, is also a product of the reaction. This substance, the concentration of which remains constant as the reaction proceeds, is said to be a catalyst for the reaction. An example of this type of behavior is the hydrolysis of an ester in the presence of hydrogen ions, which enter into the reaction with the ester (p. 140) but which are regenerated so that their concentration remains unchanged. A constant specific rate coefficient for such a reaction can be calculated using Eq. (15), so that the reaction may be said to be of the first order. If experiments are carried out at different hydrogen-ion concentrations, it is found that the specific rate coefficient so calculated is almost exactly proportional to the hydrogen-ion concentration. Such a reaction in aqueous solution, although obeying Eq. (15), is in reality of the third over-all order, since the rate varies with the concentration of (1) the ester, (2) the hydrogen ions, and (3) the water.[1]

Second-order Kinetics. When the rate of a chemical reaction is proportional to the product of two concentrations, two possibilities exist: the rate may be proportional to the product of two equal initial concentrations, or to two different ones. The former case may correspond to a reaction involving a single reactant, in which case the process can be represented as

$$2A \longrightarrow \text{products}$$

or to one between two different substances at equal initial concentrations

$$A + B \longrightarrow \text{products}$$

In either case the rate may be expressed as

$$\frac{dx}{dt} = k(a - x)^2 \tag{17}$$

which rearranges to

$$\frac{dx}{(a - x)^2} = k\,dt \tag{18}$$

This equation integrates to

$$\frac{1}{a - x} = kt + k' \tag{19}$$

where k' is the constant of integration. When $t = 0$, $x = 0$, so that $k' = 1/a$; hence

$$\frac{1}{a - x} - \frac{1}{a} = kt \tag{20}$$

[1] *Cf.* H. B. Friedman and G. V. Elmore, *J. Am. Chem. Soc.*, **63**, 864 (1941).

or

$$\frac{x}{a(a - x)} = kt \tag{21}$$

The constant k is thus given by

$$k = \frac{x}{at(a - x)} \tag{22}$$

An equation of this type was first deduced by Berthelot[1] in 1862 to account for the rate of reaction between acetic acid and ethyl alcohol, and was also employed by Harcourt and Esson and by Guldberg and Waage.

The application of the equation may be illustrated by some data on the hydrolysis of ethyl nitrobenzoate by hydroxyl ions in aqueous solution,[2] both substances being at the initial concentration of 0.05 mole per liter. The constancy of the specific rate k shown in Table 3 is evidence that the reaction is in fact of the second order.

TABLE 3. ALKALINE HYDROLYSIS OF ETHYL NITROBENZOATE

a = 0 05 mole per liter

t, sec	percentage change	$k \times 10^2$, liters mole^{-1} sec^{-1}
120	32.95	8.19
180	41.75	7.96
240	48.8	7.94
330	58.05	8.39
530	69.0	8.40
600	70.35	7.92

When the rate is proportional to the concentration of two different substances, the concentrations of which are initially a and b, the rate after an amount x has reacted is given by

$$\frac{dx}{dt} = k(a - x)(b - x) \tag{23}$$

This rearranges to

$$\frac{dx}{(a - x)(b - x)} = k\,dt \tag{24}$$

which may be integrated by the method of partial fractions; thus it may be written as

$$\left(\frac{A}{a - x} + \frac{B}{b - x}\right) dx = k\,dt \tag{25}$$

[1] Berthelot, *loc. cit.* (3), **66**, 110 (1862).

[2] W. B. S. Newling and C. N. Hinshelwood, *J. Chem. Soc.*, 1357 (1936).

where A and B are to be determined. The quantity within the brackets must equal $1/(a - x)(b - x)$,

$$\frac{A}{a - x} + \frac{B}{b - x} = \frac{1}{(a - x)(b - x)} \tag{26}$$

and by equating coefficients it is found that

$$A = \frac{1}{b - a} \quad \text{and} \quad B = \frac{1}{a - b} \tag{27}$$

Equation (25) therefore becomes

$$\left[\frac{1}{(b - a)(a - x)} + \frac{1}{(a - b)(b - x)}\right] dx = k\, dt \tag{28}$$

This integrates to

$$-\frac{\ln (a - x)}{b - a} - \frac{\ln (b - x)}{a - b} = kt + k' \tag{29}$$

where k' is the constant of integration. When $t = 0$, $x = 0$, so that

$$k' = \frac{\ln a}{a - b} - \frac{\ln b}{a - b} \tag{30}$$

Thus

$$\frac{1}{a - b} \ln \frac{a - x}{b - x} = kt + \frac{1}{a - b} \ln \frac{a}{b} \tag{31}$$

or

$$\frac{1}{a - b} \ln \frac{b(a - x)}{a(b - x)} = kt \tag{32}$$

The specific rate can therefore be calculated using the equation

$$k = \frac{1}{t(a - b)} \ln \frac{b(a - x)}{a(b - x)} \tag{33}$$

This equation has been found to be obeyed by a large number of reactions, among which may be mentioned the hydrolysis of esters by hydroxyl ions, many esterifications, the hydrolysis of amides by hydroxyl ions, and the diazotization of amines.

The General Case. The rate equation for a reaction of the nth order, all the initial concentrations being the same, is

$$\frac{dx}{dt} = k(a - x)^n \tag{34}$$

or

$$\frac{dx}{(a - x)^n} = k\,dt \tag{35}$$

This integrates to

$$\frac{1}{(n - 1)(a - x)^{n-1}} = kt + k' \tag{36}$$

where k' is the constant of integration. When $t = 0$, $x = 0$, so that

$$k' = \frac{1}{(n - 1)a^{n-1}} \tag{37}$$

hence

$$\frac{1}{(n - 1)(a - x)^{n-1}} = kt + \frac{1}{(n - 1)a^{n-1}} \tag{38}$$

or

$$k = \frac{1}{t(n - 1)}\left[\frac{1}{(a - x)^{n-1}} - \frac{1}{a^{n-1}}\right] \tag{39}$$

This equation is valid for any case except $n = 1$, for which the treatment leading to Eq. (15) is necessary. For the case of $n = 2$, Eq. (39) reduces to Eq. (22); for $n = 3$ it gives rise to

$$k = \frac{1}{2t}\left[\frac{1}{(a - x)^2} - \frac{1}{a^2}\right] \tag{40}$$

which is therefore the equation for a third-order reaction. If $n = \frac{3}{2}$, Eq. (39) becomes

$$k = \frac{2}{t}\left[\frac{1}{(a - x)^{\frac{1}{2}}} - \frac{1}{a^{\frac{1}{2}}}\right] \tag{41}$$

which is an equation for a reaction of the three-halves order. If $n = \frac{1}{2}$, the equation becomes

$$k = \frac{2}{t}[a^{\frac{1}{2}} - (a - x)^{\frac{1}{2}}] \tag{42}$$

Summary of Rate Equations. In the preceding section have been derived a number of expressions giving in explicit form the amount x of product formed as a function of the time. As has been seen, the order of a reaction is frequently determined by finding out which equation is obeyed by the experimental results; this is known as the method of integration. The rate equations, in both differential and integrated forms, are given in Table 4 for various values of the order, the initial concentrations being

assumed to be the same. In the last column a set of units appropriate for the specific rate is given.

It may be mentioned that the absolute values of the rate and of the specific rate of a given reaction may depend on the substance whose forma-

TABLE 4. SUMMARY OF RATE EQUATIONS

Order	Rate equation: Differential form	Rate equation: Integrated form	Units of the specific rate
0	$\frac{dx}{dt} = k$	$k = \frac{x}{t}$	Moles liter^{-1} sec^{-1}
½	$\frac{dx}{dt} = k(a - x)^{1/2}$	$k = \frac{2}{t}[a^{1/2} - (a - x)^{1/2}]$	Moles$^{1/2}$ liter$^{-1/2}$ sec^{-1}
1	$\frac{dx}{dt} = k(a - x)$	$k = \frac{1}{t} \ln \frac{a}{a - x}$	Sec^{-1}
3/2	$\frac{dx}{dt} = k(a - x)^{3/2}$	$k = \frac{2}{t}\left[\frac{1}{(a - x)^{1/2}} - \frac{1}{a^{1/2}}\right]$	Liters$^{1/2}$ mole$^{-1/2}$ sec^{-1}
2	$\frac{dx}{dt} = k(a - x)^2$	$k = \frac{1}{t} \frac{x}{a(a - x)}$	Liters mole^{-1} sec^{-1}
3	$\frac{dx}{dt} = k(a - x)^3$	$k = \frac{1}{2t} \frac{2ax - x^2}{a^2(a - x)^2}$	Liters^2 mole^{-2} sec^{-1}

tion or disappearance is under consideration. This may be shown with reference to the third-order reaction between nitric oxide and bromine, for which the stoichiometric equation is

$$2NO + Br_2 = 2NOBr$$

The rate of this reaction may be expressed in three ways, as follows, the square brackets indicating concentrations:

1. The rate of disappearance of nitric oxide, $-d[NO]/dt$
2. The rate of disappearance of bromine, $-d[Br_2]/dt$
3. The rate of appearance of nitrosyl bromide, $d[NOBr]/dt$

Since the disappearance of one molecule of bromine corresponds to that of two molecules of nitric oxide and to the appearance of two molecules of nitrosyl bromide, it follows that the three rate expressions are related by

$$-\frac{d[NO]}{dt} = -2\frac{d[Br_2]}{dt} = \frac{d[NOBr]}{dt} \tag{43}$$

The rates are related to the specific rates as follows:

$$-\frac{d[NO]}{dt} = k_{NO}[NO]^2[Br_2] \tag{44}$$

$$-\frac{d[Br_2]}{dt} = k_{Br_2}[NO]^2[Br_2] \tag{45}$$

and

$$\frac{d[\mathrm{NOBr}]}{dt} = k_{\mathrm{NOBr}}[\mathrm{NO}]^2[\mathrm{Br_2}] \tag{46}$$

where k_{NO}, $k_{\mathrm{Br_2}}$, and k_{NOBr} are the specific rates which correspond to the three different methods of expressing the rates. Comparison of these three equations shows that

$$k_{\mathrm{NO}} = 2k_{\mathrm{Br_2}} = k_{\mathrm{NOBr}} \tag{47}$$

In stating a rate or a specific rate it is therefore sometimes necessary to express not only the concentration units but the substance to which the rate refers.

Determination of Order and Specific Rate. After the concentration of a reactant or a product has been determined at various times, the order of the reaction and the specific rate may be calculated using a number of different methods, of which one, the method of integration, has already been described. Some of these methods will now be considered and will be compared later.

Method of Integration. The most direct method is the one that has been described; it involves taking the various equations in their integrated forms (see Table 4) and finding whether one of them gives a specific rate constant which does not drift as the value of t increases. It is then concluded that the particular law used is obeyed; the specific rate so calculated is taken to be the best one for the reaction under consideration, and the order of the reaction is that corresponding to the rate equation used. This procedure is not very sensitive for distinguishing between orders (*e.g.*, between orders of unity and three-halves), particularly if measurements are not made over a large fraction of the complete reaction. It also has the disadvantage of being misleading if applied to a complex reaction

Half-period Method. A related method involves determining the time at which one-half of the original substance has disappeared; this time is known as the half period, or half life, of the reaction and may be denoted by the symbol τ. Its value is readily calculated for a reaction of a given order in terms of the specific rate k and the initial concentration a by setting x, the amount of substance reacted, equal to $a/2$ in the appropriate rate expression. Thus for a first-order reaction the half life is given by

$$k = \frac{1}{\tau} \ln \frac{a}{a - (a/2)} \tag{48}$$

whence

$$\tau = \frac{1}{k} \ln 2 \tag{49}$$

In this case the half life is seen to be independent of the initial concentration.

For a second-order reaction the half life is given by

$$k = \frac{a/2}{\tau a(a - a/2)} \tag{50}$$

whence

$$\tau = \frac{1}{ak} \tag{51}$$

In this case the half life is inversely proportional to the initial concentration. In the general case of a reaction of the nth order the half period is found to be

$$\tau = \frac{2^{n-1} - 1}{(n - 1)ka^{n-1}} \tag{52}$$

It is thus inversely proportional to the $(n - 1)$th power of the initial concentration,

$$\tau \propto \frac{1}{a^{n-1}} \tag{53}$$

This relationship is obeyed provided that all substances are present at the same molar concentration. If two experiments are carried out at initial molar concentrations a_1 and a_2, it follows that the half lives are related by

$$\frac{\tau_1}{\tau_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \tag{54}$$

whence

$$n = 1 + \frac{\log (\tau_1/\tau_2)}{\log (a_2/a_1)} \tag{55}$$

The half lives can readily be determined from a plot of concentration vs. time, and then the value of n can be calculated. An example of the use of this method will be found later in connection with the reaction between nitric oxide and hydrogen. The method is due to Ostwald[1] and can be applied with suitable modification to any fraction of the total reaction.

Differential Method. The differential method, which was introduced by van't Hoff,[2] is based upon the fact that the instantaneous rate of a reaction of the nth order involving only one reacting substance is proportional to the nth power of its concentration,

$$-\frac{dc}{dt} = kc^n \tag{56}$$

[1] W. Ostwald, *Z. physik. Chem.*, **2**, 127 (1888).

[2] J. H. van't Hoff, "Etudes de dynamique chimique," p. 87, F. Muller and Company, Amsterdam, 1884.

If two experiments are carried out at different initial concentrations c_1 and c_2 it follows that

$$-\frac{dc_1}{dt} = kc_1^n \tag{57}$$

and

$$-\frac{dc_2}{dt} = kc_2^n \tag{58}$$

If logarithms are taken of each expression and the results subtracted, it is found, on rearrangement, that

$$n = \frac{\log\,(-dc_1/dt) - \log\,(-dc_2/dt)}{\log c_1 - \log c_2} \tag{59}$$

The order can therefore be determined from a concentration vs. time curve by measuring slopes $(-dc/dt)$ at two different concentrations and introducing the values into this equation.

A better procedure is to plot log $(-dc/dt)$ against log c for a number of values corresponding to an appreciable fraction of the total reaction (*e.g.*, from 5 to 50 per cent of the reaction. If the reaction proceeds without complexity, a straight line will be obtained, the slope being the order n; an example of the use of this procedure is shown in Fig. 2. If on the other hand the plot exhibits curvature, it is at once known that the reaction has some complicating feature and that it does not have a simple order. A further advantage of this method is that the initial rate of the reaction is obtained immediately by extrapolation. If this is done for a series of initial concentrations, the logarithms of the initial rates can be plotted against the logarithms of the initial concentrations; again a straight line will be obtained if the reaction is not complex, and the slope will be the order. As will be seen later, if the reaction is complex these two orders may not be the same. The initial rate is of some considerable significance, especially in complex reactions, as it is only at the beginning of the reaction that the experimental conditions are known with certainty.

The differential method has also been extended to the evaluation of the order with respect to one of two or more reactants. If, for example, the reaction is of the αth order with respect to A and of the βth order with respect to B, the rate is given by

$$v = k[A]^\alpha[B]^\beta \tag{60}$$

If values of v are obtained for two different values of $[A]$ but at the same value of $[B]$, the order obtained by use of Eq. (59) or by the graphical method is clearly that with respect to A, *viz.*, α. Similarly β can be determined by keeping $[A]$ constant and varying $[B]$.

A simpler procedure that may frequently be satisfactory involves dividing values of v at the beginning of the reaction, corresponding to various initial concentrations of A but to a constant concentration of B, by $[A]$, $[A]^2$, etc. If it is found that v divided by $[A]^\alpha$ is independent of $[A]$, it follows that the reaction is of the αth order with respect to A. An example of the use of this method will be seen later for the reaction between nitric oxide and hydrogen.

Isolation Method. It was pointed out by Harcourt and Esson that if all the reactants except one are present in excess, the apparent order will be

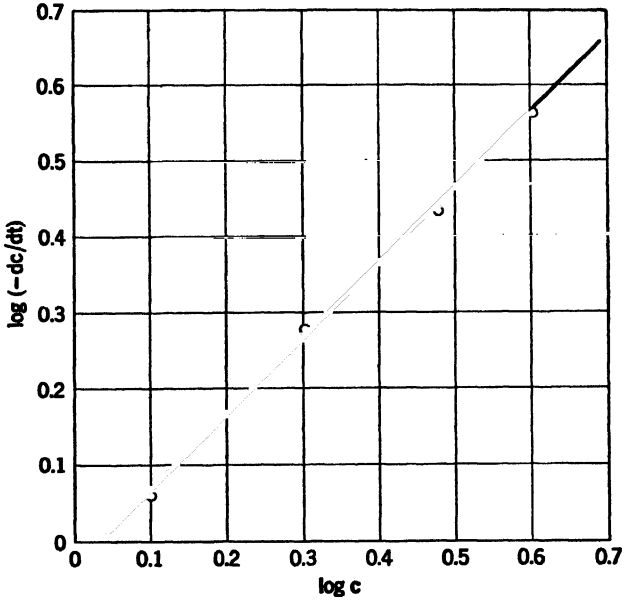


FIG. 2. The conversion of *N*-chloroacetanilide into *p*-chloroacetanilide; a plot of log (rate) against log c. The slope, equal to unity, is the order; the rate extrapolated to $c = 48.3$ is the initial rate (data in Table 1, p. 6).

the order with respect to the one reactant "isolated," since the concentrations of those in excess will not change sensibly during the course of reaction. This method was generalized by Ostwald[1] as follows: if a reaction is of the αth order with respect to A, of the βth order with respect to B, and of the γth order with respect to C, and if B and C are in excess of A, the apparent order, determined by any of the methods described above, will correspond to α; β and γ can be determined in a similar way. The method should always be employed in conjunction with other methods of

[1] W. Ostwald, "Lehrbuch der allgemeinen Chemie," Vol. 2, Part 2, p. 238, Akademische Verlagsgesellschaft, Leipzig, 1902.

determining the order, however, as in many cases it does not yield reliable results; thus if the reaction under investigation is complex, involving a number of stages, its mechanism may be influenced by the concentration changes, so that different mechanisms may be occurring under the different conditions of isolation.

Comparison of Methods. The most widely employed method of determining the order of a reaction and its initial rate is undoubtedly the method of integration. Although this procedure is entirely satisfactory in ideal cases, it is unfortunately not always reliable, and it is well to consider its defects.

In the first place, the most common forms of the integrated rate equations are those pertaining to an integral order. When the method of integration is used, the results therefore tend to be constrained to fit an integral-order law, although frequently the experimental data are better fitted by a law involving a nonintegral order. Too often are slight drifts in calculated specific rates attributed to ill-defined complexities.

A second and more fundamental objection to the method is that it characterizes a reaction according to the way in which the concentration of a product or a reactant varies with the time, and this may give rise to misleading deductions about the way in which the rate varies with the concentration of reactants. This matter has been discussed in some detail by Letort,[1] who quotes as an example the decomposition of acetaldehyde. When the method of integration is applied to this reaction, the data are found to fit the second-order equation [Eq. (22)] with good accuracy; on the other hand the initial rate is found to vary with the three-halves power of the initial concentration. These facts can be represented by the equation

$$-\frac{d[CH_3CHO]}{dt} = \frac{k[CH_3CHO]^2}{[CH_3CHO]_0^{1/2}} \tag{61}$$

where $[CH_3CHO]_0$ represents the initial concentration of acetaldehyde and $[CH_3CHO]$ the concentration at time t. That the reaction, although of three-halves order with respect to the concentration, obeys the second-order law with respect to the method of integration means that as the reaction proceeds, the rate falls off more rapidly than it should according to its variation with concentration, and this can only mean that the reaction products are inhibiting the process.

Letort has proposed that this type of complication can be treated systematically by defining two distinct orders of a reaction:

1. The order with respect to concentration, which relates the rate to the concentration, *i.e.*, is three-halves in the above example

[1] M. Letort, Thesis, University of Paris, 1937; *J. chim. phys.*, **34**, 206 (1937); *Bull. soc. chim. France*, **9**, 1 (1942).

2. The order with respect to time, which is the order that would be obtained using the method of integration; this is two for the acetaldehyde decomposition

Since it is only at the beginning of the reaction that the conditions are known with certainty, it is evident that the order with respect to concentration is the more fundamental and useful quantity, and Letort also calls it the *true order*. When the order with respect to time differs from the true order, it can be inferred that the products are interfering with the reaction. If the true order is less than the order with respect to time, it has been seen that inhibition by products is occurring. When on the other hand the order with respect to time is less than the true order, the reaction rate is not falling off as rapidly as is indicated by its variation with concentration; this means that the products are catalyzing the process, which is then said to be autocatalytic.

The most important quantities to be measured are clearly the true order and the initial rate; from them the specific rate can be obtained. Since these quantities are given by the differential method, particularly when the graphical procedure is employed, this must be considered the most reliable method. Its disadvantage is that it involves the measurements of tangents to the concentration-time curves, but if this is done at a number of points and the graphical procedure employed, the results can be obtained accurately. At first the method of integration and the half-period method should be used only in a subsidiary manner for obtaining information as to the influence of the products on the rate; however if it is established that the two orders are the same, it is satisfactory to employ these methods for determining specific rates.

The isolation method of Ostwald has been seen to be applicable in conjunction with any of the other three methods; it is clearly best used with the differential method.

It may be observed at this point that there are many reactions which do not admit of the assignment of an order; *i.e.*, their rates are not simple power functions of the concentrations. Such reactions cannot be treated satisfactorily by the method of integration, which may indeed yield quite misleading conclusions. Application of the graphical differential method to such a reaction generally gives a curve instead of a straight line, and the variation of the slope gives an indication of the type of complication that is occurring. The elucidation of the exact kinetic law then requires carefully planned experiments in which the influences of products and reactants are studied systematically.

Opposing Reactions. One complication that frequently exists, and for which due allowance must be made, is that a reaction may proceed to a state of equilibrium which differs appreciably from completion. The

simplest case of this is when both forward and reverse reactions are of the first order, so that the situation can be represented as

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

k_1 and k_{-1} being the specific rates in forward and reverse directions. If the experiment is started using pure A, of concentration a, and if after the time t the concentration of B is x, that of A is $a - x$. The net rate of production of B is then given by

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}x \tag{62}$$

since B is being produced by the forward reaction (first term) and removed by the reverse reaction (second term). If x_e is the concentration of B at equilibrium, when the net rate of reaction is zero,

$$k_1(a - x_e) - k_{-1}x_e = 0 \tag{63}$$

which rearranges to

$$k_{-1} = \frac{k_1(a - x_e)}{x_e} \tag{64}$$

Substitution of this expression in Eq. (62) gives

$$\frac{dx}{dt} = k_1(a - x) - \frac{k_1(a - x_e)x}{x_e} \tag{65}$$

$$= \frac{k_1 a}{x_e}(x_e - x) \tag{66}$$

Integration of this equation, using the fact that $x = 0$ when $t = 0$, gives

$$k_1 = \frac{x_e}{at} \ln \frac{x_e}{x_e - x} \tag{67}$$

If x_e is known, it is therefore possible to calculate k_1 from measurements of x as a function of the time. For certain purposes it is convenient to have this equation in a different form. Equation (63) rearranges to

$$x_e(k_1 + k_{-1}) = k_1 a \tag{68}$$

whence

$$\frac{x_e}{a} = \frac{k_1}{k_1 + k_{-1}} \tag{69}$$

Equation (67) may therefore be written as

$$k_1 = \frac{k_1}{k_1 + k_{-1}} \frac{1}{t} \ln \frac{x_e}{x_e - x} \tag{70}$$

or

$$k_1 + k_{-1} = \frac{1}{t} \ln \frac{x_e}{x_e - x} \tag{71}$$

Comparison of this equation with Eq. (15) for a simple first-order reaction shows that the two are formally analogous, x_e replacing a and $k_1 + k_{-1}$ replacing k.

In the foregoing derivation it has been assumed that the initial concentration of the product B is zero. If this is not the case, and the initial concentrations of A and B are a and b, the net rate at time t is given by

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}(b + x) \tag{72}$$

By methods similar to those used earlier it can be shown that this equation integrates to

$$k_1 + k_{-1} = \frac{1}{t} \ln \frac{k_1 a - k_{-1} b}{k_1 a - k_{-1} b - (k_1 + k_{-1})x} \tag{73}$$

If the quantity x_e' is defined by

$$x_e' = \frac{k_1 a - k_{-1} b}{k_1 + k_{-1}} \tag{74}$$

Eq. (73) reduces to

$$k_1 + k_{-1} = \frac{1}{t} \ln \frac{x_e'}{x_e' - x} \tag{75}$$

which has the same form as Eq. (71).

The application of Eq. (71) may be illustrated with reference to some early data[1] on the conversion of γ-hydroxybutyric acid into its lactone, the initial concentration of the lactone being zero. At equilibrium it was

TABLE 5. CONVERSION OF γ-HYDROXYBUTYRIC ACID INTO ITS LACTONE

t, sec	x	$x_e - x$	$(k_1 + k_{-1}) \times 10^4$, sec^{-1}
1,260	2.41	10.87	1.59
3,000	4.96	8.32	1.56
6,000	8.11	5.17	1.58
7,200	8.90	4.38	1.52
9,600	10.35	2.93	1.58
13,200	11.55	1.73	1.55

found that $x_e = 13.28$, and values of $k_1 + k_{-1}$ at various times, calculated using Eq. (71), are shown in Table 5; the constancy of the values in the

[1] P. Henry, *Z. physik. Chem.*, 10, 98 (1892).

last column indicates that the law is obeyed. Since k_1/k_{-1} can be calculated from the values of a and x_e, the individual constants k_1 and k_{-1} can be found. This law has also been found to be valid for the conversion of α- into β-methylglucoside,[1] the mutarotation of glucose, the conversion of ammonium thiocyanate into thiourea,[2] and the formation of ethyl formate from ethyl alcohol and formic acid;[3] in the latter case the alcohol was in excess so that the forward reaction was of the first order. Since the procedure involves the method of integration, it is applicable only to reactions proceeding without complexity.

Other cases will be referred to only briefly. If a first-order reaction is opposed by a second-order one,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + C$$

and the initial concentration of A is a, the concentrations of B and C being initially zero, the net rate of the forward reaction is

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}x^2 \tag{76}$$

If x_e is the concentration of B and C at equilibrium, this equation integrates to

$$k_1 = \frac{x_e}{t(2a - x_e)} \ln \frac{ax_e + x(a - x_e)}{a(x_e - x)} \tag{77}$$

This equation has been found to be obeyed by the hydrolysis of ethyl acetate.[4]

For the converse case in which the concentrations of B and C are initially a while that of A is zero, the rate equation integrates to

$$k_{-1} = \frac{x_e}{t(a^2 - x_e^2)} \ln \frac{x(a^2 - xx_e)}{a^2(x_e - x)} \tag{78}$$

x_e is now the equilibrium concentration of A and k_{-1} is the specific rate for the *formation* of A. This law has been verified for the reaction between ethanol and acetic acid.[5]

If two second-order reactions oppose each other, the situation can be represented by

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

[1] C. L. Jungius, *Proc. Koninkl. Akad. Wetenschap. Amsterdam*, 99 (1903), 779 (1904).

[2] J. Waddell, *J. Phys. Chem.*, **2**, 523 (1898).

[3] W. Kistiakowsky, *Z. physik. Chem.*, **27**, 250 (1898).

[4] O. Knoblauch, *Z. physik. Chem.*, **22**, 268 (1897).

[5] *Ibid.*

If A and B are initially at a concentration of a, and if C and D are not present initially but are present at a concentration of x moles per liter after time t and of x_e at equilibrium, the equation integrates to

$$k_1 = \frac{x_e}{2ta(a - x_e)} \ln \frac{x(a - 2x_e) + ax_e}{a(x_e - x)} \tag{79}$$

The use of this equation will be discussed in connection with the decomposition of hydrogen iodide into hydrogen and iodine.

Consecutive Reactions. Another type of complication that can occur is seen when the products of one reaction undergo further reaction to give other products. The simplest example of this type that can occur has both of the reactions of the first order, a case that was treated by Harcourt and Esson.[1] This situation can be represented as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

where k_1 and k_2 are the two specific rate constants (the reverse reactions are neglected). The rate of disappearance of A is given by

$$-\frac{d[A]}{dt} = k_1[A] \tag{80}$$

which integrates to

$$[A] = [A]_0 e^{-k_1 t} \tag{81}$$

where $[A]_0$ is the initial concentration of A. The rate of formation of C is given by

$$\frac{d[C]}{dt} = k_2[B] \tag{82}$$

while the net rate of production of B, which is the rate of its formation from A minus that of its reaction to give C, is

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \tag{83}$$

Introduction of Eq. (81) into Eq. (83) gives

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B] \tag{84}$$

which contains only the variables $[B]$ and t. It integrates to

$$[B] = [A]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{85}$$

[1] A. V. Harcourt and W. Esson, *Proc. Roy. Soc.* (London), **14**, 470 (1865); *Phil. Trans*, **156**, 193 (1866); **157**, 117 (1867).

The rates of change of $[A]$ and $[B]$ are thus given by Eqs. (81) and (85); that of $[C]$ is readily deduced by means of the relationship

$$[A] + [B] + [C] = [A]_0 \tag{86}$$

Equations of this type are obeyed by elements undergoing radioactive decomposition,[1] but very few chemical reactions of this character are known.

The treatment described above was applied by Harcourt and Esson to the reaction between potassium permanganate, oxalic acid, and manganous sulfate in sulfuric acid solution. This reaction may be considered briefly. When the reactants are mixed, manganese dioxide is formed with great rapidity and subsequently undergoes further reactions which are slow; it is first oxidized by the permanganate to an intermediate product, which was taken to be Mn_2O_7, and then reduced by oxalic acid to MnO. Both the permanganate and oxalic acid were present in great excess in the experiments under consideration, so that the reaction rates depend only on the concentrations of the manganese dioxide and the Mn_2O_7; the reaction can therefore be written as

$$MnO_2 \rightarrow Mn_2O_7 \rightarrow MnO$$

and may be expected to obey Eq. (85).

The progress of the reaction was followed by the addition of potassium iodide at various times, the iodine liberated being titrated with standard sodium thiosulfate solution; this determines the amounts of MnO_2 and of Mn_2O_7 present, *i.e.*, $[A] + [B]$. From Eqs. (81) and (85) it can be deduced that

$$[A] + [B] = [A]_0 \left(\frac{k_2}{k_2 - k_1} e^{-k_1 t} - \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \tag{87}$$

which may be written as

$$[A] + [B] = WX^t - YZ^t \tag{88}$$

where W, X, Y, and Z are defined by

$$W = \frac{[A]_0 k_2}{k_2 - k_1}, \qquad X = e^{-k_1}, \qquad Y = \frac{[A]_0 k_1}{k_2 - k_1}, \qquad Z = e^{-k_2} \tag{89}$$

The procedure was then to fit the $([A] + [B])$ vs. t curves by means of four empirical constants W, X, Y, and Z. In one investigation the data were fitted to the equation

$$[A] + [B] = 28.5(0.82)^t + 2.7(0.98)^t \tag{90}$$

[1] E. Rutherford and F. Soddy, *J. Chem. Soc.*, **81**, 321, 837 (1902).

where t is expressed in minutes. The satisfactory agreement between the observed values and this equation is shown by the figures in Table 6. It is to be noted that this does not represent a complete solution of the problem, since there is an infinite set of values of W, X, Y, and Z which would give equally good agreement; the procedure therefore does not allow an evaluation of the specific rates k_1 and k_2. The constant k_1 can, however, be found by measuring the rate of disappearance of the initial substance.

TABLE 6. REDUCTION OF MANGANESE DIOXIDE

t, min	$[A] + [B]$	
	Calculated	Observed
0.5	25.9	25.9
1.0	21.4	21.6
1.5	17.8	17.9
2.0	14.9	14.9
2.5	12.5	12.5

When the orders of two consecutive reactions are other than first, the equations are much more complicated and generally have to be integrated by numerical methods. An example of a reaction of this type is the reaction between potassium permanganate, oxalic acid, and manganese sulfate when the oxalic acid is not present in excess. The first reaction is the formation of manganese dioxide and is of the first order with respect to the permanganate; the subsequent reaction is of the second over-all order, being of the first order with respect to both manganese dioxide and oxalic acid. The rate equation was integrated in an infinite series, and values of the two specific rates were found which fitted the data.

PROBLEMS

1. (*a*) The rate constant of a first-order reaction is 2.5×10^{-6} sec^{-1}, and the initial concentration is 0.1 mole per liter. What is the initial rate in mole liter^{-1} sec^{-1}, in mole cc^{-1} sec^{-1}, and in mole cc^{-1} min^{-1}?

(*b*) The initial rate of a second-order reaction is 5.0×10^{-7} mole liter^{-1} sec^{-1}, and the initial concentrations of the two reacting substances are 0.2 mole per liter. What is the rate constant in liter mole^{-1} sec^{-1}, in cc mole^{-1} min^{-1}, and in cc molecule^{-1} sec^{-1}?

2. A first-order reaction is 40 per cent complete at the end of 50 min; what is the value of the rate constant, in sec^{-1}? In how many minutes will the reaction be 80 per cent complete?

3. The three-halves-order decomposition of a gas, initially present at 1 atm pressure, is 60 per cent complete in one hour; what is the value of the rate constant?

4. The half period for the decomposition of radium is 1,590 years; calculate

the rate constant in sec^{-1}. In how many years will three-quarters of a given amount of radium have disappeared?

5. Obtain an expression for the average life period for an aggregate of molecules undergoing first-order decomposition, in terms of the rate constant k.

6. A second-order reaction involving reactants initially present at 0.1 mole per liter is found to be 20 per cent complete in 40 min. Calculate (*a*) the rate constant, (*b*) the half period, and (*c*) the time it would take for the reaction to be 20 per cent complete if the initial concentrations were 0.01 mole per liter.

7. The following values were given by Letort[1] for the rate of decomposition of acetaldehyde corresponding to various degrees of decomposition:

Per cent decomposed	*Rate of decomposition, mm Hg per min*
0	8.53
5	7.49
10	6.74
15	5.90
20	5.14
25	4.69
30	4.31
35	3.75
40	3.11
45	2.67
50	2.29

Plot log v against log (per cent acetaldehyde present), and thus determine the order of the reaction with respect to time. This is an illustration of the use of van't Hoff's differential method.

8. The following results have been obtained for the reaction between triethylamine and methyl iodide in nitrobenzene solution, both substances being present in initial concentrations of 0.02 mole per cc:

Time, sec	*Per cent reacted*
325	31.4
1,295	64.9
1,530	68.8
1,975	73.7

Calculate the second-order rate constant, using the method of integration.

9. The following results were obtained in a study of the enzymatic oxidation of lactic acid, of initial concentration a equal to 0.320 mole per liter:

Time, min	$x \times 10^3$, *moles per liter*
5	2.55
8	4.12
10	5.11
13	6.71
16	8.16

Calculate the first-order rate constant corresponding to each time.

Plot log $(a - x)$ against t, and determine k from the slope of the line.

[1] M. Letort, Thesis, University of Paris, 1937.

10. The following data were obtained for the reaction between dimethyl-*p*-toluidine and methyl iodide in nitrobenzene solution, the initial concentration of each being 0.05 mole per liter:

Time, min	*Per cent change*
10.2	17.5
26.5	34.3
36.0	40.2
78.0	52.3

Calculate the ordinary second-order coefficient corresponding to each of the four times, and note that it shows a marked downward drift. This is due to the fact that the reaction approaches an equilibrium, the reverse reaction being of the second order. The rate law is thus Eq. (79). The equilibrium constant $K = k_{-1}/k_1$ was found directly to be 69.8. Calculate k_{-1} corresponding to each of the four times given, note its constancy, and determine the average.

CHAPTER 2

EXPERIMENTAL METHODS

In the present chapter will be described some of the experimental procedures used in the study of reaction kinetics. No attempt at completeness is made; some general methods will be indicated, and a few typical examples will be discussed in some detail.

Reactions in solution

Reactions in solution will be considered first, since the methods of measuring their rates are considerably more straightforward than those used in the investigation of gas-phase reactions. The rate of a reaction has been seen to be defined as the rate of disappearance of a reactant or the rate of appearance of a product, and in the investigation of reactions in solution by far the most common procedure involves chemical analysis for one of these species at various stages during the course of reaction, the time corresponding to each analysis being determined accurately.

Since reactions are very sensitive to the temperature, it is necessary for the reaction to be carried out in an accurately thermostatted system. For work between 0 and 60°C water baths may be used; for temperatures above the temperature of the room these are usually heated electrically, the heat being automatically cut off when the temperature reaches the desired temperature by means of a mercury thermoregulator and a relay system. For lower temperatures the bath may be cooled by a refrigeration coil, thermostatic control being effected in the same way as above. At temperatures above 60°C evaporation of the water may be prevented by placing a layer of oil on the surface, or alternatively a bath of pure oil may be used. For temperatures above the boiling point of water a convenient method of achieving a constant-temperature system involves the use of a liquid which boils at the desired temperature; this can be continuously refluxed in a suitably constructed vessel to which is attached a manostat to maintain the pressure, and hence the boiling temperature, constant.

If the reaction is one that occurs very slowly at room temperature, it is satisfactory to place in tubes aliquot amounts of the reacting substances present in the solvent; the tubes are then sealed (to prevent evaporation of the solvent and the reactants and products) and placed in the thermo-

stat, the time of insertion being noted. A correction to this time should be made to allow for the fact that the system takes an appreciable time to attain the temperature of the bath; this correction may be determined directly by measuring the rate of heating of the system. A number of tubes are placed in each bath, and after various intervals of time are removed, rapidly cooled in order to inhibit the progress of the reaction, and the contents analyzed for either a reactant, a product, or both. If the reaction can also be stopped by chemical means, this may be done; thus if the reaction involves hydrogen ions but does not occur in alkaline solution, the addition of alkali is an effective means of "quenching" the reaction.

If the reaction occurs at an appreciable rate at room temperatures, the method is a little different and may be illustrated with reference to a reaction involving two substances. Solutions of each are prepared, and a sample of each solution is placed in the thermostat. After the solutions have attained the temperature of the bath, an aliquot portion of one is placed in a flask or tube, and an aliquot portion of the other solution added rapidly, the time corresponding to one-half addition being noted This mixture can be prepared in such an amount that quantities may be removed after various times and analyzed, or alternatively a number of equivalent mixtures can be made and analyzed after various times. For reactions of this type "quenching" may be effected by cooling to a lower temperature, or, alternatively, chemical methods of stopping the reaction may be employed.

In addition to methods involving following a reaction by chemical analysis after various times, physical methods of following a chemical change may be used in certain cases. If the reaction involves a change in the total volume of the solution, the progress of the reaction may be followed by a dilatometric method; an example of such a procedure will be considered later in connection with the mutarotation of glucose. Since this reaction involves a change in optical rotation, polarimetric methods have also been used in studying it.

Formation of Quaternary Ammonium Salts. The reaction between an alkyl iodide and a tertiary amine will be taken to illustrate the kinetic study of a reaction by chemical methods. This type of reaction was the subject of some classical investigations by Menschutkin[1] in 1890. One of the reactions studied was that between triethylamine and ethyl iodide, tetraethylammonium iodide being formed,

$$N(C_2H_5)_3 + C_2H_5I \rightarrow N(C_2H_5)_4I$$

This reaction was studied by Menschutkin in a large number of different solvents, but at one temperature only, *viz.*, 100°C.

[1] N. Menschutkin, *Z. physik. Chem.*, **5**, 589 (1890); **6**, 41 (1890).

The experimental procedure was extremely simple. A solution was prepared containing the base and the iodide in equimolecular proportions (reaction being very slow at ordinary temperatures), and aliquot portions of the solution were introduced into small glass tubes, which were then sealed. The tubes were placed in a temperature-controlled bath at 100° and the time noted. After various intervals of time the tubes were removed, cooled in ice water so as to reduce the rate of reaction rapidly to a negligible figure, and the contents analyzed. The analytical method employed depended on the fact that the product of the reaction contains iodine in the ionized form, so that it can be estimated by titration. The tubes were broken and the contents introduced into a flask containing a small amount of water, under which conditions the iodide ions pass almost completely into the aqueous phase; the free base was then neutralized with dilute nitric acid, and the solution titrated with silver nitrate solution in the presence of a few drops of potassium chromate solution (Volhard's method).

In calculating the rate constant, allowance was made for the fact that a short period of time elapses while the temperature of the reaction tubes is reaching the temperature of the thermostat. This was done by removing the first tube after 1 min, by which time temperature equilibrium had been effectively achieved; the conditions at this time were regarded as representing the beginning of the reaction, the times being measured from this instant. If a represents the initial concentration, and x_0 the change in concentration after 1 min, the initial concentration of reactants was therefore taken to be $a - x_0$; the rate equation therefore becomes

$$\frac{dx}{dt} = k(a - x_0 - x)^2 \tag{1}$$

the reaction having been shown to obey the second-order law. This equation integrates to

$$k = \frac{1}{t(a - x_0)} \frac{x}{(a - x_0 - x)} \tag{2}$$

which is therefore the equation used in calculating the specific rate.

The method of calculation is best illustrated with reference to some more recent work on a similar reaction, the reaction between pyridine and ethyl iodide in benzene solution. This reaction, together with a number of others of the same type, was studied by Winkler and Hinshelwood,[1] and the specific rates determined at four different temperatures. The experimental method was essentially that of Menschutkin; electrically controlled thermostatted baths were used for the lower temperatures and, for temperatures of 100°C or more, specially constructed boiling-liquid thermo-

[1] C. A. Winkler and C. N. Hinshelwood, *J. Chem. Soc.*, 1147 (1935).

stats. The solutions were made up by weight using carefully purified material and were $0.2N$ before using; equivalent quantities of the solutions of base and iodide were used so that the final concentrations were $0.1N$ in the reaction mixture. The alkyl halide stayed in the benzene layer after addition of water at the end of the reaction, and the ionizable iodide readily passed into the aqueous layer; the progress of the reaction was followed by estimation of the iodide ions by Volhard's method.

Some results obtained at 100°C are shown in Table 7. The figures in the first column give the times in minutes after which the tubes were

TABLE 7. REACTION BETWEEN PYRIDINE AND ETHYL IODIDE

$T = 100°C$ $a = 0.10$ mole per liter

t, min	x, moles per liter	$k \times 10^4$, liters mole^{-1} sec^{-1}
179	0.0120	1.27
420	0.0240	1.25
737	0.0350	1.22
1,054	0.0445	1.27
1,530	0.0530	1.22
2,497	0.0655	1.27
4,020	0.0750	1.24

removed from the bath and cooled, and those in the second column (x) give the corresponding concentrations of iodide ions in the mixture, expressed as moles per liter. In the last column the specific rate, equal to $x/ta(a - x)$ is given, the time having been converted into seconds. It is seen that the values in the last column are in satisfactory agreement with one another, showing that the reaction is of the second order with respect to time.

In the calculations given above, the device of Menschutkin for correcting for the time of heating of the tube was not employed; this could have been done, but in view of the very long times involved in the experiment the correction would have been quite insignificant. One correction is, however, important, particularly when one is working at elevated temperatures; this is to take account of the fact that the solvent expands when heated to the reaction temperature, with the result that the concentrations are somewhat lowered. If the coefficient of expansion of the solvent is known, the ratio of the volumes at the reaction temperature and at the standard temperature can be found, and the rate constant obtained in the above manner should be multiplied by this ratio to obtain the true constant.

Mutarotation of Glucose. The mutarotation of glucose, catalyzed by a number of acids and bases, was studied by Brønsted and Guggenheim,[1]

[1] J. N. Brønsted and E. A. Guggenheim, *J. Am. Chem. Soc.*, **49**, 2554 (1927).

using a dilatometric method. The apparatus is shown in Fig. 3; *A* is a mixing chamber fitted with a thermometer graduated in fiftieths of a degree centigrade, a mechanical stirrer, and a platinum heating coil. With all stopcocks closed and a plug of glass wool at *B*, a solution of the acid or base to be used as a catalyst was placed in *A* and stirred, the temperature being taken after the solution had come to equilibrium with the

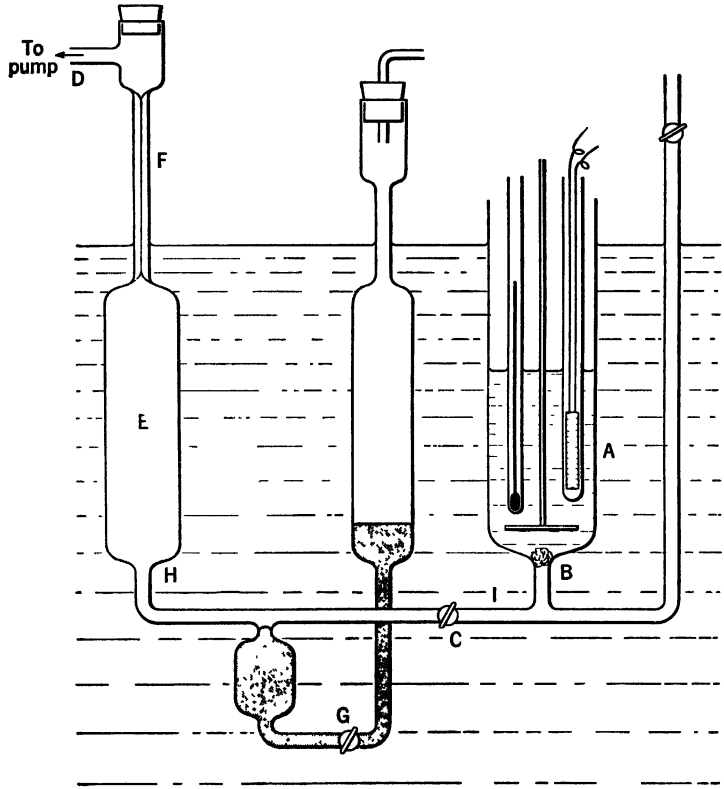


FIG. 3. Apparatus used by Brønsted and Guggenheim for studying the mutarotation of glucose.

thermostatted bath in which the apparatus was inserted. The solution was then heated through a little more than 1°C by means of the heating coil, and the glucose was introduced. Solution was rapid and brought about some cooling, but by use of the heating coil the temperature of the mixture could be brought to the initial temperature within 2 min of the introduction of the glucose. The stirrer, thermometer, and heating coil were then removed, and *A* was closed with a rubber stopper through which passed a glass tube which could be connected to a water pump, suction being applied for 1 min to remove air bubbles. The stopcock *C* was then

opened, and by evacuating through D the solution was drawn through the dilatometer E as far as the top of the capillary F; then C was closed. The stopcock G was then opened so that the mercury rose to H; the stopcock C was opened again, and the mercury allowed to flow as far as I, when C was closed. Slight suction was then applied to D to bring the surface of the solution to a convenient level in the capillary F, and G was closed.

The progress of the reaction was then followed by watching the rise of the meniscus in the capillary. Readings were taken with a magnifying glass, the meniscus being viewed through a horizontal tube about 5 cm in length so as to reduce parallax. The capillary was calibrated by weighing and measuring the lengths of threads of mercury at different positions in the tube.

This reaction proceeds to an equilibrium at which the concentrations of α- and β-glucose are equal. The equation for a reaction of the type

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

when the initial concentrations of A and B are a and b, has been seen on page 20 [Eq. (75)] to be

$$k = k_1 + k_{-1} = \frac{1}{t} \ln \frac{x_e'}{x_e' - x} \tag{3}$$

where x_e' is defined by

$$x_e' = \frac{k_1 a - k_{-1} b}{k_1 + k_{-1}} \tag{4}$$

Guggenheim[1] has developed an accurate procedure for determining the specific rates of first-order changes; its advantage is that it avoids placing unnecessarily large weight on the end value, the accuracy of which is often less than that of the other readings. The procedure, as applied to the dilatometric method, is to take a series of readings V at times t spread over an interval two or three times the half life of the reaction A second series of readings V' is then made, each at time $t + \tau$, τ being an exactly constant interval after the time of the corresponding reading V; the period τ must be at least two or three times the half life of the reaction. If ln $(V' - V)$ is then plotted against the time, a straight line will be obtained if the reaction is of the first order, and the slope of the line is $-k$ In the investigation of the mutarotation of glucose the half lives were generally 30 to 50 min, and the period chosen for τ was usually 120 min.

Some of the data obtained in one experiment are given in Table 8. The solution used for catalysis contained a mixture of sodium *o*-toluate

[1] E. A. Guggenheim, *Phil. Mag.*, **1**, 538 (1926).

and *o*-toluic acid, from the concentrations of which the concentration of the *o*-toluate ion, the catalyst, could be calculated. In the first column are given the times t in seconds, and in the second column the corresponding values of V. The third column gives the values of the readings V' at times $t + \tau$, where τ is 120 min, and the fourth gives the values of $V' - V$. After the logarithms of $(V' - V)$ were plotted against t, the slope of the best straight line gave for k the value of 1.0267×10^{-4} sec^{-1}. In the fifth column are shown the values of $V' - V$ calculated using this value of k; the agreement with the observed values is satisfactory, thus confirming the validity of the method and the fact that the reaction is of the first order.

TABLE 8. MUTAROTATION OF GLUCOSE CATALYZED BY *o*-TOLUATE IONS

Time, sec	V	V'	$V' - V$	
			Observed	Calculated
0	4.395	6.50	2.015	2.323
600	4.76	6.575	1.815	1.820
1,080	5.00	6.615	1.615	1.625
2,400	5.53	6.72	1.190	1.190
3,600	5.89	6.79	0.900	0.895
6,120	6.38	6.88	0.500	0.495

Gas reactions[1]

A common method for investigating the rate of a reaction involving gases is to introduce the reactants into a bulb maintained at the desired temperature, and to make determinations of the composition after various intervals of time; this is known as the static method. The determination of the composition of the gas may be carried out either directly, *i.e.*, by chemical analysis, or indirectly. The direct method is by all means the most satisfactory but has the disadvantage that the analyses may be extremely laborious. Some indirect methods will be mentioned briefly; when they are used, they are best supplemented by a few chemical analyses.

Manometric Methods. The most widely used indirect method of measuring the rate of a reaction involves the measurement of the pressure of the system. It is applicable to reactions in which the total number of molecules, and hence the total pressure, changes; it can also be used for reactions not involving such a change but in which one of the products

[1] For a detailed account see A. Farkas and H. W. Melville, "Experimental Methods in Gas Reactions," Macmillan & Co., London, 1939. See especially Chap. V.

can be removed by condensation or absorption, so effecting a decrease in total pressure. The pressure measurements can be made while the reaction is in progress by having a pressure-measuring device connected to the reaction vessel; liquid manometers containing mercury, oil, water, or other liquids can be used in certain cases, as can gauges of the mechanical type. Certain modifications of this general scheme have been used; *e.g.*, the reaction may be stopped after various intervals of time by cooling the reaction system with liquid air (which may also condense out certain products), and the total pressure measured, after which the system may be heated to the required temperature and the reaction allowed to continue.

In a number of reactions, particularly those in which complicated changes take place, the total pressure does not provide reliable information as to the course of the change, and conclusions drawn on the basis of such measurements are consequently in error. In many cases intermediate products are formed in measurable amounts and disappear. In all such cases extensive analyses are necessary in addition to manometric measurements.

Other Methods of Following Reactions. One or two other methods will be mentioned briefly. When the reaction involves a large change in the refractive index of the gas, this property may be measured by the use of an interferometer. Spectroscopic measurements are also used in some cases; the concentrations of atoms can, for example, be measured by exciting the atomic lines with a discharge and measuring the intensity of the lines produced. The absorption spectra of complicated molecules have also been used for estimating the concentrations of the molecules present; these spectroscopic methods are not capable of high accuracy, however, and can be used only for rough kinetic work. If in a reaction any substance reacting or being produced absorbs radiation at a convenient wave length, its concentration may be measured by means of a photometer, of which there are many types. If radiation is emitted in a reaction, the measurement of its wave length and intensity may give valuable information as to the mechanism of the process.

The Reaction Vessel. The vessel in which a chemical reaction in the gas phase is investigated is most frequently constructed of glass; for low-temperature work soft glass may be satisfactory, but at higher temperatures Pyrex must be used. One advantage of glass is that it is not attacked by most of the common gases, hydrogen fluoride being an important exception. A further advantage is that most substances other than glass allow reactions to occur on their surfaces, *i.e.*, exert a catalytic effect, so that the observed rate does not correspond to reaction in the gas phase; this behavior is also shown with glass but not quite so extensively as with other substances. Glass is also suitable for certain investigations in which it is desired to irradiate the reactants, as it is transparent over a consider-

able range of wave length. It absorbs light of wave length below about 3500 A, however, and for work in the ultraviolet quartz is usually used.

Surface Catalysis. A reaction involving a gas or a mixture of gases may occur homogeneously, *i.e.*, entirely in the gas phase, or heterogeneously, *i.e.*, on a surface, and in a number of instances a reaction may occur partly in the gas phase and partly on the surface. Whether it is desired to measure the rate of the homogeneous or the heterogeneous change, it is clearly necessary to know what fraction of the reaction goes by each mechanism. If the homogeneous reaction is under investigation, the greatest accuracy in its measurement will be achieved if the proportion of the reaction occurring on the surface is negligible, in which case the over-all rate can be identified with that of the homogeneous change; this condition is most often realized, as has been seen, with glass vessels.

The best way to determine the fraction of the reaction which is taking place on the surface is to vary the surface-volume ratio of the vessel. The rate and the specific rate of a homogeneous reaction are independent of the volume of the vessel and of the area and nature of the surface; the rate of a surface reaction is, on the other hand, proportional to the area of the surface and depends upon its nature. If a reaction is proceeding partly on the surface and partly in the gas phase, the proportion of the surface reaction is increased by increasing the surface-volume ratio, and the over-all rate will increase. The ratio can be varied by changing the size or shape of the vessel, but the extent of the alteration that can conveniently be effected in this way is limited to a factor of 10 or so. A more effective method is to pack the reaction vessel with tubes or irregular pieces of material made of the same material as the vessel; in this way the surface is increased considerably and by an amount that can be determined fairly accurately. If this procedure brings about no change in the specific rate, the surface reaction is clearly unimportant; if a change occurs, the amount of reaction occurring on the surface of the unpacked vessel can readily be calculated.

It may be mentioned that in some cases packing the reaction vessel brings about a decrease in the reaction rate. When this occurs, it can be concluded that the reaction is complex in character and that recombination of atoms or free radicals is occurring at the surface. The influence of the surface on reactions of this type is discussed in more detail later.

If it is desired to investigate the rate of a reaction on a surface, it is preferable to employ a reaction vessel which does not catalyze the reaction and to introduce the catalyst into it. If the reaction does not occur in the absence of the catalyst, the rate in its presence is clearly that of the surface-catalyzed reaction; otherwise allowance has to be made for the homogeneous reaction. Since the rate of a surface-catalyzed reaction is usually propor-

tional to the surface area of the catalyst, it is important, in a fundamental investigation of the kinetics, that the surface area be known accurately.

Photochemical Reactions.[1] Special techniques are required for the study of reactions which depend upon the absorption of radiation. Various sources of light are employed, of which mercury lamps are used most frequently; these emit a number of intense lines between 1860 and 5688 A. A number of different types of lamp are in use, some operating at low and others at high pressures. For work in the ultraviolet the lamp must be constructed of quartz, and the reaction vessel must be of quartz or at least contain a quartz window. It is necessary to use radiation within a very narrow range of wave lengths, and for this purpose monochromators or suitable filters must be used.

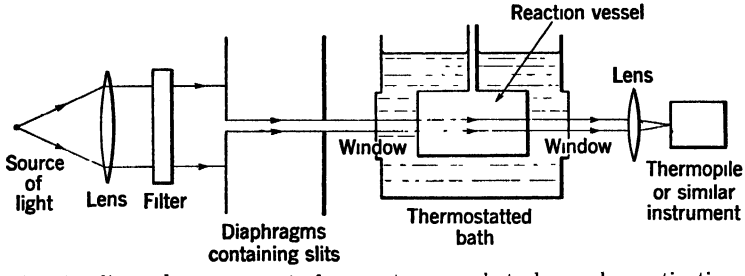


FIG. 4. General arrangement of apparatus in a photochemical investigation.

The general arrangement of the apparatus in a photochemical investigation is illustrated in Fig. 4. The light from a suitable source is made monochromatic by passage through a filter. By means of slits it is passed as a parallel beam through the reaction vessel, which must be suitably thermostatted, and then passes through a lens which focuses it upon an actinometer, which may be a thermopile, a photoelectric cell, or a chemical actinometer, for measurement of its final intensity. Many modifications of this arrangement are possible, however: sometimes the lamp is specially constructed so as to surround the reaction vessel. The progress of a photochemical reaction may be followed by any of the methods used for thermal reactions.

Since the rate of a photochemical reaction depends upon the intensity of the light absorbed, it is necessary to measure the intensity of the light passing through the reaction system in the absence of the reacting substances and that passing through when the reaction is actually occurring; the difference is the intensity absorbed by the reaction system. Various methods of measuring the radiation intensity are available, of which the most common are chemical actinometers, which depend on the measure-

[1] *Cf.* W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corporation, New York, 1941.

ment of the amount of chemical reaction brought about by the light passing into them. The uranyl oxalate actinometer is an example of this type: a weighed quantity of a solution of uranyl oxalate is placed in a suitable cell and exposed to the radiation for a known period of time. Radiation of wave lengths between 2000 and 4500 A induces decomposition to carbon monoxide, carbon dioxide, and formic acid, and the amount of oxalate remaining at the end of the period is determined by titration with acid permanganate. Chemical actinometers of this type ultimately have to be calibrated against more absolute standards, such as a thermopile.

Reactions in Flow Systems.[1] In addition to the static method of studying a chemical reaction, in which the gases are confined in a reaction vessel and the change in composition determined, flow systems may also be used. The principle of this method is that the gas or mixture of gases under investigation is led at a known rate of flow through a reaction vessel of known volume maintained at a definite temperature. Sampling tubes are usually connected to the entrance and exit ends of the vessel, and by means of them samples can be removed for analysis; however, in some cases the tube at the entrance end is dispensed with, the assumption being made that the composition is the same as that of the original mixture passed in. From the volume of the reaction vessel and the rate of flow it is possible to calculate the mean time spent by the reaction mixture in the vessel, and the difference between the compositions at the entrance and the exit represents the amount of reaction that has occurred in this time; this divided by the time of contact is therefore the rate. The order of the reaction can be determined by varying the rate of flow through the chamber and the concentrations of the entering gases.

One source of error in this method arises from the fact that it is impossible to define exactly the effective chamber volume; at each end of the vessel the temperature varies from the furnace temperature to room temperature, and some kind of mean volume has to be estimated. This error is sometimes reduced by the use of a preheater through which the gases are passed immediately before entering the reaction chamber and which brings them to the temperature of the chamber. In this case it is necessary for the initial sampling tube to be inserted between the preheater and the reaction chamber, since some reaction occurs in the preheater. The error at the exit end of the chamber can be reduced by connecting the sampling tube to the chamber inside the furnace. If these modifications are employed, the effective volume of the chamber is clearly that between the two sampling tubes.

For accurate work other refinements of the flow method must be ap-

[1] *Cf.* O. A. Hougen and K. M. Watson, "Chemical Process Principles," John Wiley & Sons, Inc., New York, 1947. For a discussion of the theory of flow systems, see H. M. Hulburt, *Ind. Eng. Chem.*, **36**, 1012 (1944); **37**, 1063 (1945).

plied; these will be mentioned only briefly. If the reaction is accompanied by a volume change the mean rate of flow through the reaction system will differ somewhat from its value before the gas is admitted to the vessel, and the time of contact must be corrected to take account of this. This correction is particularly important if an appreciable fraction of the total reaction takes place in the reaction system but may be neglected if the amount of reaction is only slight. In certain systems the gas does not flow smoothly through the vessel, and an allowance has to be made for the amount of diffusion that is occurring.

The general experimental procedures described above will now be illustrated by a number of typical examples.

Thermal Decomposition of Nitrogen Pentoxide in the Gas Phase. The work of Daniels and Johnston[1] on the decomposition of nitrogen pentoxide, which follows the stoichiometric equation

$$2N_2O_5 = 2N_2O_4 + O_2$$

is one of the earliest studies of a first-order gas reaction, and since the methods employed are typical of those used in many subsequent investigations of gas reactions, they will be discussed in some detail.

The nitrogen pentoxide was prepared by dehydrating anhydrous nitric acid with phosphorus pentoxide and subliming from the mixture at 40°C. Resublimation in the presence of ozone and more phosphorus pentoxide gave pure crystals, from which the gas was produced in the reaction vessel by allowing the crystals to sublime.

The apparatus in which the rates were measured is shown in Fig. 5. The pure nitrogen pentoxide crystals were kept in the U tube A, which was connected to the reaction vessel B through two stopcocks, between which there was a connection to a pump. The reaction vessel was immersed completely in a large thermostatted bath maintained at the required temperature to within 0.02 to 0.03°C.

An important feature of the method is the technique for measuring the pressure in the reaction vessel. This was done by means of a platinized glass diaphragm which separated the reaction vessel from an outer space, the pressure in which was measured by a mercury manometer. When the pressure in the reaction vessel was equal to or greater than that outside, the platinized diaphragm made electrical contact with a platinized glass knob, and there being a source of current and a galvanometer in series, a deflection of the galvanometer indicated contact. Since the reaction is sensitive to light, the whole apparatus was painted black.

In order to carry out a determination of the rate, the apparatus was completely evacuated by means of the pump, and the external pressure

[1] F. Daniels and E. H. Johnston, *J. Am. Chem. Soc.*, **43**, 53 (1921).

was adjusted until contact was just broken; this usually occurred at a pressure of about 20 to 30 mm. This was the excess pressure required to force the diaphragm from the knob, and in all subsequent pressure readings a correction was made to allow for this. The crystals were then partially evaporated by pumping, in order to remove air from the U tube, and the stopcocks were turned so that gaseous nitrogen pentoxide passed over into the reaction chamber, which was sealed off when the desired pressure was reached.

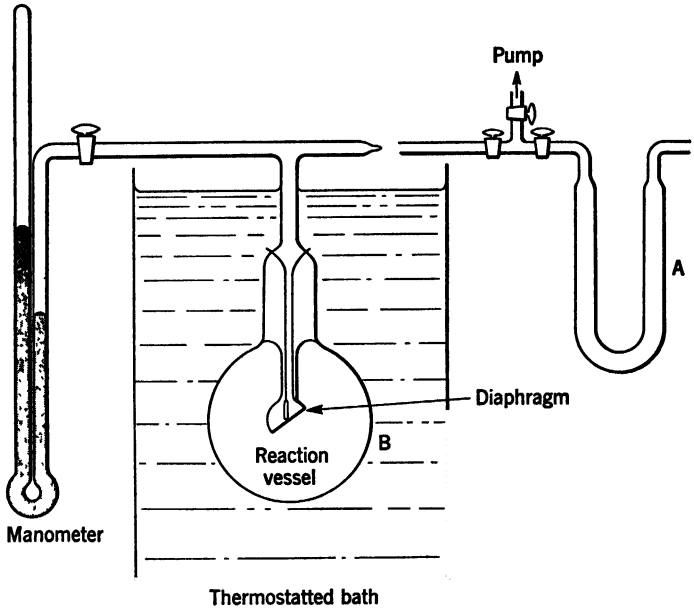


FIG. 5. Apparatus used by Daniels and Johnston for studying the thermal decomposition of nitrogen pentoxide.

The course of the reaction was then followed by making the pressure on the outside of the diaphragm somewhat greater than that inside, so that the circuit was broken. As the reaction proceeded, the pressure increased until the diaphragm was forced against the contact, and the time at which the deflection occurred was measured with a stop watch. The pressure was then increased again, and the time of the second deflection recorded. This process could be repeated as frequently as desired until no further increase in pressure was observed. The concentration of nitrogen pentoxide at any time can be determined from the total pressure, but the calculation is complicated by the fact that nitrogen dioxide, one of the products of the reaction, undergoes association, and that the equilibrium shifts as the pressure changes during the course of reaction. The method

of determining, from the pressure-time data, the initial pressure of nitrogen pentoxide and its pressure at any time, is as follows:

The over-all reaction may be represented by the equation

$$2N_2O_5 = \begin{matrix} 4NO_2 \\ \downarrow\uparrow \\ 2N_2O_4 \end{matrix} + O_2$$

After the reaction has reached completion, it is clear that the number of moles of oxygen is one-half the original number of moles of nitrogen pentoxide; hence the initial pressure, $P(i)$, is twice the partial pressure $p_{O_2}(f)$ at completion.

$$P(i) = 2p_{O_2}(f) \tag{5}$$

If α is the degree of dissociation of the N_2O_4, the number of moles of NO_2 at any time is 4α times the number of moles of oxygen; hence, at completion,

$$p_{NO_2}(f) = 4\alpha p_{O_2}(f) \tag{6}$$

and similarly the final partial pressure of N_2O_4 is

$$p_{N_2O_4}(f) = 2(1 - \alpha)p_{O_2}(f) \tag{7}$$

At the end of the reaction the system contains N_2O_4, NO_2, and O_2, and the total pressure is the sum of the partial pressures of these substances,

$$P(f) = p_{N_2O_4}(f) + p_{NO_2}(f) + p_{O_2}(f) \tag{8}$$

$$= 2(1 - \alpha)p_{O_2}(f) + 4\alpha p_{O_2}(f) + p_{O_2}(f) \tag{9}$$

$$= 3p_{O_2}(f) + 2\alpha p_{O_2}(f) \tag{10}$$

so that by Eq. (5) the final pressure is related to the initial pressure by

$$P(f) = (3/2 + \alpha)P(i) \tag{11}$$

The dissociation constant, and hence the value of α, was known, and therefore the initial pressure could be calculated from the final pressure. This is a much more satisfactory method of determining the initial pressure than extrapolating the pressures back to zero time, since the reaction is initially rapid and temperature equilibrium may not be attained in the early stages.

The method of determining the partial pressure of the nitrogen pentoxide remaining at any time is somewhat similar. The total pressure P at any time t is the sum of the partial pressures of N_2O_5, N_2O_4, NO_2, and O_2,

$$P = p_{N_2O_5} + p_{N_2O_4} + p_{NO_2} + p_{O_2} \tag{12}$$

This may be written as

$$P = P(i) + p_{N_2O_4} + p_{NO_2} + p_{O_2} - p \tag{13}$$

where $P(i)$ is the initial pressure and p is the partial pressure corresponding to the N_2O_5 that has decomposed up to the time t. The pressure p is equal to $2p_{O_2}$, and p_{NO_2} and $p_{N_2O_4}$ can be expressed in terms of p_{O_2} as before; hence

$$P = P(i) + 2(1 - \alpha)p_{O_2} + 4\alpha p_{O_2} + p_{O_2} - 2p_{O_2} \tag{14}$$

$$= P(i) + p_{O_2} + 2\alpha p_{O_2} \tag{15}$$

The pressure increase at time t is therefore given by

$$\Delta P = P - P(i) = p_{O_2} + 2\alpha p_{O_2} \tag{16}$$

so that if P is measured, p_{O_2} can be calculated; the partial pressure p of N_2O_5 decomposed is then twice this quantity.

A set of data determined in this manner is shown in Table 9. The total pressures corresponding to the various times at which measurements were made are given in the second column, and the corresponding pressure rise in the third column. The values in the fourth column, representing the amount of nitrogen pentoxide decomposed, were obtained in the

TABLE 9. DECOMPOSITION OF NITROGEN PENTOXIDE

T = 45°C Initial pressure = 348.4 mm

Time, sec	P, mm	$P - p_i$, mm	p, mm	$p_{N_2O_5}$, mm	$k \times 10^4$, sec^{-1}
600	462	114	101	247	
1,200	518	170	163	185	5.2
2,400	585	237	243	105	4.8
3,600	623	274	290	58	4.8
5,400	649	301	324	24	4.9
7,200	660	312	338	10	4.8
9,600	666	317	346	3	5.2
∞	668		348	0	

manner explained previously. The concentration of undecomposed nitrogen pentoxide is given in the fifth column, and the rate constant given in the last column is calculated using the first-order equation, *i.e.*, Eq. (8) on page 5.

Reaction between Nitric Oxide and Hydrogen. A number of gas-phase reactions involving nitric oxide have been found to be of the third order; these include the reactions between nitric oxide and chlorine and bromine.

the rates of which follow the laws[1]

$$-\frac{d[\mathrm{NO}]}{dt} = k[\mathrm{NO}]^2[\mathrm{X_2}] \tag{17}$$

where X_2 represents chlorine or bromine. For these processes the kinetic laws are consistent with the stoichiometric equation

$$2\mathrm{NO} + \mathrm{X_2} = 2\mathrm{NOX}$$

The reaction between nitric oxide and hydrogen gives rise to nitrogen and water and can be represented by the equation

$$2\mathrm{NO} + 2\mathrm{H_2} = \mathrm{N_2} + 2\mathrm{H_2O}$$

This reaction is not, however, of the fourth order, as might have been supposed from its equation, but is of the third order: the rate is proportional to the square of the concentration of the nitric oxide and to the first power of the hydrogen concentration. The reason for this difference between the stoichiometric equation and the order will be considered in Chap. 7.

The reaction was first studied kinetically by Hinshelwood and Green,[2] whose experimental procedure will now be described. The over-all reaction is attended by a decrease in pressure, even when the water is not allowed to condense, so that the rate can be measured manometrically. The apparatus is shown in Fig. 6; the reaction vessel A was of clear fused silica and was heated in an electric furnace, the temperature of which was measured by means of a thermocouple and controlled to within a degree centigrade by manual regulation of the heating current. The reaction vessel was sealed to a long T piece of fine silica capillary tubing, which communicated with the manometer C. In order to prevent condensation of the water produced in the reaction, the T piece was heated to about 140°C. This prevented diffusion of the water vapor out of the reaction vessel into the cooler parts of the apparatus such as the capillary of the manometer. The silica of the capillary tube was joined to the glass parts of the apparatus by rubber joints, the silica and glass making good contact beneath the joints. The vessel B is a reservoir in which the gases were mixed before being passed into the reaction vessel. The nitric oxide used was prepared by the nitrometer method and stored in contact with concentrated sulfuric acid; the hydrogen used was prepared electrolytically, purified from oxygen by passage over a hot platinum wire, and dried with phosphorus pentoxide.

The over-all order of the reaction was investigated by using equimolecular amounts of nitric oxide and hydrogen, and determining the

[1] Concentrations are represented by square brackets.

[2] C. N. Hinshelwood and T. E. Green, *J. Chem. Soc.*, **129**, 730 (1926).

time τ in seconds for half of the reaction to proceed. This was done at a number of initial pressures, and the order determined using the relationship [*cf.* Eq. (54), p. 14]

$$\frac{\tau_2}{\tau_1} = \left(\frac{p_1}{p_2}\right)^{n-1} \tag{18}$$

where the p's are the initial pressures. Some values obtained in this way

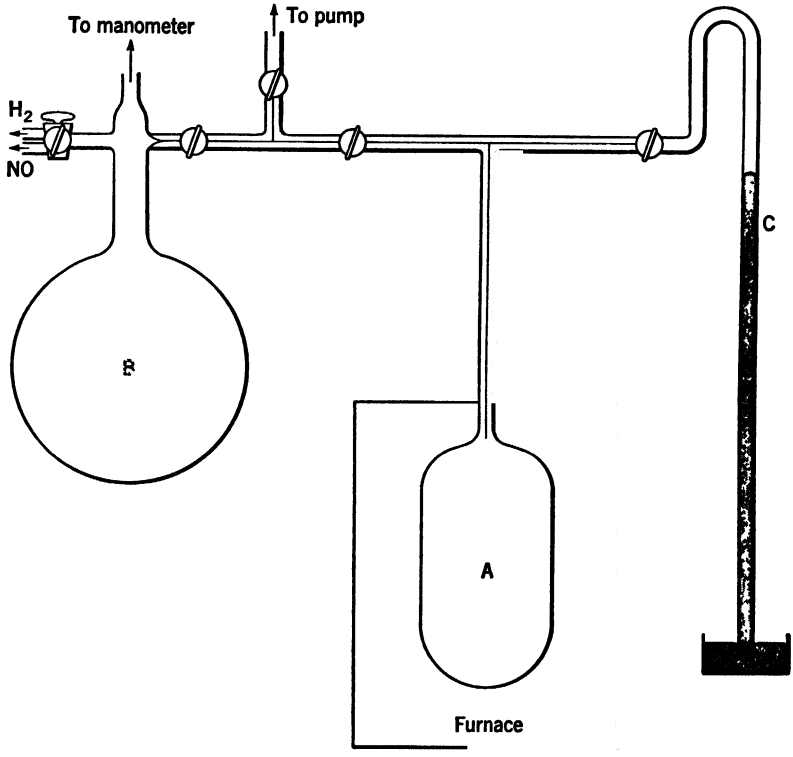


FIG. 6. Apparatus used by Hinshelwood and Green for the study of the nitric oxide–hydrogen reaction.

are given in Table 10. The order obtained in this way is seen to be somewhat less than three, a fact that will be discussed later.

Experiments were also carried out with the object of determining the influence on the rate of the concentrations of the individual gases. In order to study the influence of nitric oxide, runs were made at a fixed initial pressure of hydrogen and various initial pressures of nitric oxide. Curves were plotted showing the decrease of the pressure as a function of the time, and the initial rates determined by drawing tangents at the origin. In Table 11 are shown relative rates for three different initial

nitric oxide concentrations, and in the last two columns are shown values of rate divided by [NO] and of rate divided by $[NO]^2$. It is seen that the figures in the last column are practically constant, indicating that the rate is proportional to the square of the nitric oxide concentration. Similar investigations with a constant initial pressure of nitric oxide and a variable

TABLE 10. REACTION BETWEEN NITRIC OXIDE AND HYDROGEN: THE OVER-ALL ORDER

p_1, mm	τ_1, sec	p_2, mm	τ_2, sec	n
354	81	202	224	2.81
340.5	102	288	140	2.89
340.5	102	243	176	2.62
375	95	251	180	2.60

hydrogen pressure showed that the rate was proportional to the first power of the hydrogen concentration. The influence of the reaction products, steam and nitrogen, was studied by measuring the rate after various amounts of these substances had been added; no appreciable influence was found.

TABLE 11. REACTION BETWEEN NITRIC OXIDE AND HYDROGEN: THE ORDER WITH RESPECT TO NITRIC OXIDE

Initial NO concentration, mm	Initial rate, mm per sec	Rate/[NO], sec^{-1}	Rate/$[NO]^2$, $mm^{-1}\ sec^{-1}$
359	1.50	0.00418	0.0000116
300	1.03	0.00343	0.0000114
152	0 25	0.00164	0 0000108

The investigations thus show that the reaction is of the second order with respect to nitric oxide and of the first order with respect to hydrogen: the rate can therefore be expressed as

$$v = k[NO]^2[H_2] \tag{19}$$

If a is the initial pressure of nitric oxide and b that of hydrogen, this can be written as

$$\frac{dx}{dt} = k(a - x)^2(b - x) \tag{20}$$

where x is the amount reacted at time t. This equation integrates to

$$kt = \frac{1}{(a - b)^2} \ln \frac{b(a - x)}{a(b - x)} + \frac{1}{a - b}\left(\frac{1}{a} - \frac{1}{a - x}\right) \tag{21}$$

The most convenient way of calculating the rate constant is to determine, from the plot of pressure increase against time, the time for half change, τ. When hydrogen is in excess, half change corresponds to $x = a/2$, and one obtains

$$k = \frac{1}{\tau}\left[\frac{1}{(b-a)^2}\ln\frac{b}{2b-a} + \frac{1}{a(b-a)}\right] \tag{22}$$

When nitric oxide is in excess, half change corresponds to $x = b/2$, and under these conditions

$$k = \frac{1}{\tau}\left[\frac{1}{(a-b)^2}\ln\frac{2a-b}{a} + \frac{1}{b-a}\,\frac{b}{a(2a-b)}\right] \tag{23}$$

If the gases are in equimolar proportions, $k = 3/2\tau a^2$.

TABLE 12. SPECIFIC RATE CONSTANTS FOR THE REACTION $2NO + 2H_2 = 2H_2O + N_2$ AT 866° C

Initial NO concentration, mm	Initial hydrogen concentration, mm	τ, sec	$k \times 10^7$, mm^{-2} sec^{-1}
299	244	112	1.24
405	147	50	1.06
232	313	152	1.19
178	220	238	1 45
144	323	227	1.10
288	288	140	1 29

The specific rates shown in Table 12 have been calculated in this way. The values of k are seen to be quite constant in spite of the wide variations in the initial concentrations.

The influence of the surface of the reaction vessel was also investigated and shown to be small under the conditions used. A series of experiments was carried out in a silica bulb smaller than that employed in obtaining the results quoted above and containing some powdered silica. It was found that for experiments in which the initial pressures of nitric oxide and hydrogen were both greater than 300 mm, the specific rates were 1.18×10^{-7} mm^{-2} sec^{-1} in the smaller bulb containing silica, and 1.17×10^{-7} in the larger, empty, bulb. A greater difference was found in the experiments at lower pressures, but the results indicate that in the experiments in the empty bulb the fraction of reaction occurring on the surface is very small. The fact that the order is found to be somewhat less than three is probably attributable to the small amount of reaction occurring on the surface.

Reaction between Atomic and Molecular Hydrogen. The reaction between a hydrogen atom and a hydrogen molecule,

$$H + H_2 \rightarrow H_2 + H$$

is the simplest example of a chemical change; its measurement is made possible by the fact that molecular hydrogen exists in two forms, designated ortho (*o*) and para (*p*). The forms differ in the nuclear spins: in *o*-hydrogen the nuclei spin in the same direction, while in *p*-hydrogen the spins are opposite. *p*-Hydrogen can be prepared in the pure form by passing ordinary hydrogen through a tube containing a suitable catalyst and immersed in liquid air. Hydrogen at room temperature consists of a mixture of three parts of *o*-hydrogen and one of *p*-hydrogen; by reaction with hydrogen atoms it is found that pure *p*-hydrogen is converted into the equilibrium mixture. This is due to the occurrence of the two reactions

$$H + p\text{-}H_2 \rightarrow p\text{-}H_2 + H$$

and

$$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$$

the second reaction taking place three times as rapidly as the first. When these reactions occur, the attacking hydrogen atom forms a bond with one of the hydrogen atoms in the molecule, the bond between the hydrogen atoms in the original molecule being broken.

The rate of the reaction between atomic and molecular hydrogen was first measured by Geib and Harteck,[1] who caused atomic hydrogen to interact with hydrogen consisting largely of the para variety and determined the net rate of production of *o*-hydrogen in the mixture. Their experimental procedure involved the passing of a stream of hydrogen atoms and *p*-hydrogen through a reaction vessel, and determining the concentrations of *p*- and *o*-hydrogen in the issuing gas by making use of the fact that there is a small difference in thermal conductivity between the two forms.

The atomic hydrogen was prepared by a method developed by Wood[2] and modified by Bonhoeffer.[3] This depends upon the fact that when a silent discharge is passed through hydrogen gas at low pressure, hydrogen atoms are produced and may be detected by means of their spectra. The apparatus used by Geib and Harteck for obtaining a stream of atomic hydrogen, equivalent to that devised by Bonhoeffer, is illustrated in Fig. 7. A stream of hydrogen enters at the position indicated and passes through

[1] K. H. Geib and P. Harteck, *Z. physik. Chem., Bodenstein-Festband*, 849 (1931).
[2] R. W. Wood, *Proc. Roy. Soc.* (*London*), **A, 97,** 455 (1920); **A, 102,** 1 (1922).
[3] K. F. Bonhoeffer, *Z. physik. Chem.*, **113,** 199 (1924); **116,** 391 (1926).

the tube between the two electrodes E_1 and E_2, the potentials at which differed by 3,000 volts; the current passing was 200 milliamp. The auxiliary electrode E_a was used for cleaning the reaction tube, certain impurities which destroy atoms being removed by the action of the discharge. The hydrogen was prepared electrolytically, and was freed from oxygen by heating in an oven filled with platinum-asbestos and from other impurities by freezing them out with liquid air.

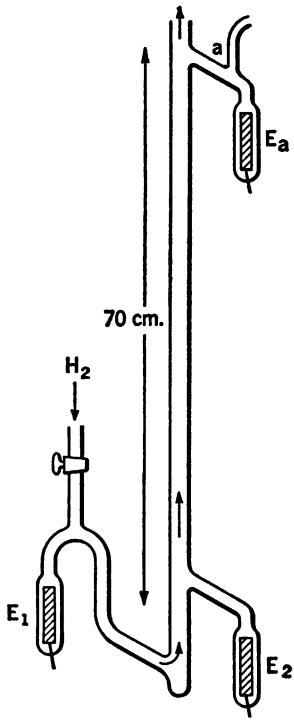


FIG. 7. Apparatus used by Bonhoeffer, and by Geib and Harteck, for producing atomic hydrogen by the silent-discharge method.

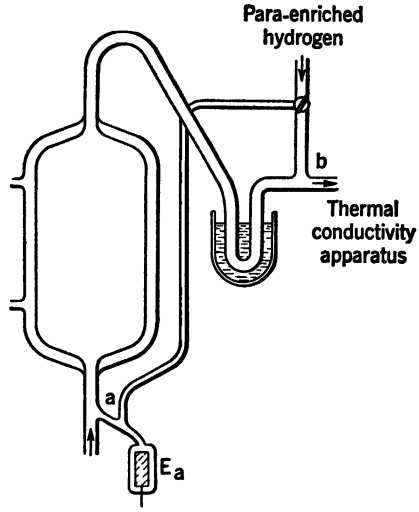


FIG. 8. Reaction vessel used by Geib and Harteck in the study of the para-ortho hydrogen conversion.

The reaction vessel is shown in Fig. 8; it had a volume of 1,030 cc and by introducing water or steam into its jacket could be brought to the desired temperature. On leaving the reaction vessel the mixture was passed through a U tube immersed in liquid air, which removed the atomic hydrogen from the mixture. The gases were then passed into the apparatus for measuring the thermal conductivity, which allowed the ratio of the concentrations of the ortho and para forms to be determined.

The hydrogen enriched with *p*-hydrogen was prepared by passing hydrogen through charcoal contained in a vessel cooled in liquid air. It was

introduced into the reaction vessel at two different points a and b. The point a was 70 cm from the position at which the atomic hydrogen left the discharge tube; the second point of introduction, b, was after the atomic hydrogen had been removed by cooling with liquid air. The results obtained using this procedure constituted a blank, since no reaction should occur. Some measurements were also taken after the para-enriched hydrogen had been passed over platinized asbestos at 800°C, a process which converts the para form into the equilibrium mixture.

The concentration of atomic hydrogen was measured by means of a gauge devised by Harteck[1] and Wrede.[2] The principle of the method is that if a stream of gas containing atomic hydrogen passes an orifice, the diameter of which is less than the mean free path of the atoms at the pressure employed, the hydrogen atoms passing through will all be converted into molecular hydrogen; a sintered-glass plug may be used instead of a simple orifice.[3] There is thus a difference in pressure between the two sides of the orifice which can be measured by means of a manometer. At equilibrium equal masses of gas traverse the orifice in opposite directions, and if x is the fraction of atomic hydrogen in the stream, and p_1 and p_2 are the pressures in the flow tube and at the other side of the orifice, it follows that[4]

$$p_2 M_{H_2}^{\frac{1}{2}} = x p_1 M_H^{\frac{1}{2}} + (1 - x) p_1 M_{H_2}^{\frac{1}{2}} \tag{24}$$

the M being the molecular weights. Since $M_{H_2} = 2M_H$, it follows that

$$x = \frac{\sqrt{2}}{\sqrt{2} - 1} \frac{p_1 - p_2}{p_1} \tag{25}$$

so that x can be calculated if p_1 and p_2 are known.

As has been seen, the rate measurements were carried out under four sets of conditions, which may be summarized as

1. H + p-H_2
2. H_2(normal) + p-H_2
3. H + H_2(normal)
4. H_2(normal) + H_2(normal)

In each case the concentration of p-hydrogen was determined, and it can be seen that the difference between the results of (2) and (4) gives the total amount of p-hydrogen when no reaction with atomic hydrogen has occurred. The difference between (1) and (3) gives the total amount of

[1] P. Harteck, *Z. physik. Chem.*, **A, 139,** 98 (1928).

[2] E. Wrede, *Z. Physik.*, **54,** 53 (1929).

[3] H. M. Chadwell and T. Titani, *J. Am. Chem. Soc.*, **55,** 1363 (1933).

[4] The number of molecules entering the orifice is proportional to $pM^{-\frac{1}{2}}$, and the mass therefore to $pM^{\frac{1}{2}}$.

p-hydrogen after interaction with a known amount of atomic hydrogen; the difference between the two differences therefore indicates how much *p*-hydrogen has been removed by interaction with hydrogen atoms.

The rate of disappearance of *p*-hydrogen, and hence the rate of the reaction $H + H_2 \rightarrow H_2 + H$, could therefore be calculated; it was found to be proportional to the hydrogen-atom concentration and also to the concentration of *p*-hydrogen. The reaction is therefore of the second order, and a second-order specific rate can be calculated; actually a somewhat different procedure was employed in the original paper.

Thermal Decomposition of Ethane. The thermal decomposition of ethane has been studied kinetically by a number of workers using a wide variety of experimental techniques. In order to illustrate the use of flow

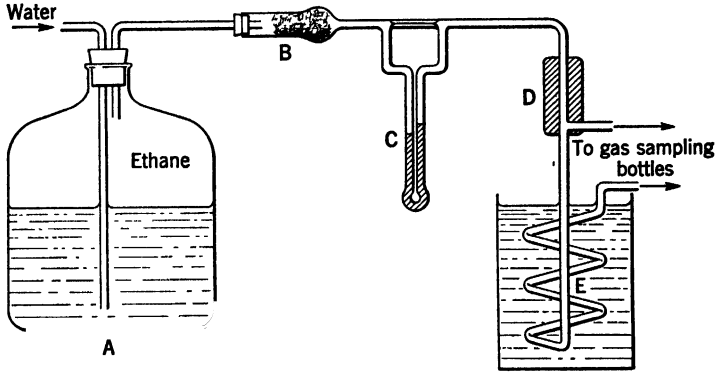


FIG. 9. Flow system used by Marek and McCluer for investigating the ethane decomposition.

methods in investigations of this kind, the study of Marek and McCluer[1] will be considered here.

The apparatus is shown schematically in Fig. 9. The ethane, prepared by passing pure ethylene and hydrogen over a reduced nickel catalyst supported on pumice, was stored in the reservoir *A*, from which it could be forced by air-free water. It was passed through a calcium chloride tube *B*, and the rate of its flow into the reaction system was measured using the calibrated flowmeter *C*.

The reaction system consisted of a preheater *D* and a reaction coil *E*. The preheater *D* consisted of a copper block electrically heated to a temperature somewhat higher than that of the reaction coil. The gas passed through a hole drilled through the length of the block, and its temperature was measured by a thermocouple situated at the lower end of the hole. A sampling tube in the lower part of the preheater allowed a sample of

[1] L. F. Marek and W. B. McCluer, *Ind. Eng. Chem.*, **23**, 878 (1931).

gas to be removed so that the composition of the gas entering the reaction coil was known exactly.

The reaction coil was made from a copper-lined steel tube 12 ft long, the internal volume being 30 cc. The coil was immersed in an electrically heated lead bath, the temperature of which was measured by a thermocouple. During the run the temperature of the preheater was regulated so that the temperature of the gas entering the reaction vessel was the same as that of the lead bath.

The analyses were made on a Burrell gas-analysis apparatus. Hydrogen was determined by combustion over copper oxide at 320°C and ethylene by absorption in bromine water. In the case of one of the runs the products were fractionated in a liquid-air column in order to determine the amount of methane produced; negligible amounts were found.

TABLE 13. THERMAL DECOMPOSITION OF ETHANE AT 649°C

Time of contact, sec	$x_{C_2H_4}$	x_{H_2}	$x'_{C_2H_4}$	x'_{H_2}	$x_{C_2H_6}$	$x'_{C_2H_6}$	$k \times 10^3$, sec^{-1}
6.66	0.013	0.007	0.033	0 030	0.980	0.937	6.74
3 96	0.012	0 015	0.021	0 030	0.973	0 949	6.28
5.16	0 010	0 014	0 021	0 025	0.971	0.954	4.42
9.70	0.013	0 013	0 043	0.043	0.974	0.914	6.55
13.18	0.014	0.015	0.052	0.055	0.971	0.889	6.69

The principle used in calculating the specific rate of the reaction involved a determination of the amount of ethane present in the stream entering the reaction coil and that in the stream leaving it. If, as determined by the analyses, $x_{C_2H_4}$ was the mole fraction of the ethylene entering the coil and x_{H_2} was that of the hydrogen, the mole fraction of the ethane, the only other substance present, is given by $x_{C_2H_6} = 1 - x_{C_2H_4} - x_{H_2}$; similarly the mole fraction $x'_{C_2H_6}$ of the ethane in the stream leaving the coil is $1 - x'_{C_2H_4} - x'_{H_2}$, where $x'_{C_2H_4}$ and x'_{H_2} are the corresponding mole fractions in the stream leaving the coil. If t is the mean time spent by the gas in the coil (as determined from the rate of flow and the volume of the coil), the first-order specific rate is given by [*cf.* Eq. (15), p. 6]

$$k = \frac{2.303}{t} \log_{10} \frac{1 - x_{C_2H_4} - x_{H_2}}{1 - x'_{C_2H_4} - x'_{H_2}} \tag{26}$$

The method of treating the data obtained at 649°C is illustrated in Table 13. In the first column is given the time of contact, and in columns 2 to 5 are the mole fractions of ethylene and hydrogen in the streams entering and leaving the reaction coil. In the sixth and seventh columns are

given the mole fractions of ethane, and in the last column the values of k calculated using Eq. (26). From the fact that k shows no systematic variation with the time of contact it is concluded that the reaction is approximately of the first order. In the original paper a slight correction was applied to allow for the fact that the equilibrium does not quite correspond to complete reaction.

Decomposition of Hydrogen Iodide. Gaseous hydrogen iodide decomposes thermally to give an equilibrium mixture of hydrogen, iodine, and hydrogen iodide according to the stoichiometric equation

$$2HI = H_2 + I_2$$

The reaction is of particular interest on account of its kinetic simplicity and has been studied in great detail; its investigation by Bodenstein[1] constituted the first comprehensive study of a reaction occurring in the gas phase. In addition to measuring the rates of the forward and the reverse reactions, Bodenstein determined directly the equilibrium constant; all this work was carried out at various temperatures, ranging from 283 to 508°C.

The experimental technique for studying the decomposition of hydrogen iodide consisted in sealing pure hydrogen iodide in bulbs, which were maintained in a vapor bath at the required constant temperature for various intervals of time, and were then removed and cooled rapidly. The contents were then analyzed for all three constituents; since there is no volume change, an analytical method was necessary.

In determining the specific rate from the data, it is necessary to take into account the fact that the reaction does not go to completion. At the temperatures used only about 20 per cent decomposition occurred. It has been seen on page 22 that if A and B are initially at a concentration of a, and the equilibrium concentration of the products is x_e, the specific rate of the forward reaction is given by

$$k_1 = \frac{x_e}{2ta(a - x_e)} \ln \frac{x(a - 2x_e) + ax_e}{a(x_e - x)} \tag{27}$$

The value of x_e was known from direct determinations of the equilibrium constant; consequently from the fraction x decomposed at time t the specific rate k_1 can be calculated. In Table 14 are given some results obtained at 410°C; the values of x at various times are given in the second column, and in the third the value of k_1 calculated from the above expression. The bulbs were filled at 0°C and 760 mm pressure, and hence the initial concentration is 1 mole in 22.4 liters, or 4.46×10^{-2} mole per

[1] M. Bodenstein, *Z. physik. Chem.*, **13**, 56 (1894); **22**, 1 (1897); **29**, 295 (1899).

liter; the equilibrium concentration of product, x_e, was 0.938×10^{-2} mole per liter at this temperature.

Subsequently to Bodenstein's investigations the reaction has been studied by a number of workers, some of whose methods may be mentioned briefly. H. A. Taylor[1] used a flow system, the hydrogen iodide being streamed through a heated Pyrex tube of 600 sq cm surface. The fraction of decomposition was found by analyzing the ensuing gas mixture, and from the rate of flow and the volume of the tube the time of contact could be estimated; the specific rate could therefore be calculated. One of the objects of this investigation was to see if the reaction was occurring to an appreciable extent on the walls; on introducing Pyrex glass powder into the tube the rate was very much increased, indicating that under the conditions of the experiments an appreciable amount of the reaction occurred on the surface. However the specific rates obtained by Taylor were about 100 times those of Bodenstein; it therefore appears that Taylor's result may be due to his use of another type of glass, and, as will be seen later, there is good reason to believe that in Bodenstein's work the surface reaction was negligible. A very comprehensive study of the reaction was carried out by Kistiakowsky,[2] who used the same general method as Bodenstein but investigated the reaction over a much wider range of pressures; the concentrations ranged from 0.02 to 7 moles per liter, the latter value corresponding to a pressure of 150 atm. Using a quartz vessel, he found that the reaction was almost entirely homogeneous.

TABLE 14. DECOMPOSITION OF HYDROGEN IODIDE AT 410°C

t, sec	$x \times 10^3$, moles per liter	$k \times 10^1$, liters mole^{-1} sec^{-1}
3,000	2.79	5.08
6,000	4.95	5.04
9,000	6.16	4.59
12,000	7.37	4.89

Reaction between Hydrogen and Iodine. The reverse reaction, between hydrogen and iodine, was studied by Bodenstein using similar methods to those he used for the hydrogen iodide decomposition; hydrogen and iodine were sealed in bulbs, heated at the required temperature, cooled rapidly, and the contents analyzed. It was not possible to seal equimolar amounts, so that the rate expression to be used is

$$\frac{dx}{dt} = k_{-1}\left(a - \frac{x}{2}\right)\left(b - \frac{x}{2}\right) - k_1 x^2 \qquad (28)$$

[1] H. A. Taylor, *J. Phys. Chem.*, **28**, 984 (1924).

[2] G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **50**, 2315 (1928).

where k_1 and k_{-1} are the specific rates for the decomposition and formation, respectively, of hydrogen iodide, a and b are the initial concentrations of hydrogen and iodine, and x is the amount of hydrogen iodide formed at time t. The constants k_1 and k_{-1} are related to the equilibrium constant K by $K = k_1/k_{-1}$, and elimination of k_1 gives

$$\frac{dx}{dt} = k_{-1}\left(a - \frac{x}{2}\right)\left(b - \frac{x}{2}\right) - k_{-1}Kx^2 \tag{29}$$

This can be integrated by the method of partial fractions to give

$$k_{-1} = \frac{2}{mt} \ln \frac{\left(\frac{a + b - m}{1 - 4K} - x\right)(a + b - m)}{\left(\frac{a + b + m}{1 - 4K} - x\right)(a + b + m)} \tag{30}$$

where m is defined by

$$m = [(a + b)^2 - 4ab(1 - 4K)]^{\frac{1}{2}} \tag{31}$$

The constant for the reaction, k_{-1}, can therefore be calculated from the values of x at various times, a, b, and K being known. Measurements were made at a number of initial pressures, and k_{-1} was found to be satisfactorily constant.

Decomposition of Ammonia on the Surfaces of Tungsten and Platinum. As final examples of reactions involving gases will be considered the investigations of Hinshelwood and Burk[1] on the decomposition of ammonia occurring on tungsten and platinum surfaces.

The homogeneous decomposition of ammonia has been shown to occur extremely slowly, except at very high temperatures. Consequently the observed rates of decomposition in the presence of surfaces may be attributed to the surface decompositions alone.

The experimental methods used in these investigations were of the greatest simplicity. For the work with tungsten the reaction vessel was a commercial tungsten-filament lamp, to which were sealed capillary tubes leading to a pump, to the ammonia supply, and to a mercury manometer, the volume of all connections being negligible compared with that of the bulb. The filament was heated electrically to a constant temperature, which was measured by determining its resistance, since the relationship between resistance and temperature is known. The reaction vessel was kept in melting ice, and the change in pressure under these conditions was a measure of the amount of decomposition.

Runs were carried out at different initial ammonia concentrations, some being made after hydrogen had been added initially. Some of the results, obtained at 856°C, are plotted in Fig. 10. It is seen that the addition of

[1] C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 1105 (1925).

hydrogen causes no change in the rate of reaction, in contrast with the behavior found on a platinum surface (see below). It is to be noted that the initial slopes, *i.e.*, initial rates, corresponding to different initial concentrations are the same, indicating that the rate is independent of the ammonia concentration. This conclusion that the reaction is of zero order is supported by the fact that the curves approach linearity more closely than they approach the type of curvature found with first-order reactions. Application of the half-life method leads to the same conclu-

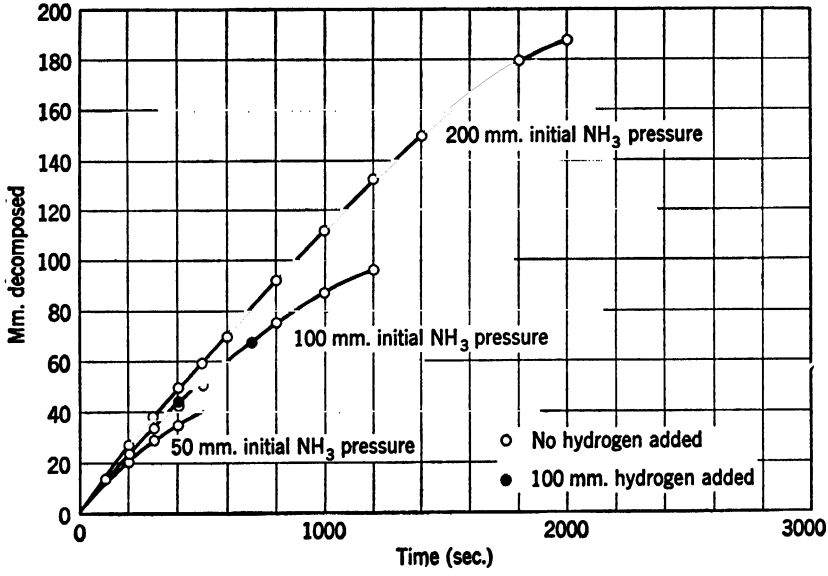


FIG. 10. Pressure-time curves obtained in the decomposition of ammonia on a tungsten surface (Hinshelwood and Burk).

sion: the half lives at 50, 100, and 200 mm initial pressure are found to be in the ratio 1:1.92:3.52. Half lives have been seen to be proportional to a^{1-n}; for a zero-order reaction the predicted ratios would be 1:2:4, while for a first-order reaction the lives would be independent of the initial concentration. The results clearly approximate to zero-order kinetics more closely than to first-order kinetics.

The apparatus used for the study of the decomposition on platinum was somewhat similar: a platinum wire was supported in a bulb and heated electrically, its temperature being kept constant and measured in the same manner as with tungsten. In this case the rate of decomposition was found to be inversely proportional to the initial concentration of hydrogen but independent of the concentration of nitrogen; the rate

equation when there is no initial addition of hydrogen is therefore of the form

$$\frac{dx}{dt} = \frac{k(a - x)^n}{x} \tag{32}$$

where x is the amount of hydrogen formed at time t. The value of n may be found by a modification of the half-life method; in the case of a reaction inhibited by a product it may be shown that the half life varies as a^{2-n}. At 1138°C the half periods corresponding to initial ammonia pressures of 100 and 200 mm were found to be 180 and 360 sec, respectively, *i.e.*, to be in the ratio 1:2. The half life is therefore directly proportional to the initial concentration, which leads to the result that n is equal to unity. The kinetic law obeyed is therefore established as $dx/dt = k(a - x)/x$, and using this, the specific rate k can readily be calculated from the experimental data.

CHAPTER 3

THE MECHANISMS OF ELEMENTARY PROCESSES

As knowledge of the mechanisms of chemical reactions has advanced, it has become increasingly clear that the formation of the final products from the initial reactants always takes place by one or more relatively simple steps in each of which the amount of atomic rearrangement is at a minimum. As a result of this general principle the number of over-all processes which take place in a single stage is quite small; indeed practically all of those which occur in the gas phase will be considered in the next chapter. A large fraction of the work now being carried out in the field of chemical kinetics consists of the elucidation of the individual reaction steps by which chemical changes occur, a matter that will be treated in the latter part of this book. The individual steps which take place are generally spoken of as "elementary" processes, and before proceeding to a discussion of complex reactions some consideration will be given to the characteristics and mechanisms of elementary processes. The theoretical work that has been done on these processes will be treated in the present chapter and in more detail in Chap. 13. The three chapters following the present one are devoted largely to a study of the special features of reactions occurring in the gas phase, in solution, on surfaces, and in the solid state.

Molecularity of an elementary reaction

In considering the mechanisms of elementary reactions, an important question concerns the number of reactant molecules which come together in the course of reaction, forming a complex which directly gives rise to the products of reaction; this number is known as the "molecularity" of the reaction. Whereas the order of a reaction is deduced directly from the experimental results, the molecularity can be determined only on the basis of additional arguments about which there is sometimes some uncertainty.

At first sight it might appear that it would be possible to identify the molecularity of an elementary reaction with its over-all order, *i.e.*, the order which is obtained after due regard has been paid to the influence of substances in excess and of catalysts. In fact such identification is correct except for unimolecular gas reactions, which are not necessarily of the first order: it will be seen later in the present chapter that they become of

the second order at low pressures. If a gas reaction is found to be of the first over-all order under any pressure conditions, it may be inferred that it is unimolecular; if it is second order and becomes first order at higher pressures, it is also unimolecular. There is always some doubt about the molecularity of second-order gas reactions which involve only one reacting gas and which remain of the second order at all pressures, as it is always possible that at higher pressures than those investigated they would become of the first order and hence reveal themselves as unimolecular.

In all other cases the molecularity of an elementary reaction may safely be identified with the over-all order, it being assumed that in establishing the over-all order the influence of every possible reactant has been investigated.

The Arrhenius law

That increasing the temperature frequently causes a marked increase in the rates of reactions has been known for many years; for reactions in solution a useful rough generalization is that the rate is doubled by a rise in temperature of 10°C. In 1887 van't Hoff,[1] arguing on the basis of the variation of the equilibrium constant with the temperature, pointed out that the logarithm of the specific rate of a reaction should be a linear function of the reciprocal of the absolute temperature. This idea was extended by Arrhenius[2] and was successfully applied by him to the data relative to a number of reactions; on account of his work the law, which may be expressed as

$$\log k = B - \frac{A'}{T} \tag{1}$$

where A' and B are constants, is usually referred to as the Arrhenius law.

The arguments of van't Hoff and Arrhenius proceeded as follows: The variation of the equilibrium constant obeys the law

$$\frac{d \ln K_c}{dT} = \frac{E}{RT^2} \tag{2}$$

where K_c is the equilibrium constant expressed in terms of concentrations and E is the energy change. On the hypothesis that equilibrium is dynamic, the equilibrium conditions for a reaction $A + B \rightleftharpoons C + D$ can be formulated by equating the rates of the two opposing reactions,

$$k_1[A][B] = k_{-1}[C][D] \tag{3}$$

[1] J. H. van't Hoff, "Etudes de dynamique chimique," F. Muller and Company, Amsterdam, 1884.

[2] S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

where k_1 and k_{-1} are the second-order specific rates for the reactions. The equilibrium constant is therefore equal to k_1/k_{-1}:

$$\frac{[C][D]}{[A][B]} = \frac{k_1}{k_{-1}} = K_c \tag{4}$$

The reaction isochore [Eq. (2)] may therefore be written as

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_{-1}}{dT} = \frac{E}{RT^2} \tag{5}$$

which may be split into the two equations

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} + I \tag{6}$$

and

$$\frac{d \ln k_{-1}}{dT} = \frac{E_{-1}}{RT^2} + I \tag{7}$$

where $E_1 - E_{-1} = E$. Experimentally it was found that I can be set equal to zero, the rate constant therefore being related to the temperature by the equation

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \tag{8}$$

This integrates to

$$\ln k_1 = -\frac{E_1}{RT} + \text{const.} \tag{9}$$

or

$$k_1 = Ae^{-E_1/RT} \tag{10}$$

where A is a constant. It is usually known as the *frequency factor* of the reaction.[1] If $\ln k_1$ is plotted against $1/T$, a straight line is therefore expected, and its slope is equal to $-E_1/R$. In this way E_1, known as the energy of activation, can readily be determined experimentally. In Fig. 11 is shown a plot of $\log_{10} k$ against $1/T$ for the thermal decomposition of hydrogen iodide.

This result, and Arrhenius's interpretation of it in terms of molecular behavior, is still accepted today as being essentially correct; failure to obey the Arrhenius law is, in fact, taken as evidence that the kinetics are complex. Arrhenius suggested that in order for reaction to occur, the reactant molecules must become activated, and that there exists an equi-

[1] This is not a particularly happy term; A has the same dimensions as the rate constant itself, and is therefore only a frequency for a first-order reaction (see p. 12).

librium between normal and activated molecules. The energy E represents the energy the molecules have to acquire in order to be capable of undergoing reaction and accounts for the high temperature coefficient of the rate, since a rise in temperature increases markedly the proportion of active molecules. This concept was extended along statistical lines by Marcelin,[1] Rice,[2] Trautz,[3] and others.

The collision theory

The interpretation of the factor A occurring in Eq. (10) offered more difficulty. The solution, which was given by W. C. McC. Lewis,[4] was

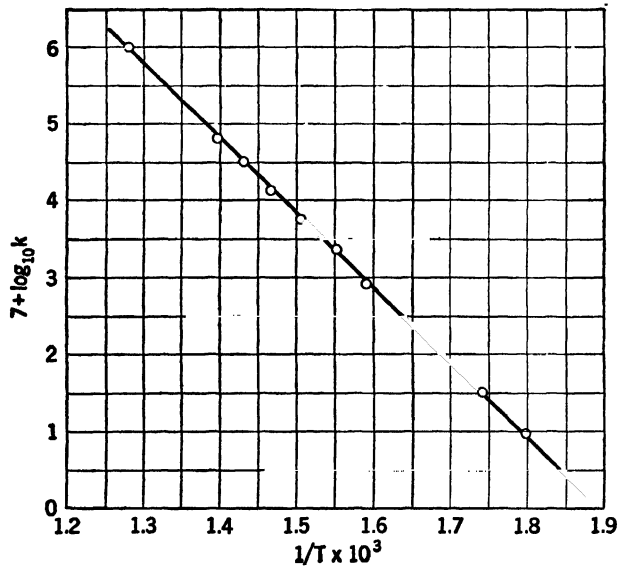


FIG. 11. A plot of $\log_{10} k$ against $1/T$ for the thermal decomposition of hydrogen iodide. The slope is equal to $E/2.303R$, whence $E = 44.0$ kcal.

that, for reactions of higher order than the first, A is equal to the frequency of collisions between the reacting molecules; thus for a reaction between two molecules A and B, the rate in molecular units was expressed as

$$v = ze^{-E/RT} \quad \text{molecules cc}^{-1} \text{ sec}^{-1} \tag{11}$$

[1] A. Marcelin, *Ann. phys.*, **3**, 158 (1915).

[2] J. Rice, *Brit. Assoc. Advancement Sci., Rept.*, 397 (1915).

[3] M. Trautz, *Z. Elektrochem.*, **15**, 692 (1909).

[4] W. C. McC. Lewis, *J. Chem. Soc.*, **113**, 471 (1918); *cf.* K. F. Herzfeld, *Z. Elektrochem.*, **25**, 301 (1919); *Ann. Physik*, **59**, 635 (1919); M. Polanyi, *Z. Elektrochem.*, **26**, 48, 228 (1920).

where z is the number of collisions per second between A and B in 1 cc of gas This frequency of collision is given by kinetic theory as

$$z = n_A n_B \sigma_{AB}^2 \left[8\pi \mathbf{k} T \left(\frac{m_A + m_B}{m_A m_B} \right) \right]^{1/2} \quad \text{molecules cc}^{-1} \text{ sec}^{-1} \quad (12)$$

where σ_{AB} is the average of the molecular diameters of A and B, m_A and m_B are the molecular masses, $\mathbf{k}$ is the Boltzmann constant, and the n's are the concentrations in molecules per cubic centimeter. The physical meaning of Eq. (11) is that the rate is the number of molecules colliding per second and having a joint energy E in excess of the mean energy. Since the rate v is related to the rate constant k by $v = kn_A n_B$, it is evident that

$$k = \sigma_{AB}^2 \left[8\pi \mathbf{k} T \left(\frac{m_A + m_B}{m_A m_B} \right) \right]^{1/2} e^{-E/RT}$$

$$= Ze^{-E/RT} \quad \text{cc molecule}^{-1} \text{ sec}^{-1} \quad (13)$$

where Z, equal to $\sigma_{AB}^2 [8\pi \mathbf{k} T(m_A + m_B)/m_A m_B]^{1/2}$, is known as the collision number; it is the number of collisions per second when there is only one molecule of each reactant per cubic centimeter.

Equation (13) can be written in terms of its temperature-independent part Z', and $T^{1/2}$, so that the rate constant can be written as

$$k = Z' T^{1/2} e^{-E/RT} \quad (14)$$

Taking logarithms,

$$\ln k = \ln Z' + \frac{1}{2} \ln T - \frac{E}{RT} \quad (15)$$

According to this, a plot of $\ln k$ against $1/T$ will not be exactly linear, but normally the departure from linearity is only slight; however a more accurate value of the energy of activation can be obtained by plotting $\ln(k/T^{1/2})$ against $1/T$.

The collision number can readily be calculated using molecular diameters derived from viscosity data, or in other ways, and since E can be determined from the experimental variation of the rate with the temperature, it is easy to test the theory. In many instances the agreement is satisfactory,[1] within a factor of 10 or so. This is true for gas reactions involving relatively simple molecules and for many reactions in solution, particularly those in which at least one of the reactants is a simple molecule or ion. However a number of reactions, especially those involving more complex molecules, take place at rates which are markedly different

[1] *Cf.* E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," p. 71, Oxford University Press, New York, 1947.

from those calculated on the basis of the collision theory. For example, certain gaseous isomerizations take place much more slowly than expected,[1] while the addition of tertiary amines to alkyl iodides in solution frequently proceeds at rates which are 10^{-5} to 10^{-8} of the calculated values.[2] At one time the anomalies in solution were thought to be due to solvent effects, but in some instances the rates were shown to be low in the gas phase also (see Chap. 5). Certain reactions were found to proceed more rapidly than calculated; these include certain reactions of the first order, (which, however, present a separate problem and will be considered later), and some ionic reactions in solution.

In order to account for deviations from the simple collision theory, it was postulated that the number of effective collisions may be less than that given by kinetic theory, since for reaction to take place a critical orientation of the molecules on collision may be necessary. The rate constant was therefore written as

$$k = PZe^{-E/RT} \tag{16}$$

where P is referred to as a *probability*, or *steric*, factor.

Several weaknesses of the collision treatment have become apparent in recent years. In the first place, attempts to correlate the value of P with the structures and properties of the reacting molecules have not been very successful. Secondly, it is hardly possible to interpret on this basis the abnormally high rates that are sometimes observed. Furthermore a logical weakness of the collision treatment becomes apparent when reversible reactions are considered;[3] thus for the reaction

$$A_2 + B_2 = 2AB$$

the rate constant for the forward reaction would be given as

$$k_1 = P_1Z_1e^{-E_1/RT} \tag{17}$$

while that for the reverse reaction is

$$k_{-1} = P_{-1}Z_{-1}e^{-E_{-1}/RT} \tag{18}$$

The equilibrium constant K, equal to k_1/k_{-1}, is therefore given by

$$K = \frac{k_1}{k_{-1}} = \frac{P_1Z_1}{P_{-1}Z_{-1}}\, e^{-(E_1-E_{-1})/RT} \tag{19}$$

[1] G. B. Kistiakowsky and M. Nelles, *Z. physik. Chem., Bodenstein-Festband,* 369 (1931); G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56,** 638 (1934); **57,** 269 (1935); **58,** 766, 1043, 2428 (1936).

[2] C. A. Winkler and C. N. Hinshelwood, *J. Chem. Soc.*, **1147** (1935).

[3] A. E. Stearn and H. Eyring, *J. Chem. Phys.*, **3,** 113 (1937).

However, from thermodynamics the equilibrium constant is equal to

$$K = e^{-\Delta F/RT} \tag{20}$$

$$= e^{\Delta S/R} e^{-\Delta H/RT} \tag{21}$$

where ΔF, ΔS, and ΔH are the increases in free energy, entropy, and heat content. Comparing these expressions for K, it is clear that the terms $e^{-(E_1-E_{-1})/RT}$ and $e^{-\Delta H/RT}$ correspond; consequently the ratio $P_1Z_1/P_{-1}Z_{-1}$ must be equal to $e^{\Delta S/R}$. If the molecules A_2, B_2, and AB are of comparable dimensions, Z_1 will be practically equal to Z_{-1}, so that the entropy term $e^{\Delta S/RT}$ must be approximately equal to the ratio of the probability factors. It is therefore not sufficient to correlate the probability factors with the probability of certain reacting groups being together on collision: they should be interpreted in terms of entropy factors in a precise manner. In view of these unsatisfactory features of the simple collision theory as applied to chemical reactions, a somewhat different point of view will here be presented. Reactions will still be regarded as taking place on collision between reacting molecules, but the nature of a collision will be defined more precisely. As a result the number of collisions, and hence the rate constant, will be calculated with greater accuracy than is possible on the basis of the treatment outlined above.

Equilibrium and rate of reaction

In considering chemical reactions it is important to distinguish clearly between two aspects of the problem: one is concerned with the direction and extent of chemical change, the other with the rate with which it takes place. There is no general connection between these two problems. Two chemical substances, A and B, may react together to give C and D; if A and B are brought together under constant external conditions, they will react at a rate which is a function of their concentrations and which will become less and less as reaction proceeds. Theoretically, equilibrium between A, B, C, and D will be reached only after an infinite time, but in practice it is found that after a certain lapse of time (which in some cases may be extremely long) no further change in the system can be detected. The concentrations will then obey the relationship

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K_c \tag{22}$$

where a, b, c, and d are the numbers of molecules of A, B, C, and D which react according to the stoichiometric equation, and K_c is a constant which does not depend on the concentrations but which does depend on the temperature.

If at a given temperature the equilibrium constant K_c has a high value, it is clear that at equilibrium the concentrations of C and D are higher than those of A and B; A and B have therefore reacted to a considerable extent and may be said to have a high affinity for one another. If on the other hand the constant K_c is a small fraction, there will be little of C and D at equilibrium, and the reacting substances A and B have a low mutual affinity.

The affinity of chemical substances for one another, defined in the above manner, is found to be in no way related to the velocity with which the chemical change takes place. The two molecules may have a very high affinity for one another, but the time for even a very small fraction of the molecules to react may be extremely long. Hydrogen and oxygen, for example, have a very high affinity at ordinary temperatures: the equilibrium is well over on the side of the water, but a mixture of the two gases may be kept for an indefinite period without a measurable amount of reaction taking place.

It is only with the second aspect, the rates of chemical reactions, that this book is primarily concerned; the theory of equilibrium is treated in works on thermodynamics and statistical mechanics. There is, however, a close relationship between the theory of rates and the theory of equilibria, in spite of there being no general connection between equilibrium and rate constants. This is so because molecules undergoing reaction pass through activated states which to a good approximation can be regarded as in equilibrium with the molecules in their normal states. The concentration of activated molecules can therefore be calculated by ordinary equilibrium theory, so that if the probability of the decomposition of activated molecules is known, the rate of reaction can be calculated. The problem of calculating rates therefore resolves itself into two parts: the first is the calculation of the concentrations of activated molecules, the second the calculation of the rates of reaction of the activated molecules. In the following section a brief outline of the statistical-thermodynamical theory of equilibrium will be presented.

Statistical mechanics of chemical equilibrium[1]

According to statistical mechanics, the equilibrium constant for a reaction

$$aA + bB = cC + dD$$

[1] For reviews see R. H. Fowler, "Statistical Mechanics," Cambridge University Press, New York, 1936; R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, New York, 1939; S. Glasstone, "Theoretical Chemistry," D. Van Nostrand Company, Inc., New York, 1946; G. S. Rushbrooke, "Introduction to Statistical Mechanics," Oxford University Press, New York, 1949.

defined by Eq. (22), is equal to

$$K_c = \frac{F_C^c F_D^d}{F_A^a F_B^b} e^{-E_0/RT} \tag{23}$$

where the F's are known as the partition functions of the molecules A, B, C, and D, and E_0 is the energy increase at the absolute zero when a moles of A react with b moles of B to form c moles of C and d moles of D, all substances being in their standard states. The manner of evaluating the partition functions will now be described briefly.

The partition function F for a molecule is defined by

$$F = \sum_i g_i e^{-\epsilon_i/kT} \tag{24}$$

where ϵ_i is the energy, with respect to the zero-point energy, for a given energy level of the molecule, and g_i is the number of states corresponding to that level; the summation is taken over all states, *i.e.*, electronic, translational, rotational, and vibrational. Since these various types of energy are to a good approximation independent of one another, the total energy corresponding to a given energy level may be written as

$$\epsilon_i = e_i + t_i + r_i + v_i \tag{25}$$

where the four terms on the right-hand side represent the four types of energy corresponding to the ith state. The partition function therefore becomes

$$F = \sum_i g_{e,i} e^{-e_i/kT} g_{t,i} e^{-t_i/kT} g_{r,i} e^{-r_i/kT} g_{v,i} e^{-v_i/kT} \tag{26}$$

the g_i having factorized as well as the exponential terms. This equation may be written as

$$F = f_e f_t f_r f_v \tag{27}$$

where f_e, f_t, f_r, and f_v are separate partition functions, each referring to one type of energy. The partition function has thus been factorized, so that each term may be evaluated separately.

The partition function for electronic energy is calulated directly, from the observed electronic levels of the atom or molecule, using the relationship

$$f_e = \sum_i g_{e,i} e^{-e_i/kT} \tag{28}$$

At ordinary temperatures the excited energy levels of an atom or molecule are usually too high to make a significant contribution to the partition function. If the lowest state is a singlet state, the statistical weight g_e is unity, so that if the lowest state is taken as the zero level and all other

levels are sufficiently high, the partition function is approximately unity; as a rough guide it may be assumed that excited electronic levels may be neglected if their energy is more than $4\mathbf{k}T$. For nitric oxide, oxygen, and one or two other molecules the lowest level is not a singlet, so that the partition function is no longer unity.

The partition function for the translational motion of a molecule of mass m having three degrees of translational motion can be shown to be

$$f_t = \frac{(2\pi m\mathbf{k}T)^{3/2}}{\mathbf{h}^3} \tag{29}$$

where $\mathbf{h}$ is Planck's constant. The rotational partition function for a linear molecule, which has only two degrees of rotational freedom, is given by

$$f_r = \frac{8\pi^2 I\mathbf{k}T}{\mathbf{h}^2} \tag{30}$$

where I is the moment of inertia of the molecule; for a homonuclear molecule this function must be divided by 2. For a polyatomic molecule having no axis of symmetry the rotational partition function is given by

$$f_r = \frac{8\pi^2(8\pi^3 ABC)^{1/2}(\mathbf{k}T)^{3/2}}{\mathbf{h}^3} \tag{31}$$

where A, B, and C are the moments of inertia about any three mutually perpendicular axes. This expression also requires modification if the molecule has certain types of symmetry.

The total number of degrees of freedom of a molecule is equal to $3N$, where N is the number of atoms in the molecule. Of this number, three relate to the translational motion, and in the case of a nonlinear molecule three are for rotational energy; the remainder, $3N - 6$, therefore apply to vibrational energy. If the molecule is linear, there are only two degrees of rotational freedom and hence $3N - 5$ degrees of vibrational freedom. In the case of a diatomic molecule there is clearly only one degree of vibrational freedom. The partition function for vibrational motion is equal to

$$f_v = \prod_i (1 - e^{-\mathbf{h}\nu_i/\mathbf{k}T})^{-1} \tag{32}$$

where ν_i is the vibrational frequency in sec^{-1},† the product being taken over all the modes of vibration; *i.e.*, there is a factor corresponding to each of the $3N - 6$ or $3N - 5$ degrees of freedom. For a diatomic molecule the partition function consists of a single function $(1 - e^{-\mathbf{h}\nu/\mathbf{k}T})^{-1}$, while for a

† If wave numbers (ω, cm^{-1}) are provided, they must be multiplied by the velocity of light ($\nu = \omega c$).

polyatomic molecule each of the factors will have its characteristic ν corresponding to the normal mode of vibration to which it is related.

The theory of absolute reaction rates[1]

The treatment of chemical equilibrium in terms of partition functions, making use of relationships like Eq. (23), now has to be extended to the calculation of the rates of chemical reactions. In order for any chemical change to take place, it is necessary for the atoms or molecules involved to come together to form an activated complex. This complex is regarded as being situated at the top of an energy barrier lying between the initial and final states, and the rate of the reaction is controlled by the rate with which the complex travels over the top of the barrier. This type of formulation of the process seems first to have been put forward by Marcelin,[2] who considered the reacting molecules to cross a "critical surface in phase space," and the idea was somewhat further developed by Rodebush[3] and later by O. K. Rice and Gershinowitz.[4] The first calculation of the rates of reactions in terms of specific potential-energy surfaces was done by Pelzer and Wigner[5] who calculated the rate of the reaction between hydrogen atoms and molecules. A particularly clear formulation of the problem was made by Eyring,[6] who has applied his method with considerable success to a large number of physical and chemical processes. A somewhat similar formulation of the problem was made by Polanyi and Evans.[7] The method of Eyring will be employed here, but a simplified development of the basic equation will be given.

Consider a reaction

$$A + B \rightleftharpoons C + D$$

which has proceeded to equilibrium. Under these conditions the activated complexes, which may be denoted as $X^{\ddagger}$, will also be in equilibrium with the reactants and products, and their concentration may therefore be

[1] For a detailed treatment, see S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, Inc., New York, 1941.

[2] A. Marcelin. *Ann. phys.*, **3**, 158 (1915); *cf* A. March, *Physik. Z.*, **18**, 53 (1917); R. C. Tolman, *J. Am. Chem. Soc.*, **42**, 2506 (1920); **44**, 75 (1922); E. P. Adams, *ibid.*, **43**, 1251 (1921).

[3] W. H. Rodebush, *ibid.*, **45**, 606 (1923); *J. Chem. Phys.*, **1**, 440 (1933); **3**, 242 (1935); **4**, 744 (1936).

[4] O. K. Rice and H. Gershinowitz, *ibid.*, **2**, 853 (1934); **3**, 479 (1935); G. B. Kistiakowsky and J. R. Lacher, *J. Am. Chem. Soc.*, **58**, 123 (1936).

[5] H. Pelzer and E. Wigner, *Z. physik. Chem.*, **B**, **15**, 445 (1932).

[6] H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); W. F. K. Wynne-Jones and H. Eyring, *ibid.*, **3**, 492 (1935).

[7] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **31**, 875 (1935); **33**, 448 (1937); **M. Polanyi, *J. Chem. Soc.*, 629 (1937).**

calculated accurately by statistical mechanics in terms of the concentrations of A and B. The assumption is now made that even when equilibrium is not established between A, B, C, and D, the complex $X^{\ddagger}$ is in equilibrium with the reactants A and B. This is an approximation that has been made in practically every theory of chemical change (including collision theory); its justification is largely the success with which it predicts the results of experiments, but in addition it has been found that similar results are given by more rigorous theoretical treatments.[1]

The equilibrium condition may be written as

$$\frac{[X^{\ddagger}]}{[A][B]} = K^{\ddagger} \tag{33}$$

where $K^{\ddagger}$ is the equilibrium constant. As seen in the previous section, this equilibrium constant may be written in terms of the appropriate partition functions,

$$\frac{[X^{\ddagger}]}{[A][B]} = \frac{F^{\ddagger}}{F_A F_B} e^{-E_0/RT} \tag{34}$$

where E_0 is now the difference between the zero-point energy per mole of the activated complexes and that of the reactants. Since this energy is the amount of energy that the reactants must acquire at 0°K before they can react, E_0 is the energy of activation at this temperature. The partition functions in this expression must be evaluated with respect to the zero-point levels of the respective molecules.

As was seen earlier, these functions can be factorized into terms corresponding to translational, rotational, vibrational, and electronic energy. If, for example, the molecule A consists of N_A atoms, there will be $3N_A$ such partition functions, of which three are for translational motion, three for rotational motion (or two if the molecule is linear), and therefore $3N_A - 6$ for vibrational motion ($3N_A - 5$ for a linear molecule). The same is true for the activated complex, which consists of $N_A + N_B$ atoms, giving $3(N_A + N_B) - 6$ vibrational terms if the molecule is nonlinear. One of these vibrational terms is of a different character from the rest, since it corresponds to a very loose vibration which allows the complex to dissociate into the products C and D. For this one degree of freedom one may therefore employ, in place of the ordinary factor $(1 - e^{-h\nu/kT})^{-1}$, the value of this function calculated in the limit at which ν tends to zero. This is evaluated by expanding the exponential and taking only the first term,

$$\lim_{\nu \to 0} \frac{1}{1 - e^{-h\nu/kT}} = \frac{1}{1 - [1 - (h\nu/kT)]} = \frac{kT}{h\nu} \tag{35}$$

[1] B. J. Zwolinski and H. Eyring, *J. Am. Chem. Soc.*, **69**, 2702 (1947).

The equilibrium constant may therefore be expressed by including this term $\mathbf{k}T/\mathbf{h}\nu$ and replacing $F^{\ddagger}$ by $F_{\ddagger}$, which now refers only to $3(N_A + N_B) - 7$ degrees of vibrational freedom [$3(N_A + N_B) - 6$ for a linear complex]; the resulting expression is

$$\frac{[X^{\ddagger}]}{[A][B]} = \frac{F_{\ddagger}(\mathbf{k}T/\mathbf{h}\nu)}{F_A F_B} e^{-E_0/RT} \tag{36}$$

This expression rearranges to

$$\nu[X^{\ddagger}] = [A][B] \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_{\ddagger}}{F_A F_B} e^{-E_0/RT} \tag{37}$$

The frequency ν is the frequency of vibration of the activated complexes in the degree of freedom corresponding to their decomposition; it is therefore the frequency of decomposition. The expression on the left-hand side of Eq. (37) is therefore the product of the concentration of complexes $X^{\ddagger}$ and the frequency of their decomposition; it is therefore the rate of reaction, which is thus given by the expression on the right-hand side of the equation, *viz.*,

$$v = [A][B] \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_{\ddagger}}{F_A F_B} e^{-E_0/RT} \tag{38}$$

The result that the rate is proportional to the product $[A][B]$ arose from the assumption that the activated complex is composed of one molecule of A and one of B; in the more general case of a complex composed of $A_a B_b \cdots$, the rate would be proportional to $[A]^a[B]^b \cdots$. The molecularity of a reaction is in fact equal to the number of reactant molecules that occur in the activated complex.

The specific rate of the reaction, the rate of which is given by Eq. (38), is given by

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_{\ddagger}}{F_A F_B} e^{-E_0/RT} \tag{39}$$

The quantity $\mathbf{k}T/\mathbf{h}$ which appears in these expressions is of great importance in rate theory; it has the dimensions of a frequency, and its value is about 6×10^{12} sec^{-1} at 300°K.

The problem of calculating the specific rate has thus been reduced to that of evaluating the partition functions for the normal and activated states; for this to be done, the nature of the activated complex clearly must be known or be postulated. In principle, the structure of the activated complex can be determined by the methods of quantum mechanics, as will be discussed in Chap. 13, but the procedure is laborious and not very accurate; however, in many cases the structure of the activated complex

can be estimated with sufficient accuracy on the basis of our general knowledge of molecular structure, and examples in which this is done will be given in later chapters.

Although the theory of absolute reaction rates outlined above is closely linked with the theory of chemical equilibrium, it is important to realize that equilibrium theory alone can give no information about rates. In the present application, equilibrium theory is concerned solely with the calculation of the concentration of activated complexes in terms of those of the reactants; additional theory was required to deal with the question of the frequency with which they decompose.

The Transmission Coefficient. To allow for the possibility that not every activated complex reaching the top of the potential-energy barrier is converted into a reaction product, it is convenient to introduce a "transmission coefficient" κ, the specific rate being written as

$$k = \kappa \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_{\ddagger}}{F_A F_B} e^{-E_0/RT} \tag{40}$$

The function

$$\frac{F_{\ddagger}}{F_A F_B} e^{-E_0/RT}$$

may be regarded as a modified equilibrium constant between the normal and activated states, the modification being the removal of the vibrational factor for the decomposition of the complex. Denoting this equilibrium constant by K^*, the rate expression becomes

$$k = \kappa \frac{\mathbf{k}T}{\mathbf{h}} K^* \tag{41}$$

This expression has been derived on the assumption that the specific reaction rate is expressed in terms of concentrations; under these conditions K^* is a concentration equilibrium constant. If pressure units are employed, the same expression holds, but K^* is now a pressure equilibrium constant. The expressions involving partition functions are, however, valid only for concentration units.

For a great many reactions the transmission coefficient is equal to unity, which means that every activated complex becomes a product; there are, however, two important classes of reactions for which the coefficient may be considerably less than unity. The first comprises bimolecular atom recombinations in the gas phase and the reverse decompositions of diatomic molecules. When two atoms collide in the gas phase, there is no energy of activation, and an activated complex may therefore be said to be formed on every collision; however the resulting molecule still contains, largely as vibrational energy, the energy of the initial atoms and will

therefore decompose in the period of its first vibration; the transmission coefficient of such a reaction is therefore extremely low and would be zero except for the possibility that the complex loses some of its energy by radiation. If on the other hand the complex is formed in the presence of a "third body," which may be a gas molecule or part of a surface, the energy may be removed by the third body, and the product is therefore stabilized; the transmission coefficient may then approach unity. In the case of the decomposition of a diatomic molecule into atoms, a third body is similarly necessary in order to provide the molecule with the energy required for decomposition. The effectiveness of third bodies is discussed in Chap. 13.

The second class of reactions in which the transmission coefficient may be appreciably less than unity comprises those in which there is a change from one type of electronic state to another. A certain number of reactions are known in which there is a transition between states of differing multiplicities. Such "electronic switches" occur with only a low probability, and the transmission coefficient assigned to the reaction takes account of this. In the case of certain cis-trans isomerizations it appears that there are two transitions of this kind, the first from a singlet to a triplet state, and the second from the triplet to a singlet; the reactions consequently occur with a low transmission coefficient and hence with a low frequency factor. Processes of this type are discussed further in Chap. 13.

Reactions between Atoms.[1] The first example to which the general theory of absolute reaction rates will be applied is a reaction between two atoms A and B.† The activated complex will in this case be the diatomic molecule AB, which has three degrees of translational freedom and two of rotational; if it were a normal diatomic molecule, it would have one degree of vibrational freedom, but as it is an activated complex, this corresponds to decomposition and is therefore omitted. The partition function $F_\ddagger$, with this omission, is therefore

$$F_\ddagger = \frac{[2\pi(m_A + m_B)\mathbf{k}T]^{3/2}}{\mathbf{h}^3} \frac{8\pi^2 I \mathbf{k}T}{\mathbf{h}^2} \tag{42}$$

where m_A and m_B are the atomic masses and I is the moment of inertia of the diatomic complex. The first term in this expression is the contribution from the three degrees of translational freedom, while the second is for

[1] *Cf.* H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 1536 (1935); **32**, 178 (1936); C. N. Hinshelwood, *J. Chem. Soc.*, 635 (1937); R. P. Bell, *Ann. Repts. on Progress Chem. (Chem. Soc., London)*, **36**, 82 (1939).

† The question of the necessity for a third body in atomic reactions is ignored in the present section.

rotation. If σ_{AB} is the distance between the centers of the atoms in the activated complex, the moment of inertia is given by

$$I = \sigma_{AB}^2 \frac{m_A m_B}{m_A + m_B} \tag{43}$$

The atoms A and B have only translational degrees of freedom, so that the respective partition functions are

$$F_A = \frac{(2\pi m_A \mathbf{k}T)^{3/2}}{\mathbf{h}^3} \tag{44}$$

and

$$F_B = \frac{(2\pi m_B \mathbf{k}T)^{3/2}}{\mathbf{h}^3} \tag{45}$$

If the transmission coefficient κ is taken as unity, the specific rate of the reaction is therefore [*cf.* eq. (39)]

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_\ddagger}{F_A F_B} e^{-E_0/RT} \tag{46}$$

$$= \sigma_{AB}^2 \left[8\pi \mathbf{k}T \left(\frac{m_A + m_B}{m_A m_B} \right) \right]^{1/2} e^{-E_0/RT} \tag{47}$$

It was seen in Eq. (13) that an identical expression was given by collision theory, on the assumption that the atoms are hard spheres having diameters σ_A and σ_B such that $\frac{1}{2}(\sigma_A + \sigma_B)$ is equal to σ_{AB}; Eq. (12) in fact gave the total number of collisions at unit concentration, and at once gives Eq. (47) if the fraction $e^{-E_0/RT}$ of the collisions are sufficiently energetic to lead to reaction.

Agreement between the two treatments is not, however, found when reactions between molecules are considered, as will now be seen.

Reactions between Molecules.[1] The treatment given for atoms can be extended to reactions between molecules of any complexity; however, the equations become rather involved, and a simplified treatment is to be preferred. For this purpose the approximation will be made of regarding the partition function for each type of energy as consisting of equal terms, one for each degree of freedom. This procedure is justified from the point of view of the numerical values of the partition functions, which do not vary to any great extent with the molecular masses or moments of inertia; thus partition functions for a single degree of translational freedom are generally of the order of 10^8, while those for rotation are often between 10 and 100; those for vibration are close to unity except at elevated temperatures.

[1] *Cf.* Bawn, *loc. cit.*

Denoting the contributions of single translational, rotational, and vibrational degrees of freedom as f_T, f_R, and f_V, the total partition function F for a molecule may be written as

$$F = f_T^t f_R^r f_V^v \tag{48}$$

where t, r, and v are the numbers of the degrees of freedom contributing. For the case of reaction between two atoms, already considered,

$$F_A = f_T^3, \qquad F_B = f_T^3, \qquad F_\ddagger = f_T^3 f_R^2 \tag{49}$$

so that the specific rate of the reaction is given by

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_\ddagger}{F_A F_B} e^{-E_0/RT} \tag{50}$$

$$= \frac{\mathbf{k}T}{\mathbf{h}} \frac{f_R^2}{f_T^3} e^{-E_0/RT} \tag{51}$$

If the general case is now considered, where A and B are complex nonlinear molecules containing N_A and N_B atoms, respectively,

$$F_A = f_T^3 f_R^3 f_V^{3N_A-6} \tag{52}$$

$$F_B = f_T^3 f_R^3 f_V^{3N_B-6}$$

and

$$F_\ddagger = f_T^3 f_R^3 f_V^{3(N_A+N_B)-7} \tag{53}$$

the activated complex having one degree of vibrational freedom less than a normal molecule with $N_A + N_B$ atoms. The rate constant is now found to be

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{f_V^5}{f_T^3 f_R^3} e^{-E_0/RT} \tag{54}$$

The specific rate therefore differs from that obtained in the atomic case by the factor $(f_V/f_R)^5$; the collision theory, by treating the molecules as hard spheres in all cases, is therefore in error by this factor. Since f_V is usually of the order of unity, while f_R may be from 10 to 100 in the case of a complex molecule, the ratio f_V/f_R is 10^{-1} to 10^{-2}, so that $(f_V/f_R)^5$ is 10^{-5} to 10^{-10}. Reactions between complex molecules may therefore be expected to proceed very much more slowly than is calculated on the basis of collision theory, and this is in fact found to be the case, both in the gas phase and in solution. With less complex reacting species the discrepancy is not as great; thus with an atom and a diatomic molecule, forming a nonlinear activated complex, the factor is f_V/f_R, *i.e.*, 10^{-1} to 10^{-2}.

When the specific rates of bimolecular reactions are calculated using

molecular units, the results are in the units cubic centimeters per molecule per second; for comparison with experiment these may be converted into liters per mole per second. It is convenient to express both calculated and observed specific rates in the form $Ae^{-E/RT}$, where E is the energy of activation and A is known as the frequency factor; A has the same units as the specific rate. For reactions between relatively simple molecules, A generally has a value of the order of 10^9 to 10^{11} liters per mole per second but for reactions between complex molecules may be as low as 10^5. For unimolecular reactions, A has the units sec^{-1}; its magnitude will be considered later. The case of trimolecular reactions will be considered in the next chapter.

Thermodynamical formulation of reaction rates

The equilibrium constant K for a chemical reaction is related to the *standard* free energy increase ΔF by the equation

$$-\Delta F = RT \ln K \tag{55}$$

It is clear from this equation that the sign of ΔF determines whether K is greater or less than unity; if, for example, ΔF is positive, K is less than unity, and the equilibrium consequently favors the reactants A and B rather than the products. The equation may be expressed by the qualitative statement that molecules tend to react if by so doing they approach a state of lower free energy; the free energy is therefore the analogue of the potential energy of a mechanical system, which tends to assume a position of minimum potential energy.

The analogy with mechanical systems can to some extent be extended to the problem of the rates of chemical reactions. A mechanical system can pass to a region of lower potential energy only if it is not separated from it by a region of higher energy; in a similar way the progress of a chemical system to a system of lower free energy will be inhibited if the process involves a preliminary change to a state of higher free energy. However the analogy must not be pursued too far, as it would imply a *zero* rate of reaction in the case of an intermediate state of higher free energy. The difference between the two systems is due to the marked statistical fluctuations in the energies of individual molecules; these do not occur to an appreciable degree in bulk matter. The molecular situation may be represented as in Fig. 12, which represents schematically the standard free energies of the reactants $A + B$, of the products $C + D$, and of the intermediate complex represented by $X^{\ddagger}$. The change from $A + B$ to $C + D$ involves a decrease of standard free energy, so that the equilibrium, when attained, favors $C + D$. Passage from $A + B$ to $X^{\ddagger}$ involves an increase in standard free energy, $\Delta F_1^{\ddagger}$, while the passage

from $X^{\ddagger}$ to $C + D$ involves a decrease, $-\Delta F^{\ddagger}_{-1}$; these two free-energy changes are related to the over-all decrease in standard free energy, $-\Delta F$, by

$$\Delta F = \Delta F^{\ddagger}_{1} - \Delta F^{\ddagger}_{-1} \tag{56}$$

By collisions with other molecules the reacting molecules A and B may acquire sufficient joint free energy to reach the activated state $X^{\ddagger}$, which can then dissociate into C and D. The greater the free-energy increase $\Delta F^{\ddagger}_{1}$, the less is the probability of the formation of $X^{\ddagger}$, and the lower will be the rate of reaction. It is clear from this point of view that the activated complex is the state of maximum free energy during the course of reaction, rather than of maximum total energy as envisaged by Arrhenius. Frequently the configuration of maximum free energy corresponds fairly closely to that of maximum total energy, but a number of important exceptions are known.

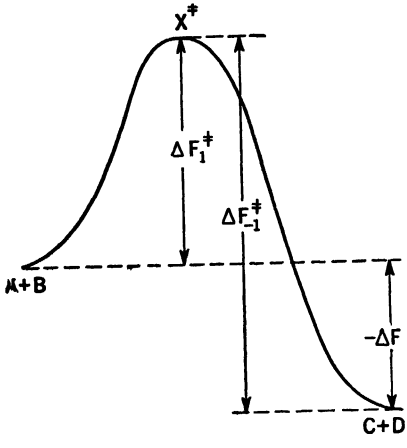


FIG. 12. Relative free energies of reactants, products, and activated complex.

The equilibrium constant $K^{\ddagger}_{1}$ defined by $[X^{\ddagger}]/[A][B]$ is related to the standard-free-energy change $\Delta F^{\ddagger}_{1}$ by

$$-\Delta F^{\ddagger}_{1} = RT \ln K^{\ddagger}_{1} \tag{57}$$

Similarly for the reverse reaction between C and D, for which $K^{\ddagger}_{-1}$ is equal to $[X^{\ddagger}]/[C][D]$,

$$-\Delta F^{\ddagger}_{-1} = RT \ln K^{\ddagger}_{-1} \tag{58}$$

At complete equilibrium between A, B, C, D, and $X^{\ddagger}$

$$\frac{[C][D]}{[A][B]} = K = \frac{K^{\ddagger}_{1}}{K^{\ddagger}_{-1}} \tag{59}$$

$$= e^{-(\Delta F^{\ddagger}_{1} - \Delta F^{\ddagger}_{-1})/RT} \tag{60}$$

$$= e^{-\Delta F/RT} \tag{61}$$

using Eq. (56). This is the required expression for ΔF in terms of the concentrations of A, B, C, and D.

The standard-free-energy change ΔF for the over-all process is related to the heat (ΔH) and entropy (ΔS) changes by

$$\Delta F = \Delta H - T\,\Delta S \tag{62}$$

so that the equilibrium constant K is given by

$$K = e^{-\Delta F/RT} = e^{\Delta S/R} e^{-\Delta H/RT} \tag{63}$$

Similarly for the change from $A + B$ to $X^\ddagger$,

$$\Delta F_1^\ddagger = \Delta H_1^\ddagger - T\,\Delta S_1^\ddagger \tag{64}$$

and

$$K_1^\ddagger = e^{-\Delta F_1^\ddagger/RT} = e^{\Delta S_1^\ddagger/R} e^{-\Delta H_1^\ddagger/RT} \tag{65}$$

For the reverse reaction between C and D,

$$\Delta F_{-1}^\ddagger = \Delta H_{-1}^\ddagger - T\,\Delta S_{-1}^\ddagger \tag{66}$$

so that

$$K_{-1}^\ddagger = e^{-\Delta F_{-1}^\ddagger/RT} = e^{\Delta S_{-1}^\ddagger/R} e^{-\Delta H_{-1}^\ddagger/RT} \tag{67}$$

Since $K = K_1^\ddagger/K_{-1}^\ddagger$, it is easily seen that

$$\Delta S = \Delta S_1^\ddagger - \Delta S_{-1}^\ddagger \tag{68}$$

and

$$\Delta H = \Delta H_1^\ddagger - \Delta H_{-1}^\ddagger \tag{69}$$

The specific rate for the reaction between A and B has been seen on page 69 [Eq. (41)] to be given by

$$k_1 = \frac{\mathbf{k}T}{\mathbf{h}} K_1^* \tag{70}$$

(taking the transmission coefficient as unity) where the equilibrium constant K_1^* differs from that used in the present section by lacking a term corresponding to the degree of freedom for decomposition. Since this term involves the entropy and not the heat, we may write

$$-RT \ln K_1^* = \Delta F_1^* = \Delta H_1^\ddagger - T\,\Delta S_1^* \tag{71}$$

where ΔF_1^* and ΔS_1^* differ from $\Delta F_1^\ddagger$ and $\Delta S_1^\ddagger$ by a small amount owing to the removal of this degree of freedom. This equation rearranges to

$$K_1^* = e^{\Delta S_1^*/R} e^{-\Delta H_1^\ddagger/RT} \tag{72}$$

so that the specific rate is equal to

$$k_1 = \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S_1^*/R} e^{-\Delta H_1^\ddagger/RT} \tag{73}$$

On taking logarithms, one obtains

$$\ln k_1 = \ln \left(\frac{\mathbf{k}}{\mathbf{h}} e^{\Delta S_1^{\ddagger}/R} \right) + \ln T - \frac{\Delta H_1^{\ddagger}}{RT} \tag{74}$$

If, as is usually the case, ΔS_1^* does not vary greatly with the temperature, and since ln T is usually insignificant compared with $\Delta H_1^{\ddagger}/RT$, a plot of ln k_1 against $1/T$ will give an approximate straight line of slope $-\Delta H_1^{\ddagger}/R$.

Equation (74) is seen to resemble the corresponding equation [Eq. (15)] obtained on the basis of collision theory; however the temperature now appears as ln T instead of as $\frac{1}{2}$ ln T, and the function $(\mathbf{k}/\mathbf{h})e^{\Delta S_1^{\ddagger}/R}$ replaces the term Z'.

The idea of introducing an entropy term into the rate equation is really the logical extension of Arrhenius's concept of splitting the reaction isochore into two parts, one for the forward and the other for the reverse reaction. Equations of the form

$$k = Ae^{-\Delta F_{\ddagger}^0/RT} \tag{75}$$

$$= Ae^{\Delta S^*/R} e^{-\Delta H^{\ddagger}/RT} \tag{76}$$

were first proposed many years ago,[1] and in particular a modification to the collision theory of the form

$$k = Ze^{\Delta S^*/R} e^{-\Delta H^{\ddagger}/RT} \tag{77}$$

was proposed by LaMer[2] to account for the variation with temperature of the experimental activation energies of a number of reactions.

Unimolecular reactions

Since unimolecular reactions present some special features, the present section will be devoted to them. A unimolecular reaction is one in which the activated complex consists of a single, activated, reactant molecule and is to be distinguished from a bimolecular and a trimolecular reaction, in which two and three molecules, respectively, are united in the activated complex. Unimolecular reactions are of the first order under certain circumstances, but, as will be seen later, they become of the second orde at low pressures.

The history of unimolecular changes has been a somewhat confused one, and even today some important details of the theoretical treatment are

[1] P. Kohnstamm and F. E. C. Scheffer, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, **13**, 789 (1911); F. E. C. Scheffer and W. F. Brandsma, *Rec. trav. chim.*, **45**, 522 (1926); W. F. Brandsma, *ibid.*, **47**, 94 (1928); **48**, 1205 (1929).

[2] V. K. LaMer, *J. Chem. Phys.*, **1**, 289 (1933); V. K. LaMer and M. L. Miller, *J. Am. Chem. Soc.*, **57**, 2674 (1935); see also E. A. Moelwyn-Hughes, *Proc. Roy. Soc (London)*, **A, 164**, 295 (1938).

not fully understood. For a long time no unimolecular reaction was known, and it was generally held that none existed. A number of organic decompositions were then found to be of the first order, as was the decomposition of nitrogen pentoxide. These reactions were at first regarded as elementary processes, and the general theory of unimolecular reactions was applied to them directly; however, it is now known that only a very small number of unimolecular reactions (indeed of any reactions) proceed in an elementary fashion. The decomposition of organic molecules, for example, frequently proceeds by two mechanisms which take place side by side: one is the direct rearrangement of the molecules to form the products of the reaction, and the other is the dissociation of the molecules into free radicals which may give rise to a chain of reactions. Under certain circumstances the order of the over-all chain process may be the first, and the products may be identical with those formed by direct rearrangement; in such a case the reaction appears to be elementary and can be detected as a complex reaction only by the use of special techniques to be described later. In other cases the order of the chain process may be different from unity, and different products may be formed; it is then evident from the kinetics that the reaction is not simple.

A few reactions are known in which the occurrence of free radicals seems to be very unlikely; these include certain rearrangements and isomerizations. In other reactions, such as the decomposition of acetaldehyde, the fraction of decomposition that takes place by means other than direct rearrangement is fairly small. The theory of elementary unimolecular reactions can be applied to the former group of reactions without reservations and to the latter with very little error. It is also applicable to such individual steps in chain mechanisms as proceed in a unimolecular fashion.

As soon as a few unimolecular reactions had been discovered, some difficulty arose as to the manner in which the molecules became activated. The reactions that were known were assumed to be elementary—probably without serious error—and it appeared that activation by collisions would give rise to second-order kinetics, the number of collisions being proportional to the square of the concentration. At the time it was believed that activation was brought about by the absorption of radiation, and it was suggested in 1919 by Perrin[1] that the existence of unimolecular reactions was further evidence for this theory. Since the specific rate of a unimolecular reaction in the gas phase is independent of the pressure, it appeared that a gas could be expanded to infinite volume and continue to react at the same rate; collisions can no longer be responsible for the activation, and the radiation theory appeared to offer the only alternative explanation.

[1] J. Perrin, *Ann. phys.*, (9), **11**, 1 (1919).

The error in Perrin's argument is that actually the specific rate of a unimolecular reaction does not remain constant if the gas is expanded to a very large volume, although this fact was discovered only some time later. In the meantime Lindemann[1] showed how it is possible for activation by collision to give rise to first-order kinetics. If the activated molecules decompose only slowly compared with the rate with which they are deactivated, a stationary concentration of them may be built up, and since the activated molecules are in equilibrium with the normal molecules, their concentration will be proportional to that of the normal molecules. The rate of reaction, being proportional to the concentration of activated molecules, will thus be proportional to the concentration of normal molecules, *i.e.*, the reaction will be of the first order. This situation, however, will no longer exist at sufficiently low pressures; if the collisions can no longer maintain a supply of activated molecules, the rate of the reaction will depend on the rate of activation, *i.e.*, will be proportional to the square of the concentration of reacting molecules.

This may be formulated mathematically as follows: The process of activation by collision may be represented by

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

where A represents a normal reactant molecule and A^* an activated molecule. The decomposition of the activated molecule may be represented by

$$A^* \rightarrow B + C$$

and the rate of this process is equal to $k_2[A^*]$, where k_2 is the specific rate of this reaction. The rate of activation is given by $k_1[A]^2$, and the rate of deactivation by $k_{-1}[A^*][A]$, where k_1 and k_{-1} are the specific rates corresponding to the two processes. Since the concentration of A^* is small, the rate of its change as reaction proceeds will be small; consequently the rate of its formation may be set equal to the sum of the rates of decomposition and deactivation,

$$k_1[A]^2 = k_2[A^*] + k_{-1}[A^*][A] \tag{78}$$

Solution of this equation for $[A^*]$ gives

$$[A^*] = \frac{k_1[A]^2}{k_2 + k_{-1}[A]} \tag{79}$$

The rate of the reaction is therefore given by

$$-\frac{d[A]}{dt} = k_2[A^*] = \frac{k_1 k_2[A]^2}{k_{-1}[A] + k_2} \tag{80}$$

[1] F. A. Lindemann, *Trans. Faraday Soc.*, 17, 598 (1922).

At sufficiently high pressures the term $k_{-1}[A]$ is much greater than k_2, which can therefore be neglected; under these conditions the rate is given by

$$-\frac{d[A]}{dt} = \frac{k_1 k_2}{k_{-1}}[A] \tag{81}$$

so that the reaction is of the first order. At low pressures, on the other hand, $k_{-1}[A]$ will be negligible compared with k_2 and can be neglected; the rate equation then reduces to

$$-\frac{d[A]}{dt} = k_1[A]^2 \tag{82}$$

so that the reaction is now of the second order.

Such a change from first-order to second-order kinetics as the pressure is lowered has been observed experimentally in a number of instances, both for simple and for complex reactions. The evidence is therefore against the radiation theory and in favor of Lindemann's extension of the theory of collisional activation to unimolecular processes.

The change in the order of reaction on lowering the pressure can be considered from another point of view. Suppose that a first-order rate coefficient k^1 is calculated from the data, whether or not the reaction is truly of the first order; this would be defined by

$$-\frac{d[A]}{dt} = k^1[A] \tag{83}$$

It follows from Eq. (80) that

$$k^1 = \frac{k_1 k_2[A]}{k_{-1}[A] + k_2} \tag{84}$$

whence

$$\frac{1}{k^1} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1[A]} \tag{85}$$

A plot of $1/k^1$, obtained from the experimental data, against $1/[A]$ should therefore give a straight line, the slope of which would give the value of $1/k_1$; in fact, as will be seen, deviations from linearity occur and require a modification of the original theory. If k^1 is plotted against $[A]$, a curve of the form of Fig. 13 is obtained; k^1 is constant at the higher pressures but falls at lower ones.

Before turning to a discussion of the refinements of the Lindemann theory, reference will be made to another hypothesis which was put forward to account for the method of activation in unimolecular processes; this was the chain theory of Christiansen and Kramers.[1] The suggestion was

[1] J. A. Christiansen and F. Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

that the energy liberated in each single chemical transformation can activate a fresh molecule of reactant; in this way a new activated molecule replaces each activated molecule removed by chemical transformation. By this mechanism the active molecules are maintained at a constant fraction of the total concentration of the reactant molecules, so that the reaction is of the first order.

This hypothesis had some difficulties; it was necessary, for example, to introduce the rather arbitrary assumption that only reactant molecules can be activated by collision with products, since otherwise the rate would fall off as the products accumulated and took a greater share of the energy of reaction. It is now known that specific energy transfers of this kind do not take place efficiently; in general, the energy liberated on reaction becomes dissipated into translational energy and would not pass exclusively into the reactant molecules. However this idea of an "energy chain" proved most fruitful in pointing to another type of chain reaction, involving atoms and free radicals, which is important in a great many reactions.

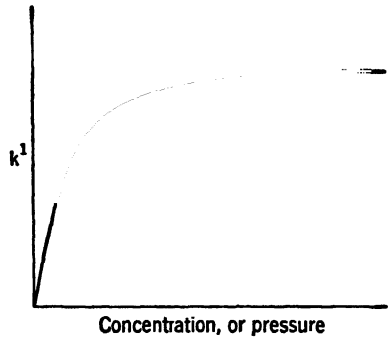


FIG. 13. The variation of k^1, the first-order specific rate, with the concentration, for a unimolecular reaction.

One difficulty that was felt in connection with the Lindemann theory of unimolecular processes was that in some instances the rate of reaction seemed to be greater than could be accounted for according to the simple collision theory. In the region of high pressures, where the kinetics are first-order, the rate of activation by collision must be greater than the rate of reaction, since otherwise the equilibrium concentration of activated molecules could not be maintained. In some instances, however, the kinetics remained of the first order down to a pressure at which, according to collision theory, the rate of activation would not be sufficient to maintain the concentration of active molecules. This difficulty was surmounted by the explanation[1] that the rate of activation of a complex molecule may be much higher than that for a simple one, since the probability that it has an energy greater than E is

$$\frac{(E/RT)^{s-1}}{(s-1)!}\, e^{-E/RT} \tag{86}$$

instead of $e^{-E/RT}$, which is the case for a simple molecule; here s represents

[1] G. N. Lewis and D. F. Smith, *J. Am. Chem. Soc.*, **47**, 1508 (1925); C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 113**, 230 (1927); R. H. Fowler and E. K. Rideal, *ibid.*, 570 (1927).

the number of degrees of vibrational freedom that may contribute to the energy of activation. The rate of activation is therefore given by

$$v = [A]^2 Z \frac{(E/RT)^{s-1}}{(s-1)!} e^{-E/RT} \tag{87}$$

where Z is the collision number. With suitable values of s this expression is considerably greater than the simple expression, and it was usually found to be possible to explain the rates of unimolecular reactions using values of s which were consistent with the actual number of degrees of vibrational freedom in the molecule.

One reaction was an apparent exception in this respect; this was the decomposition of nitrogen pentoxide, which is found to remain of the first order down to extremely low pressures, at which even the improved theory was inadequate to account for the rate of activation. Various explanations of this have been proposed,[1] and the correct one appears to be that of Ogg,[2] who has shown that the mechanism of the reaction is a complex one (see p. 222).

This explanation of the enhanced rate of activation of a complex molecule is the classical equivalent of the modern treatment of chemical processes in terms of the partition functions of the excited and normal molecules; a quantum-mechanical treatment of the problem has recently been worked out by Slater.[3] The rate of activation of a complex molecule may be written as

$$v = [A]^2 \frac{\mathbf{k}T}{\mathbf{h}} \frac{(f_T^3 f_R^3 f_V^{3N-7})_\ddagger}{(f_T^3 f_R^3 f_V^{3N-6})_A} e^{-E_0/RT} \tag{88}$$

the normal molecules and the activated ones being taken to be nonlinear molecules containing N atoms. The translational terms are identical in initial and activated states, and the rotational ones are nearly so; the vibrational factors are greater in the activated than in the normal state, so that the rate of activation is greater than

$$[A]^2 \frac{\mathbf{k}T}{\mathbf{h}} e^{-E_0/RT}$$

This rate constant is considerably greater than that corresponding to simple collision theory, which was seen on page 73 to give a frequency factor of $(\mathbf{k}T/\mathbf{h})f_R^2/f_T^3$; since f_T is of the order of 10^8 and f_R is 10 to 100, it is clear that the rate of activation of a complex molecule may be very much greater than is given by simple collision theory.

[1] For example, Fowler and Rideal, *loc. cit.*

[2] R. A. Ogg, *J. Chem. Phys.*, **15**, 337 (1947).

[3] N. B. Slater, *Proc. Roy. Soc.* (*London*), **A, 194**, 112 (1948).

A further refinement of the original Lindemann theory was necessary to account for the fact that, as referred to above, a plot of $1/k^1$ against $1/[A]$ does not give a straight line, as predicted by the theory, but shows a curvature (see Fig. 14). The experimental line is seen to agree with the theoretical at high values of $1/[A]$, *i.e.*, at low pressures, but at high pressures the rate is greater than the theory would predict. The explanation put forward to account for this[1] is that the specific rate k_2 for the decomposition of the active molecules increases with the energy possessed by the molecule in its various degrees of freedom; consequently, at high pressures, where there is a greater number of highly activated molecules, the rate will be increased. The larger the energy possessed by the excited molecule, the greater is the chance that it passes into the bond that is to be broken, and hence the greater is the rate of the decomposition. The statistical weight of a system of s degrees of vibrational freedom containing j quanta of vibrational energy is equal to the number of ways in which j objects can be divided among s boxes, each of which can contain any number; the number of such ways is

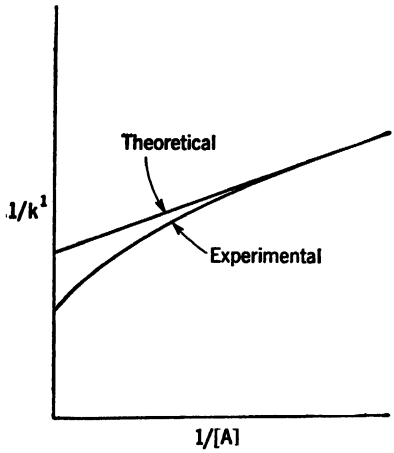


FIG. 14. The variation of $1/k^1$ with $1/[A]$, for a unimolecular reaction.

$$\frac{(j+s-1)!}{j!(s-1)!}$$

The statistical weight for states in which the s oscillators have j quanta among them and a particular one has m quanta is similarly

$$\frac{(j-m+s-1)!}{(j-m)!(s-1)!}$$

The probability that a particular oscillator has m quanta when all s oscillators have j quanta is the ratio of these,

$$\frac{(j-m+s-1)!j!}{(j-m)!(j+s-1)!}$$

which is approximately equal to

$$\left(\frac{j-m}{j}\right)^{s-1}$$

[1] O. K. Rice and H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617 (1927); **50**, 617 (1928) L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928); L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Chap. V, Reinhold Publishing Corporation, New York, 1932. See also E. Patat, *Z. Elektrochem.*, **42**, 85 (1936).

if j is very large. The rate with which the required energy passes into the particular degree of freedom is proportional to this, *i.e.*,

$$k_2 = k_2' \left(\frac{j - m}{j}\right)^{s-1} \tag{89}$$

The total number of quanta j may be taken as proportional to E, the total energy of the molecule, while m is proportional to E', the minimum energy the molecule must have for decomposition to take place; it follows, therefore, that

$$k_2 = k_2' \left(\frac{E - E'}{E}\right)^{s-1} \tag{90}$$

This expression has been applied quantitatively to the experimental results, and satisfactory agreement was obtained. All energies from E' to infinity are possible, so that the expression must be integrated using a Boltzmann distribution of energies; this has been done graphically.

As has been stated, the number of unimolecular reactions which are simple in character is very small. Many gaseous organic decompositions, which will be discussed in Chap. 9, have been shown to involve free-radical chains, and those that have not been tested for chains are naturally suspect. The theoretical treatment of unimolecular processes was largely developed with reference to reactions which are now known to be complex, but fortunately they were not so complex that erroneous conclusions were drawn. Some elementary unimolecular reactions in the gas phase will be considered in the next chapter.[1]

Influence of Foreign Gases. One piece of support for the Lindemann theory of the mechanism of unimolecular reactions came from the influence of foreign gases on the rates at low pressures. If activation takes place by collisions, it is to be expected that such gases will be able to prevent the first-order rates from falling off as the pressure is diminished, although a priori little can be said about the relative effectiveness of different substances. Most of the work done in this connection has been done on reactions which are now known to be complex, so that the evidence is less definite than it was previously thought to be. However, the contribution of chain processes to such reactions is frequently small, and in any case the first step in the chain mechanisms is unimolecular; consequently the results and the theoretical treatment are directly applicable to the first step.

[1] For recent theoretical discussions of unimolecular reactions, see J. O. Hirshfelder, *J. Chem. Phys.*, **16**, 22 (1948); R. M. Barrer, *Trans. Faraday Soc.*, **44**, 399 (1948); Slater, *loc. cit.*

Some of the earliest work in this connection was done on the decomposition of acetaldehyde,[1] but the results cannot be interpreted with certainty since the chain mechanism is important. The work with propionaldehyde[2] is more reliable; here the amount of reaction that occurs by means of chains is very small. It was found that in the presence of a sufficient concentration of hydrogen the specific rate did not fall off as the partial pressure of the aldehyde was reduced, but remained constant. No amount of hydrogen could, however, raise the constant above the limiting high-pressure value, suggesting that the phenomenon cannot be explained as due to chemical action; the hydrogen apparently acts by maintaining the normal distribution of energy among the molecules of the reacting gas.

Similar investigations have been carried out with other foreign gases, and on the decompositions of fluorine monoxide,[3] nitrous oxide,[4] and azomethane,[5] all of which are complex. The relative efficiencies of various molecules in transferring energy to the reacting molecules may be derived as follows: In the presence of a foreign substance X the activation of the molecules A by collision may occur by two alternative processes:

$$A + A \rightleftharpoons A^* + A$$

and

$$A + X \rightleftharpoons A^* + X$$

for which the forward specific rates may be represented as k_1 and k'_1 and the reverse rates as k_{-1} and k'_{-1}. The complex A^* decomposes with the specific rate k_2

$$A^* \rightarrow B + C$$

and applying the same treatment as on page 78, it is found that the rate of reaction is

$$-\frac{d[A]}{dt} = k_2[A^*] = k_2 \frac{k_1[A]^2 + k'_1[A][X]}{k_{-1}[A] + k'_{-1}[X] + k_2} \qquad (91)$$

From the influences of A and X on the reaction it is possible to calculate a value for the ratio k'_1/k_1, *i.e.*, the relative effectiveness with which X and A transfer energy to A. Some of the results obtained in the decompositions of fluorine monoxide, nitrous oxide, and azomethane are given in Table 15.

It is seen that in some instances X is more effective in transferring energy

[1] C. N. Hinshelwood and P. J. Askey, *ibid.*, **A, 116,** 163 (1927).
[2] C. N. Hinshelwood and L. A. K. Staveley, *J. Chem. Soc.*, 817 (1936).
[3] W. Koblitz and H. J. Schumacher, *Z. physik. Chem.*, **B, 20,** 460 (1933).
[4] M. Volmer *et al.*, *ibid.*, **B, 19,** 85 (1932); **B, 21,** 257 (1933); **B, 25,** 81 (1934).
[5] D. V. Sickman and O. K. Rice, *J. Chem. Phys.*, **4,** 608 (1936).

than is A itself. The efficiency is, in general, least for the inert gases, and it appears that the effectiveness of a substance is related to its tendency to undergo reaction with A. The problem of energy transfers of this kind will be discussed in detail in the last chapter of this book.

TABLE 15. RELATIVE EFFICIENCIES OF GASES IN TRANSFERRING ENERGY IN UNIMOLECULAR DECOMPOSITIONS

Gas	Decomposition of		
	F_2O (250°C)	N_2O (653°C)	Azomethane (310°C)
He	0.40	0.66	0.07
A	0.82	0.20	
Kr		0.18	
SiF_4	0.88		
N_2	1.01	0.24	0.21
O_2	1.13	0.23	
F_2	1.13		
CO		...	0.13
CH_4			0.20
CO_2		1.32	0.25
H_2O		1.5	0.46
D_2			0.46

PROBLEMS[1]

1. The rate of a reaction at 40°C is three times that at 20°C. Calculate the energy of activation.

2. On the basis of simple collision theory, calculate the probability that at 500°C the energy of a collision is (*a*) 10 kcal, (*b*) 40 kcal, and (*c*) 60 kcal in excess of the average.

3. The following data have been given for the decomposition of dibromosuccinic acid in solution:

T, °C	$k \times 10^4$, hr^{-1}
50.0	1.08
70.1	7.34
89.4	45.4
101.0	138

[1] The following constants [R. T. Birge, *Revs. Modern Phys.*, **13**, 233 (1941)] may be useful in the solution of problems in this and subsequent chapters:

$$\mathbf{k} = 1.380 \times 10^{-16} \text{ erg per deg}$$
$$\mathbf{h} = 6.624 \times 10^{-27} \text{ erg-sec}$$
$$N = 6.023 \times 10^{23} \text{ mole}^{-1}$$
$$R = 1.986 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$2.303R = 4.574 \text{ cal deg}^{-1} \text{ mole}^{-1}$$
$$c = 2.998 \times 10^{10} \text{ cm sec}^{-1}$$

Plot log k vs. $1/T$ in degrees Kelvin, and determine the activation energy from the slope of the best line. Check the answer using the method of least squares.

4. Calculate the probability that a molecule having 10 degrees of vibrational freedom has an energy 20 kcal in excess of the average, at 300°K. Compare this result with the probability obtained on the basis of simple collision theory.

5. Calculate, using collision theory, the rate of activation at 500°K of a substance of molecular weight 80 and collision diameter 5 A. Assume 12 degrees of internal freedom, an activation energy of 40 kcal, and a pressure of 1 atm. If the substance is decomposing unimolecularly with a frequency factor of 10^{14} sec^{-1}, at what pressure will the first-order coefficient begin to fall off?

6. One liter of oxygen is maintained at 400 mm pressure and 300°C. Assuming a collision diameter of 2.0 A, calculate (*a*) the total number of collisions per second, (*b*) the number of molecules colliding per second per cubic centimeter, and (*c*) the number of collisions in the 1 liter of gas in which the joint energy is 20 kcal in excess of the average.

7. The frequency factors for two unimolecular reactions occurring at 200°C are 2.75×10^{15} and 3.98×10^{13} sec^{-1}. Calculate the entropy of activation in each case. How do the values obtained depend upon the standard state used?

8. Carry out a corresponding calculation for two bimolecular gas reactions occurring at 300°C, having frequency factors of 7.4×10^{10} and 9.6×10^{9} liters $mole^{-1}$ sec^{-1}. How do the answers now depend upon the standard state used?

9. On the basis of absolute rate theory determine the dependence on temperature of the frequency factors for the following types of reactions:

1. A unimolecular reaction
2. A bimolecular reaction between two diatomic molecules, the complex being nonlinear
3. A termolecular reaction between three diatomic molecules, forming a nonlinear complex with no free rotation

In each case show how the activation energy at T°K is related to that at 0°K.

Assuming translational partition functions to be 10^8 for each degree of freedom, rotational to be 10, and vibrational to be unity, calculate frequency factors in molecular and in molar units for the above reaction types.

*** 10.** (*a*) In the linear activated complex for the reaction $H + HBr \rightarrow H_2 + Br$, the H-H distance is 1.50 A, and the shorter H-Br distance is 1.42 A. Calculate the moment of inertia of the complex and hence the rotational partition function.

(*b*) The three real vibrational frequencies in the activated complex are 2,340, 460 and 460 cm^{-1}. Calculate the vibrational partition function of the complex.

(*c*) Calculate the total partition function for the activated complex.

(*d*) Calculate the total partition functions for the reactants, H and HBr, taking the H-Br distance as 1.414 A and the vibrational frequency as 2,650 cm^{-1}.

(*e*) Obtain a value for the rate constant at 300°K, assuming the activation energy to be 1.2 kcal at that temperature.

* Problems marked with an asterisk are more advanced than the others.

CHAPTER 4

ELEMENTARY GAS-PHASE REACTIONS

Apart from reactions involving atoms and free radicals, which are chiefly of interest in connection with the part they play in free-radical mechanisms, very few gas reactions are elementary. The most important bimolecular reactions of this class are the reaction between hydrogen and iodine, the reverse decomposition of hydrogen iodide, the corresponding reactions involving deuterium instead of hydrogen, and the dimerization of cyclopentadiene; possibly the decomposition of nitrogen dioxide[1] should also be added to this list, although the reaction has not been investigated very thoroughly. There are a small number of reactions of the third order, all involving nitric oxide, which can be treated as if they involved a simple three-body collision, although it is likely that two well-defined steps could be distinguished. In addition, a few unimolecular isomerizations occur in an elementary manner, but no unimolecular decomposition appears to be of this type. A great many other gas-phase reactions have at various times been thought to be elementary, but further study has shown them to be complex. Elementary gas-phase reactions involving molecules will be treated in some detail in the present chapter, since an understanding of them provides a foundation for the study of reactions in other phases and for the study of complex processes.

Decomposition of hydrogen iodide

The work done on this reaction by Bodenstein and his coworkers has been described in Chap. 2. Subsequently to these investigations, the reaction has been studied by a number of workers. Some of the results obtained seemed to suggest that the reaction was not an elementary one, or proceeded partly on the surface, but it now seems fairly certain that under the conditions used by Bodenstein the reaction is elementary and occurs largely in the gas phase. The result of H. A. Taylor that in Pyrex vessels the reaction appears to take place to a marked extent on the surface was mentioned on page 52, where it was noted that Taylor's rates were very much greater than those of Bodenstein. Another indication that the results of Bodenstein and of Taylor are not comparable is that when log k was plotted against $1/T$ for Taylor's results, a straight line was not

[1] M. Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

obtained, indicating with certainty that simultaneous reactions are occurring. With Bodenstein's results, on the other hand, a good straight line was obtained, as shown in Fig. 11. It therefore seems likely that under the conditions used by Bodenstein the reaction takes place largely in the gas phase, and that Taylor's results arose as a result of his use of Pyrex glass.

The suggestion that the decomposition might not be an elementary reaction was made by B. Lewis and Rideal[1] on the basis of their results obtained with hydrogen iodide that had been intensively dried by means of phosphorus pentoxide. Their results appeared to indicate that the decomposition did not stop at the equilibrium position found by Bodenstein but went to completion, and they concluded that iodine atoms are involved in the reaction. However Bodenstein and Jost[2] suggested that the process of drying had introduced traces of phosphorus pentoxide into the hydrogen iodide and that this substance was reacting with the iodide to form iodine and water; this explanation is generally accepted.

The reaction was studied over a much wider range of initial concentrations by Kistiakowsky[3] (*cf.* p. 52), who found that the reaction took place almost entirely in the gas phase and was unaffected by intense drying. At the lower pressures the reaction was strictly of the second order, but deviations occurred at higher pressures; however, these could be attributed entirely to departures from ideal-gas behavior. At high concentrations the collision number is somewhat larger than that corresponding to ideal behavior, owing to the volume occupied by the molecules themselves. A correction allowing for this, involving the van der Waals constant b, was found to explain the deviations very accurately. The values of k obtained by Kistiakowsky agree very well with those of Bodenstein.

The investigations on this reaction leave little doubt that the decomposition as studied by Bodenstein and Kistiakowsky is an elementary gas-phase reaction of the second order, and it will therefore be discussed on this basis.

Application of the Arrhenius law to the decomposition was made by W. C. McC. Lewis.[4] As seen in the last chapter, the specific rate is related to the temperature by the equation

$$\ln k = \ln A - \frac{E}{RT} \tag{1}$$

so that a plot of $\log_{10} k$ against $1/T$ should give a straight line; this has been seen to be the case in Fig. 11. From the slope of the line the value of E

[1] B. Lewis and E. K. Rideal, *J. Am. Chem. Soc.*, **48**, 2553 (1926).
[2] M. Bodenstein and W. Jost, *J. Am. Chem. Soc.*, **49**, 1416 (1927).
[3] G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **50**, 2315 (1928).
[4] W. C. McC. Lewis *J. Chem. Soc.*, **113**, 471 (1918).

is found to be 44.0 kcal per mole. Actually this treatment is slightly in error, since A varies slightly with the temperature; however for the present purposes this may be ignored.

The collision theory of the absolute magnitude of the rate constant was also due largely to W. C. McC. Lewis, who developed the treatment in a number of papers, in one[1] of which the decomposition of hydrogen iodide was discussed numerically. One feature of the Lewis theory is now known to be incorrect, but fortunately it can be extracted from the treatment without invalidating the rest of the work: this was his concept that molecules acquire the activation energy by absorbing infrared radiation. The molecules of a gas at a constant temperature are in equilibrium with radiant energy, which they constantly absorb and emit, and this was believed at the time to explain the way they gain and lose energy. The frequency of the energy corresponding to a given temperature can readily be calculated, and light of this frequency should, if the hypothesis were true, cause an increase in the rate of reaction. Numerous attempts to bring about such an enhancement of the rates of various reactions by means of infrared radiation have been made, but in no case was success achieved.[2] This fact, together with the success of the Lindemann theory in explaining the behavior of unimolecular reactions, indicates that in fact molecules acquire energy by collisions with one another.

The reason that the incorrectness of the radiation theory does not vitiate Lewis's treatment is that the concentration of active molecules is related to that of normal ones by statistical laws and does not depend on the mechanism by which the energy is acquired or lost.

By equating the constant A to the number of molecules entering into collision each second, Lewis arrived at the expression

$$v = 2\sqrt{2}\pi\sigma^2\bar{u}n^2e^{-E/RT} \qquad \text{molecules cc}^{-1}\ \text{sec}^{-1} \tag{2}$$

for the rate of a second-order reaction involving like molecules; here σ is the kinetic-theory diameter, $\bar{u}$ the mean velocity, and n the number of molecules per cubic centimeter. The specific rate k_1, the rate corresponding to a value of n corresponding to 1 molecule per cubic centimeter, is thus

$$k_1 = 2\sqrt{2}\pi\sigma^2\bar{u}e^{-E/RT} \qquad \text{cc molecule}^{-1}\ \text{sec}^{-1} \tag{3}$$

For the kinetic-theory diameter Lewis assumed a value of 2×10^{-8}, which is now known to be somewhat too low; this value, together with $\bar{u} = 3.3 \times 10^4$ cm per sec and $E = 44$ kcal per mole, gives for the specific rate at 556°K

$$k_1 = 3.5 \times 10^{-7}\ \text{liter mole}^{-1}\ \text{sec}^{-1}$$

[1] *Ibid.*

[2] See especially J. E. Mayer, *J. Am. Chem. Soc.*, **49**, 3033 (1927).

This is in excellent agreement with Bodenstein's experimental value of 3.517×10^{-7} at this temperature. Lewis extended his calculations over the whole range of temperatures covered by Bodenstein, and the agreement was satisfactory throughout. The agreement is not quite so good when the more accurate value of 3.5×10^{-8} cm is taken for the molecular diameter; thus at 556°K the calculated rate constant becomes 5.3×10^{-7}, to be compared with the experimental figure of 3.517×10^{-7}. However the agreement is still satisfactory, since a very slight error in the experimental activation energy can make a big percentage change in the calculated rate. It may be noted that the frequency factor for this reaction is about 10^{11} liter mole^{-1} sec^{-1}.

Reaction between hydrogen and iodine

The experimental work of Bodenstein on this reaction was discussed on page 52. Application of the collision theory to the results was also made by Lewis, the treatment given above requiring modification since collisions between two unlike molecules are involved. The number of such collisions is given by the expression

$$\pi \sigma_{AB}^2 n_A n_B (\bar{u}_A^2 + \bar{u}_B^2)^{1/2}$$

where σ_{AB} is now the sum of the effective radii of the molecules, n_A and n_B are the numbers of molecules per unit volume, and $\bar{u}_A$ and $\bar{u}_B$ are the mean velocities of the two kinds of molecules. The specific rate is therefore given by

$$k = \pi \sigma_{AB}^2 (\bar{u}_A^2 + \bar{u}_B^2)^{1/2} e^{-E/RT} \tag{4}$$

The experimental value of E is 40 kcal per mole, and taking at 700°K, $(\bar{u}_A^2 + \bar{u}_B^2)^{1/2} = 29.7 \times 10^{-4}$ cm per sec, $\sigma_{AB} = 2 \times 10^{-8}$ cm, the calculated value of k is found to be

$$k = 14 \times 10^{-2} \text{ liter mole}^{-1} \text{ sec}^{-1}$$

This is in satisfactory agreement with the observed value of 6.42×10^{-2} at this temperature. The frequency factor is about 2×10^{11}.

The reaction has also been treated in terms of the theory of absolute reaction rates, by Wheeler, Topley, and Eyring.[1] This work includes quantum-mechanical calculations of the energy of activation of the reaction, using methods outlined in Chap. 13. The result obtained was 50 kcal, a good deal higher than the experimental value of 40 kcal; however, as will be seen, the calculations cannot be expected to yield more than a very rough approximation to the true value. The most important outcome of these calculations lies in the fact that they show why the reaction

[1] A. Wheeler, B. Topley, and H. Eyring, *J. Chem. Phys.*, **4**, 178 (1936).

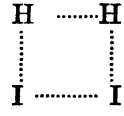
is elementary, whereas the corresponding reactions of chlorine and bromine are complex. These reactions proceed by an initial decomposition of the halogen molecule, followed by the attack on a hydrogen molecule by a halogen atom; the corresponding reactions with iodine would be

$$\tfrac{1}{2}I_2 \rightleftharpoons I$$

$$I + H_2 \rightarrow HI + I$$

The energy required to dissociate an iodine molecule is 34 kcal per mole, so the energy required for the first reaction would be just one-half of this, *i.e.*, 17 kcal. The energy of activation for the second reaction was calculated to be about 40 kcal; consequently the energy of activation required for the formation of 1 mole of hydrogen iodide by the atomic mechanism is 40 + 17 = 57 kcal. This is considerably higher than the observed activation energy and that calculated assuming the reaction to be elementary; the atomic reaction is therefore unimportant in comparison with the elementary molecular reaction.

According to the theory of absolute reaction rates, the activated complex, which is a molecule of the form



is in equilibrium with the reactants H_2 and I_2, and the rate of the reaction is controlled by the rate of decomposition of the complex. The equilibrium constant for the process

$$H_2 + I_2 \rightleftharpoons H_2I_2^{\ddagger}$$

is given by the expression

$$K_c = \frac{F^{\ddagger}}{F_{H_2}F_{I_2}} e^{-E_0/RT} \tag{5}$$

where the F are the partition functions per unit volume and E_0 is the activation energy per mole at the absolute zero. The specific rate of the reaction is thus given by [*cf.* Eq. (39), p. 68]

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_{\ddagger}}{F_{H_2}F_{I_2}} e^{-E_0/RT} \tag{6}$$

where the partition function $F_{\ddagger}$ differs from $F^{\ddagger}$ by the removal of the vibrational factor corresponding to dissociation into 2HI. The partition functions may now be expressed in terms of the translational, rotational, and vibrational factors. The functions for H_2 and I_2 both contain terms

for three degrees of translational freedom, two of rotational (being linear molecules), and one of vibrational and can be expressed as

$$F_{H_2} = \frac{(2\pi m_{H_2} kT)^{3/2}}{h^3} \frac{8\pi I_{H_2} kT}{2h^2} \frac{1}{1 - e^{h\nu_{H_2}/kT}} \tag{7}$$

and

$$F_{I_2} = \frac{(2\pi m_{I_2} kT)^{3/2}}{h^3} \frac{8\pi^2 I_{I_2} kT}{2h^2} \frac{1}{1 - e^{h\nu_{I_2}/kT}} \tag{8}$$

In the rotational factors, since the molecules are symmetrical, the symmetry numbers 2 have appeared in the denominator. The partition function for the activated complex is given by

$$F_{\ddagger} = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{4h^3} \prod^{5} \frac{1}{1 - e^{-h\nu/kT}} \tag{9}$$

The symmetry number is now 4, and there are five vibrational degrees of freedom ($3n - 7$ where $n = 4$).

TABLE 16. CALCULATED AND OBSERVED RATES FOR THE HYDROGEN-IODINE REACTION

T, °K	k_{calc}, cc mole^{-1} sec^{-1}	k_{obs}, cc mole^{-1} sec^{-1}
575	0.132	0.245
781	1,340	950

The numerical evaluation of the translational factors presents no problem, as the molecular masses are known with precision. Evaluation of the rotational factors involves the moments of inertia; these are known with accuracy for H_2 and I_2 and are known for the complex on the basis of the quantum-mechanical calculation of its properties. A little more uncertainty enters into the vibrational terms, since the calculations do not allow a very accurate determination of the frequencies in the activated complex; however the vibrational factors are not highly sensitive to these frequencies. Some adjustment to the values was made so as to give agreement at 700°K.

The partition functions being evaluated in this manner, and using the observed activation energy (this is equivalent to 39.7 kcal at the absolute zero), the rate constants were calculated; they are compared with the experimental results at 575 and 781°K in Table 16. The agreement is seen to be quite satisfactory, although it must be remembered that the treatment is somewhat artificial in view of the adjustment of the vibrational frequencies. In this application the treatment is not superior to collision theory in accuracy and is certainly much more laborious; when

the reacting molecules are more complicated, however, the theory of absolute reaction rates gives very much more accurate results.

The essential difference between this treatment and the simple collision theory is that the reacting molecules are not regarded as hard spheres. Writing the translational, rotational, and vibrational contributions for each degree of freedom as t, r, and v, the theory of absolute reaction rates expresses the rate constant in the form

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{(t^3r^3v^5)_\ddagger}{(t^3r^2v)_{H_2}(t^3r^2v)_{I_2}} e^{-E_0/RT} \tag{10}$$

while the collision theory is equivalent to

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{(t^3r^2)_\ddagger}{(t^3)_{H_2}(t^3)_{I_2}} e^{-E_0/RT} \tag{11}$$

These equations are useful for determining the predicted variation of the rate with the temperature. The translational and rotational partition functions for each degree of freedom vary with the square root of the absolute temperature, while the vibrational terms are practically temperature-independent. Separating out temperature-independent terms in Eq. (10) as k', the equation becomes

$$k = k'T \frac{(T^{3/2}T^{3/2})_\ddagger}{(T^{3/2}T)_{H_2}(T^{3/2}T)_{I_2}} e^{-E_0/RT} \tag{12}$$

$$= \frac{k'}{T} e^{-E_0/RT} \tag{13}$$

Equation (11) gives

$$k = k'T \frac{(T^{3/2}T)_\ddagger}{(T^{3/2})_{H_2}(T^{3/2})_{I_2}} e^{-E_0/RT} \tag{14}$$

$$= k'T^{1/2}e^{-E_0/RT} \tag{15}$$

The two treatments therefore differ somewhat as to the temperature dependence of the nonexponential part of the rate expression. The difference would be slightly less if the temperature dependence of the vibrational factors were taken into account.

The specific rate of the reaction can be formulated in an alternative manner, making use of the thermodynamic functions. It was seen in the last chapter [Eq. (73), p. 75] that the rate constant is given in general by

$$k_1 = \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^*/R} e^{-\Delta H^\ddagger/RT} \tag{16}$$

where $\Delta H^\ddagger$ and ΔS^* are the heat and entropy of activation. The heat of activation is not strictly equal to the energy of activation E,

and if the latter is to be used, it can easily be shown that the rate expression becomes[1]

$$k_1 = e^2 \frac{kT}{h} e^{\Delta S^*/R} e^{-E/RT} \tag{17}$$

In the above expressions the standard state for the entropy is unit concentration. The separate translational, rotational, and vibrational entropies for H_2, I_2, and the activated complex have been evaluated and are shown in Table 17. The entropies, except for the figure in the last column, all

TABLE 17. ENTROPIES OF ACTIVATION FOR THE H_2-I_2 REACTION

$T = 300°K$

The standard state for ΔS_c^* is 1 mole per liter.

Molecule	Entropy				ΔS_p^*	ΔS_c^*
	Translational	Rotational	Vibrational	Total		
H_2	28.2	2.1	0	30.3	−20 3	−13 9
I_2	42.8	17.0	0	59.8		
$H_2I_2^{\ddagger}$	42.8	23.1	3.9	69.8		

refer to a standard state of 1 atm pressure. If the rate constant is written in the form of the collision theory, *i.e.*, as

$$k = Ze^{-E/RT} \tag{18}$$

it follows that

$$Z = e^2 \frac{kT}{h} e^{\Delta S^*/R} \tag{19}$$

and Z calculated in this way is found to have a value of approximately

[1] Equation (17) is derived as follows: The experimental energy of activation E is defined by $E = RT^2\, d(\ln k)/dT$, and from Eq. (70) of page 75 it follows that

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K^*}{dT}$$

Thus $E = RT + RT^2\, d(\ln K^*)/dT = RT + \Delta E^{\ddagger} = RT + \Delta H^{\ddagger} - p\,\Delta v_{\ddagger}$, where $\Delta v_{\ddagger}$ is the increase in volume in forming the activated complex. For a gas reaction $p\,\Delta v_{\ddagger}$ is equal to $\Delta n_{\ddagger} RT$, where $\Delta n_{\ddagger}$ is the increase in the number of molecules when the activated complex is formed. Thus

$$\Delta H^{\ddagger} = E - RT + \Delta n_{\ddagger} RT$$

and insertion of this in Eq. (16) gives

$$k_1 = e^{-(\Delta n_{\ddagger} - 1)} \frac{kT}{h} e^{\Delta S^*/R} e^{-E/RT}$$

For a bimolecular gas reaction $\Delta n_{\ddagger}$ is -1, and hence Eq. (17) follows.

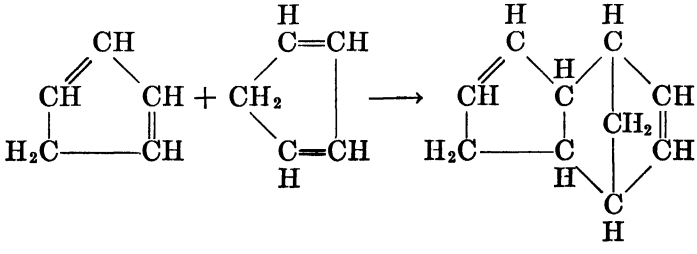
5×10^{10} liter $mole^{-1}$ sec^{-1} at 300°K; this is slightly less than the value calculated using collision theory, which gives approximately 10^{11}. For an exact correspondence between the two theories, ΔS^* must have a value of about -11.7†; however, owing to the different temperature dependence given by the two theories, the particular value of ΔS^* which gives correspondence between the treatments depends upon the temperature. For a reaction involving two atoms or simple molecules, such as the one under consideration, there is little rearrangement of energy between the various degrees of freedom in the activated state; ΔS^* will then be close to the above value and the two theories will give similar results. With more complex molecules the situation is very different, as will be seen from examples given later in this chapter.

Decomposition of deuterium iodide

The rate of decomposition of deuterium iodide has been measured by Blagg and Murphy[1] using a method which is somewhat similar to that used by Bodenstein for hydrogen iodide. The rates were measured between 660 and 719°K, and the activation energy was found to be 11.8 kcal as compared with 12.3 kcal for the hydrogen iodide decomposition. In spite of the higher activation energy, the latter reaction proceeds faster by a factor of 1.53; this is due to entropy effects, and the difference in rates is in satisfactory agreement with the calculations of Wheeler, Topley, and Eyring (p. 90), who predicted a ratio of 1.92 for the rates. The rate of the reverse reaction has not been measured directly but can be calculated, since the equilibrium constant is known accurately.[2]

Dimerization of cyclopentadiene

The dimerization of cyclopentadiene, which proceeds as follows,



has been shown by Wassermann and his coworkers to be an elementary

† Since this value of ΔS^* is obtained from Z expressed as liter $mole^{-1}$ sec^{-1} the standard state referred to is 1 mole per liter.

[1] J. C. L. Blagg and G. M. Murphy, *J. Chem. Phys.*, **4**, 631 (1936).

[2] D. Rittenburg and H. C. Urey, *J. Chem. Phys.*, **2**, 106 (1934).

reaction both in the gas phase and in various solvents. Since chief interest attaches to a comparison between the rate in the gas phase and in solution, the reaction will be discussed further in the following chapter, where references are given.

Termolecular reactions

A number of reactions take place with velocities that are proportional to the product of three concentrations. The activated complex is made up of three molecules, and although there is some doubt about the manner of formation of the activated complex, its concentration can be calculated by the usual methods of statistical mechanics. Since, moreover, the reactions appear to be comparatively free from side reactions, they may conveniently be treated as elementary.

All the known gaseous reactions of the third order involve nitric oxide as one of the reacting molecules. The first reaction of this type was studied in 1914 by Trautz,[1] who investigated the reaction between nitric oxide and chlorine over the range of temperatures from 8 to 283°C. The product of the reaction is nitrosyl chloride, so that the over-all process is

$$2NO + Cl_2 = 2NOCl$$

There is therefore a decrease in volume, so that the progress of the reaction can be followed by confining the gases in a bulb maintained at the required temperature and observing the change in pressure as a function of the time. Trautz later did further work on the reaction and on the equilibrium,[2] as did Kiss.[3] Later Krauss and Saracini[4] confirmed that the reaction is homogeneous and of the third order over a wide range of pressures.

Other reactions of the third order were studied during the same period. In 1918 Bodenstein investigated the reaction between nitric oxide and oxygen to give nitrogen dioxide[5]

$$2NO + O_2 = 2NO_2$$

the reacting gases were allowed to stream into a bulb the temperature of which was controlled, and the change in pressure was measured using a manometer containing bromonaphthalene. The rate of reaction is high

[1] M. Trautz, *Z. anorg. Chem.*, **88**, 285 (1914).

[2] M. Trautz and L. Wachenheim, *ibid.*, **97**, 241 (1916); M. Trautz and F. A. Hengheim, *ibid.*, **110**, 237 (1920); M. Trautz and H. Schlueter, *ibid.*, **136**, 1 (1924).

[3] A. von Kiss, *Rec. trav. chim.*, **42**, 112, 665 (1923); **43**, 68 (1924).

[4] W. Krauss and M. Saracini, *Z. physik. Chem.*, **A, 178**, 245 (1937).

[5] M. Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918); *Z. physik. Chem.*, **100**, 68 (1922). *Cf.* E. Briner, W. Pfeiffer, and G. Malet, *J. chim. phys.*, **21**, 25 (1924); G. Kornfeld and E. Klingler, *Z. physik. Chem.*, **B, 4**, 37 (1929).

at ordinary pressures but can be measured sufficiently accurately at low ones. The third-order law was found to be obeyed, and the rate decreased with rise of temperature.

Similar results were obtained with the reaction between nitric oxide and bromine[1]

$$2NO + Br_2 = 2NOBr$$

The reaction between nitric oxide and hydrogen[2]

$$2NO + 2H_2 = 2H_2O + N_2$$

differs from the other reactions in having a high temperature coefficient, and more recent work[3] has indicated that the reaction becomes more complicated at lower pressures. The reaction with deuterium has also been studied.[4]

There has been a good deal of speculation, on the basis of the collision theory, as to the mechanism by which these reactions take place. Although this question is entirely avoided by the theory of absolute reaction rates, a brief outline will be given of the collision-theory treatment.

A collision between three molecules will obviously take place much less frequently than one between two; consequently, if a reaction of the third order had the same activation energy as one of the second order, its rate would be much lower. The only third-order reactions that are likely to proceed at a conveniently measurable rate may therefore be expected to involve rather low activation energies. This is true for all the reactions studied except that involving hydrogen, and this takes place only at very high temperatures and is complex.

In 1916 Trautz[5] suggested that true ternary collisions between molecules are probably so rare that it is better to regard the termolecular reactions as taking place in two stages; in 1918 he proposed[6] the mechanism

$$NO + Br_2 \rightleftharpoons NOBr_2$$
$$NOBr_2 + NO \rightarrow 2NOBr$$

for the bromine reaction, and later gave corresponding mechanisms for the other reactions.[7] According to this scheme a small concentration of $NOBr_2$ is maintained in equilibrium with NO and Br_2, its concentration

[1] M. Trautz and V. P. Dalal, *Z. anorg. Chem.*, **102**, 149 (1918).

[2] C. N. Hinshelwood and T. E. Green, *J. Chem. Soc.*, 730 (1926).

[3] C. N. Hinshelwood and J. W. Mitchell, *J. Chem. Soc.*, 378 (1936); H. A. Taylor and C. Tanford, *J. Chem. Phys.*, **12**, 47 (1944).

[4] Hinshelwood and Mitchell, *ibid.*

[5] M. Trautz, *Z. Elektrochem.*, **22**, 104 (1916).

[6] Trautz and Dalal, *loc. cit.*

[7] M. Trautz and H. Schlueter, *Z. anorg. Chem.*, **136**, 1 (1924).

being proportional to $[NO][Br_2]$. The over-all rate of the reaction is determined by the collision between $NOBr_2$ and NO, so that the rate is proportional to $[NOBr_2][NO]$, *i.e.*, to $[NO]^2[Br_2]$. Increase in temperature tends to dissociate the $NOBr_2$, with the result that the rate of the reaction may be reduced.

Such mechanisms are formally equivalent to the assumption of collisions of long duration ("sticky collisions") between two of the reacting molecules—NO and Br_2 in the above example. Bodenstein[1] explained the experimental results in a rather more general way than Trautz, without specifying the molecules between which a long collision time had to be postulated. He made a rough estimate of the number of triple collisions by assuming that the ratio between the chance of a molecule hitting another molecule which is actually in collision with a third molecule and the chance that it hits a single molecule is as the molecular diameter is to the mean free path. On this basis the ratio of ternary to binary collisons came out to be about 1:1,000. However this gives about 10^5 more collisions than correspond to reaction for the cases in which the energy of activation is zero. The reason for this discrepancy is that the collision theory, by assuming the molecules to behave as hard spheres, neglects the considerable loss of entropy when three molecules become one in the activated state.

The theory of absolute reaction rates has the virtue of allowing for this effect and of circumventing the question of the mechanism by which the ternary complex is formed. As long as it can be assumed that the complex is in equilibrium with the reacting molecules, the question of the manner of its formation is irrelevant to the calculation of its concentration.

The detailed application of the theory has been worked out by Gershinowitz and Eyring.[2] For a reaction of the type

$$2NO + X_2 \rightarrow 2NOX$$

where X may be hydrogen, deuterium, oxygen, chlorine, or bromine, the specific reaction rate is given by

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_\ddagger}{F_{NO}^2 F_{X_2}} e^{-E_0/RT} \tag{20}$$

Evaluation of the partition functions in terms of their translational, rotational, and vibrational factors gives the expression

$$k = \frac{\mathbf{k}T}{\mathbf{h}} \frac{g_\ddagger}{g_s} \frac{\dfrac{(2\pi m_\ddagger \mathbf{k}T)^{3/2}}{\mathbf{h}^3} \dfrac{8\pi^2(8\pi^3 ABC)^{1/2}(\mathbf{k}T)^{3/2}}{\mathbf{h}^3\sigma_\ddagger} \prod^{11}(1 - e^{-\mathbf{h}\nu_\ddagger/\mathbf{k}T})^{-1}}{\prod^{3} \dfrac{(2\pi m_s \mathbf{k}T)^{3/2}}{\mathbf{h}^3} \prod^{3} \left(\dfrac{8\pi^2 I_s \mathbf{k}T}{\mathbf{h}^2\sigma_s}\right) \prod^{3}(1 - e^{-\mathbf{h}\nu_s/\mathbf{k}T})^{-1}} e^{-E_0/RT} \tag{21}$$

[1] M. Bodenstein, *Z. physik. Chem.*, **100**, 118 (1922); *cf.* K. F. Herzfeld, *Z. physik*, **8**, 132 (1921).

[2] H. Gershinowitz and H. Eyring, *J. Am. Chem. Soc.*, **57**, 985 (1935).

In these two equations the transmission coefficient has been taken as unity; the subscript i refers to the initial state. Since the activated complex contains six atoms, there are 11 vibrational factors. Separating out the temperature-independent factors, including the vibrational factors, which vary only slightly with the temperature, this expression may be written as

$$k = k'T^{-7/2}e^{-E_0/RT} \tag{22}$$

It is evident that if E_0 is zero or very small, the rate constant will decrease with temperature, as is actually found in the reaction involving oxygen.

In order to carry out an absolute calculation of the specific rates, it is necessary to have some knowledge of the configuration and vibration frequencies of the activated complex. For the reaction between nitric oxide and oxygen the configuration depicted in Fig. 15 has been assumed. This necessitates a slight modification to the treatment given previously [Eq. (21)] owing to the possibility of free rotation about the O-O bond. This is done by replacing one of the vibrational factors for the activated complex by the expression

$$\frac{(8\pi^3 I_D kT)^{1/2}}{h}$$

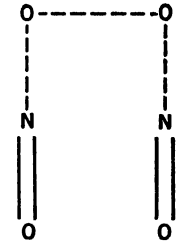


FIG. 15. Configuration of the activated complex in the nitric oxide–oxygen reaction.

where I_D is the moment of inertia for rotation about the bond. The effect of this is to replace the term $T^{-7/2}$ by T^{-3}. Upon substituting the numerical values for the universal constants and expressing molecular weights M in grams and moments of inertia in g-Å^2 per mole, it is found that the rate constant for the reaction is given by

$$k = 1.6 \times 10^{19} \frac{g_\ddagger}{g_i} \left(\frac{M_\ddagger}{\prod^3 M_i} \right)^{3/2} \frac{(ABC)^{1/2} I_D^{1/2}}{\sigma_\ddagger \prod^3 (I_i/\sigma_i)} \frac{\prod^{10} (1 - e^{-h\nu_\ddagger/kT})^{-1}}{\prod^3 (1 - e^{h\nu_i/kT})^{-1}} \frac{1}{T^3} e^{-E_0/RT} \tag{23}$$

the units being cubic centimeters squared per mole squared per second. To a good approximation the vibrational frequencies $\nu_\ddagger$ for the activated state may be taken to be the same as in N_2O_4, the values of which are known.[1] The frequencies for oxygen and nitric oxide are so high that the corresponding partition functions are practically unity. Making this approximation, and taking logarithms of both sides of Eq. (23), it is seen that a plot of

$$\ln k + 3 \ln T - \ln \prod^7 (1 - e^{h\nu_\ddagger/kT})^{-1}$$

[1] G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **A, 141**, 342 (1933).

against $1/T$ should be a straight line of slope equal to $-E_0/R$. This has been plotted in Fig. 16, in which it is seen that E_0 is extremely close to zero. This result may be associated with the fact that both nitric oxide and oxygen are paramagnetic, the former molecule having one, and the latter two, unshared electrons.

The specific rate is therefore calculated taking E_0 equal to zero. The moments of inertia were derived from spectroscopic measurements, but the evaluation of those of the activated complex requires a knowledge of its configurations and dimensions. The relevant values are not very

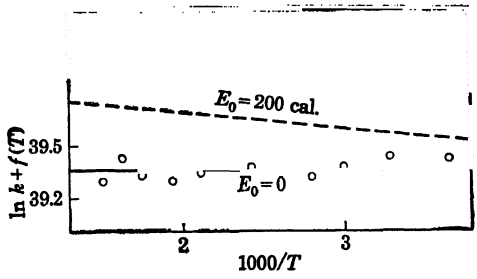


FIG. 16. A plot ln $k + f(T)$ against $1/T$ for the nitric oxide oxygen reaction.

critical, and estimates were made on the basis of the normal interatomic distances in other molecules.

The observed results, and those calculated by the methods outlined above, are shown in Table 18. The agreement is very satisfactory, es-

TABLE 18. CALCULATED AND OBSERVED SPECIFIC RATES FOR THE NITRIC OXIDE–OXYGEN REACTION

T, °K	$k \times 10^{-3}$, liter^2 mole^{-2} sec^{-1}	
	Calculated	Observed
80	86.0	41 8
143	16.2	20.2
228	5.3	10.1
300	3.3	7.1
413	2.2	4.0
564	2.0	2.8
613	2 1	2.8
662	2 0	2.9

pecially in that both theory and experiment show a minimum rate at about the same temperature; this is because the contributions of the vibrational partition function become greater the higher the temperature, and eventually overcome the decrease due to the factor T^{-3}.

The reaction between nitric oxide and chlorine has been treated in an essentially similar manner, the activated complex being assumed to have the configuration shown in Fig. 15, with a Cl_2 molecule replacing the O_2 molecule. A plot of the same function against $1/T$ again gave a straight line, but the slope was found to correspond to an energy of activation of 4.8 kcal. Using this value the specific rates given in Table 19 were

TABLE 19. CALCULATED AND OBSERVED RATES FOR THE NITRIC OXIDE–CHLORINE REACTION

T, °K	k, liter^2 mole^{-2} sec^{-1}	
	Calculated	Observed
273	1.4	5.5
333	2 2	9.5
355	8 6	27.2
401	18.3	72.2
451	25.4	182
506	64.5	453
566	120.2	1,130

calculated. The agreement between calculated and observed values is again quite satisfactory, especially in view of the assumptions made in the theory and the fact that the data are not very accurate.

The experimental results for the reaction between nitric oxide and bromine are not adequate to allow an estimate of the value of E_0 to be made; however, certain qualitative remarks can be made about the reaction. Because bromine is heavier than chlorine, the vibration frequencies are probably lower, and the activation energy will be lower since the Br-Br bond is weaker than the Cl-Cl bond. It therefore follows from Eq. (21) that the rate of this reaction should be greater than that of the reaction with chlorine at the same temperature. This conclusion is in agreement with experiment.

The satisfactory agreement with experiment that is achieved by the theory of absolute reaction rates indicates that the theory is adequate to interpret elementary reactions of the third order from the standpoint of an equilibrium between the complex and the reacting molecules. The question of the way in which the complex is formed is therefore irrelevant to the study of the rate of reaction.

Unimolecular reactions

Practically all unimolecular reactions in the gas phase have been found to be complex, by methods to be discussed in Chap. 7; in the remainder of

this chapter we shall consider, with special reference to the theory, some of the reactions of this class which are almost certainly elementary.

Rearrangement of Cyclopropane to Give Propylene. The first work on this reaction was carried out by Trautz and Winkler,[1] whose investigations indicated that reaction proceeded partly by a first-order homogeneous change and partly by a surface reaction; in addition some thermal decomposition took place. Chambers and Kistiakowsky,[2] working at lower temperatures (470 to 518°C), found that under these conditions the reaction was almost entirely homogeneous (packing the vessel gave no change in velocity) and that propylene was the only product; this was consistent with the fact that the total pressure change was only 1 per cent. The formation of propylene was followed by absorption in 3 per cent neutral

TABLE 20. CONVERSION OF CYCLOPROPANE INTO PROPYLENE; FIRST-ORDER SPECIFIC RATES

Initial pressure, mm	$k^1 \times 10^4$, sec^{-1}
70.26	5.95
37.91	5.74
19.54	5.60
10.86	5.12
5.36	4.84
3.75	4.42
2.44	4.11
1.30	4.06

potassium permanganate solution. Preliminary experiments indicate the reaction to be free from chains,[3] as indeed is to be expected from the nature of the reaction.

In agreement with the Lindemann theory of unimolecular reactions, the first-order specific rates were found to fall off at lower pressures; this is seen from the selected data in Table 20. A plot of k^1, the first-order rate coefficient, against the initial pressure gives a curve of the form of Fig. 13, while a plot of $1/k^1$ against the reciprocal of the initial pressure gives a fairly good straight line, with, however, a slight deviation of the type indicated in Fig. 14. This slight curvature indicates that the Rice-Ramsperger-Kassel refinement (*cf.* p. 82) of the theory is necessary. Detailed application of the theory indicates that about 13 vibrational degrees of freedom must contribute to the process of activation in order to account for the value of the pressure at which the rate constant begins to fall off.

[1] M. Trautz and K. Winkler, *J. prakt. Chem.*, **104**, 53 (1922).

[2] T. S. Chambers and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 399 (1934).

[3] R. N. Pease, "Equilibrium and Kinetics of Gas Reactions," p. 146, Princeton University Press, Princeton, N. J., 1942.

The specific rate of the reaction may be expressed as

$$k = 1.48 \times 10^{15} e^{-65,000/RT} \quad \text{sec}^{-1}$$

or as

$$\log_{10} k = 15.17 - \frac{65,000}{2.303RT}$$

i.e., the activation energy is 65.0 kcal, and the frequency factor 1.48×10^{15} sec^{-1}. For a unimolecular gas reaction the theory of absolute reaction rates gives for the rate constant the expression

$$k = e \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^*/R} e^{-E/RT} \quad \text{sec}^{-1} \tag{24}$$

the factor e being introduced in the change from the heat of activation $\Delta H^{\ddagger}$ to the experimental energy of activation E (*cf.* footnote, p. 94). At 500°C this expression becomes

$$k = 4.37 \times 10^{13} e^{\Delta S^*/R} e^{-E/RT} \quad \text{sec}^{-1} \tag{25}$$

from which it follows that ΔS^* has a value of about 7.0 entropy units.

Rearrangement of Pinene to Give *dl*-Limonene. D. F. Smith[1] investigated the loss of optical activity of *d*-pinene at temperatures between 184 and 237°C and over a range of pressures from 170 to 760 mm Hg. The reaction proceeded homogeneously and was of the first order, and on the assumption that the change was a simple racemization, *i.e.*, a change from the dextro to the levo form, he expressed the first-order rate constant as

$$k = 2.6 \times 10^{14} e^{-43,710/RT} \quad \text{sec}^{-1}$$

The range of pressures was not sufficient to determine whether there was a falling off of the specific rate at low pressures. The reaction was also investigated by G. N. Lewis and Mayer[2] from the point of view of the radiation theory; the pinene vapor was passed at low pressure through a vessel irradiated with infrared radiation of high intensity and of the frequency calculated to produce activation according to the radiation theory. The radiation was found to have no influence on the rate.

Later work by Conant and Carlson[3] and by Thurber and Johnson[4] has, however, shown that the reaction Smith was studying was almost cer-

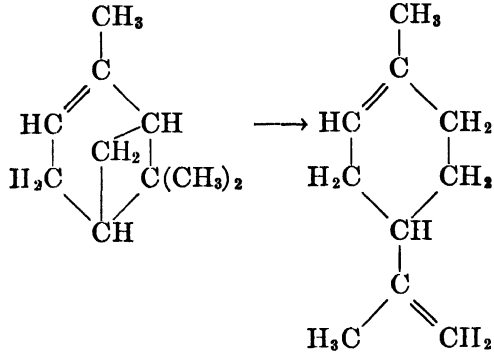
[1] D. F. Smith, *J. Am. Chem. Soc.*, **49**, 43 (1927).

[2] G. N. Lewis and J. E. Mayer, *Proc. Natl. Acad. Sci. U. S.*, **13**, 623 (1927).

[3] J. B. Conant and G. H. Carlson, *J. Am. Chem. Soc.*, **51**, 3464 (1929).

[4] F. H. Thurber and C. H. Johnson, *ibid.*, **52**, 786 (1930). *Cf.* L. S. Kassel, *ibid.*, 1935.

tainly not the simple racemization of pinene but was its conversion to *dl*-limonene:



If this interpretation is correct, Smith's rate constant requires modification: since the reaction is the formation of a dextro-levo compound rather than the levo form of pinene, the rate of reaction is twice that indicated by the change in optical activity and therefore becomes

$$k = 5.2 \times 10^{14} e^{-43{,}710/RT} \qquad \text{sec}^{-1}$$

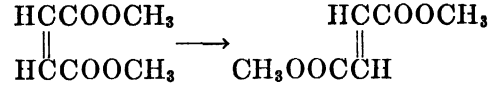
The fact that this rate constant is maintained down to at least 150 mm pressure requires the number of degrees of freedom contributing to activation to be at least eight, which is quite reasonable for a molecule as large as pinene.

At 200°C the theory of absolute reaction rates gives the rate constant as

$$k = 3.24 \times 10^{13} e^{\Delta S^*/R} e^{-E/RT} \qquad \text{sec}^{-1}$$

Comparing this with the experimental rate, it is found that ΔS^* is equal to 5.5 entropy units.

Cis-Trans Isomerizations. A group of reactions which exhibit first-order kinetics and proceed in an elementary fashion are certain cis-trans isomerizations studied by Kistiakowsky and coworkers. The first of these to be investigated was the change of dimethyl maleic ester into dimethyl fumaric ester:[1]



The work was carried out between 270 and 380°C and at pressures from 45 to 530 mm pressure. In addition to the main reaction, it was found that a slow reaction involving the elimination of carbon dioxide took place, but

[1] G. B. Kistiakowsky and M. Nelles, *Z. physik. Chem., Bodenstein-Festband*, 369 (1931).

a correction could be made for this. The experimental technique consisted in leaving a known amount of the maleic ester in a quartz vessel for a known time. The amount of the fumaric acid formed was determined by means of vapor-pressure, melting-point, and dielectric-constant measurements on the liquid formed on cooling.

The reaction was found to be almost completely homogeneous and of the first order. The activation energy was 26.5 kcal, and the rate constant could be expressed as

$$k = 1.3 \times 10^5 e^{-26,500/RT} \qquad \text{sec}^{-1}$$

The frequency factor, 1.3×10^5 is extremely low; the reason for this will be discussed later.

The rate constant was found to fall off at lower pressures, and a plot of $1/k^1$ against $1/p$ gave a straight line. Even one degree of vibrational freedom is more than enough to account for the pressure at which the rate constant falls off.

The change of dimethyl citraconate into the cis form was investigated[1] between 280 and 360°C, and from 30 to 500 mm pressure. The freezing points are here badly defined, and the reaction was followed by making use of the different miscibilities of the esters in mineral oil. As the reaction was complicated by decomposition taking place at the same time, the rate could not be determined with great accuracy, but a value of 25 kcal was obtained for the activation energy. The first-order constant was given as

$$k = 10^5 e^{-25,000/RT} \qquad \text{sec}^{-1}$$

and the frequency factor is again seen to be very low.

A similar experimental technique was used for the change from isostilbene into the trans form:[2]

$$\begin{array}{l} C_6H_5CH \\ \| \\ C_6H_5CH \end{array} \longrightarrow \begin{array}{l} C_6H_5CH \\ \| \\ HCC_6H_5 \end{array}$$

The reaction does not go to completion, and a suitable correction was made for this in calculating the specific rates. The total pressure change was small, indicating side reactions to be unimportant, and very little reaction took place on the surface. The first-order rate constant may be expressed as

$$k = 6 \times 10^{12} e^{-42,800/RT} \qquad \text{sec}^{-1}$$

The frequency factor is here normal, being not far from the value of kT/h. The first-order constant showed no signs of falling off down to 4

[1] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **56**, 638 (1934).
[2] *Ibid.*

mm pressure, and this indicates that at least 12 degrees of freedom contribute to the process of activation.

The change of methyl *cis*-cinnamate into the trans form

$$\begin{array}{l} HCC_6H_5 \\ \| \\ HCCOOCH_3 \end{array} \longrightarrow \begin{array}{r} HCC_6H_5 \\ \| \\ CH_3OOCCH \end{array}$$

is of special interest, because the reactant lies structurally between maleic acid, which has a low frequency factor, and stilbene, which has a normal one. The reaction was investigated[1] using the same method of analysis as with stilbene and dimethyl citraconate; the reaction was found to be fairly free from side reactions and to be homogeneous and of the first order. The rate constant can be expressed as

$$k = 3.5 \times 10^{10} e^{-41,600/RT} \quad \text{sec}^{-1}$$

so that the frequency factor lies between that of maleic acid and of stilbene. The specific rate began to fall at about 5 mm pressure, corresponding to about six degrees of freedom.

The change of β-cyanostyrene to the trans form,

$$\begin{array}{l} HCC_6H_5 \\ \| \\ HCCN \end{array} \longrightarrow \begin{array}{r} HCC_6H_5 \\ \| \\ NCCH \end{array}$$

was investigated using the melting-point method of analysis.[2] The reaction goes to equilibrium corresponding to about 60 per cent change, and the rate constant is given by

$$k = 4 \times 10^{11} e^{-46,000/RT} \quad \text{sec}^{-1}$$

This value is probably not very accurate, since some decomposition occurs, particularly at lower pressures; for this reason it was impossible to determine at what pressure the first-order constant began to fall.

The change of 2-butene from the cis to the trans form,

$$\begin{array}{l} HCCH_3 \\ \| \\ HCCH_3 \end{array} \longrightarrow \begin{array}{r} CH_3CH \\ \| \\ HCCH_3 \end{array}$$

proceeded homogeneously and without side reactions.[3] The activation energy was very small, 18.0 kcal, and the first-order constant is given by

$$k = 2e^{-18,000/RT} \quad \text{sec}^{-1}$$

[1] *Ibid.*, **57**, 269 (1935).
[2] *Ibid.*, **58**, 2428 (1936).
[3] *Ibid.*, 766.

The frequency factor is remarkably small. Kistiakowsky and Smith suggest that the reaction is a chain reaction; this explanation may be consistent with the low activation energy, but it in no way explains the frequency factor.

The results obtained with these cis-trans isomerizations are summarized in Table 21. It is seen that from the point of view of the kinetics the reactions fall into two classes; in one the activation energies are low, about 20 to 25 kcal, and the frequency factor is very much lower than $\mathbf{k}T/\mathbf{h}$, while in the other the activation energies and frequency factors are higher. Within the temperature range of the investigations all the reactions proceeded at roughly the same rate, so that the differences between the two classes are surprising.

TABLE 21. FREQUENCY FACTORS AND ACTIVATION ENERGIES FOR CIS-TRANS ISOMERIZATIONS

Reactant	Frequency factor, sec^{-1}	Activation energy, kcal per mole
Dimethyl maleate	1.3×10^5	26 5
Dimethyl citraconate	10^5	25
2-Butene	2	18
Isostilbene	6×10^{12}	42.8
Methyl cinnamate	3.5×10^{10}	41.6
β-Cyanostyrene	4×10^{11}	46

The reactions in the second group are normal, in that the frequency factor corresponds to an entropy of activation quite close to unity, as is to be expected for such a transformation. An explanation that has been offered[1] for the other class of reactions involves the postulation of a triplet excited state for the ethylenic derivatives, this state lying 20 to 25 kcal above the normal, singlet, state.[2] The variation in potential energy on rotation about the double bond is represented by curves I and I′ in Fig. 17, in which θ represents the angle of rotation. The normal type of reaction is envisaged as corresponding to a crossing from curve I to curve I′ at the point A. The potential-energy curve for the triplet-excited state is shown as curve II, and if it can be assumed that II cuts I and I′ at 20 to 25 kcal

[1] J. L. Magee, W. Shand, and H. Eyring, *ibid.*, **63**, 677 (1941); H. M. Hulburt, R. A. Harman, A. V. Tobolsky, and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943).

[2] For discussions of the triplet-excited state of ethylenic compounds, see R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932); H. Hartmann, *Z. physik. Chem.*, **B, 53**, 96 (1943); G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944); M. Kasha, *Chem. Revs.*, **41**, 401 (1947); R. S. Mulliken and C. J. Roothaan, *ibid.*, 219.

above the ground level, a possible mechanism for the reactions of low frequency factor involves a passage from I to I′ via II. As will be seen in Chap. 13, a transition from I to II, involving as it does a change in multiplicity, will take place only with difficulty and will therefore give rise to a low frequency factor. Detailed calculations of the frequency factors gave good agreement for dimethyl maleate but poor agreement for 2-butene.

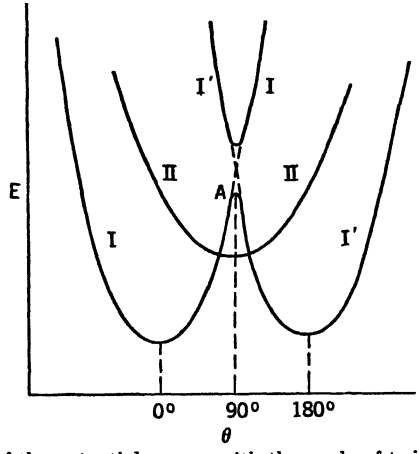
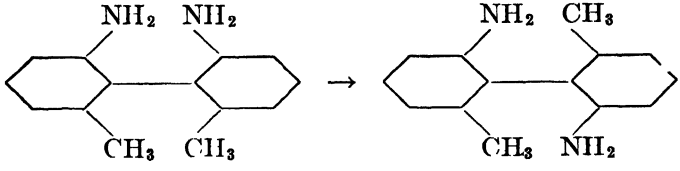


FIG. 17. The variation of the potential energy with the angle of twist about a double bond

Racemizations. Another group of reactions which almost certainly proceed in an elementary fashion comprises certain racemizations of optically active compounds, particularly substituted diphenyls. Kistiakowsky and Smith[1] have studied the kinetics of the racemization of 2,2′-diamino-6,6′-dimethyldiphenyl,



both in the gas phase and in solution. The measurements in the gas phase were made between 50 and 150 mm pressure and at temperatures between 342 and 388°C. The reaction was followed by quenching the reaction after known lengths of time, dissolving the crystals in diphenyl ether, and determining the activity of the solution. The reaction was found to be homogeneous and of the first order, and the specific rate is given by

$$k = 2.35 \times 10^{10} e^{-45{,}100/RT} \quad \text{sec}^{-1}$$

The constant showed no signs of falling off as the pressure was lowered,

[1] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **58**, 1043 (1936).

and to account for this, the participation of at least six degrees of freedom has to be assumed.

Other racemizations of this type have only been investigated in solution.

PROBLEMS

1. The following rate constants[1] are given for the reaction $H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$:

T, °K	$k \times 10^7$, *liters mole*$^{-1}$ *sec*$^{-1}$
283	3 41
330	19.8
373	73 0

Determine the experimental energy of activation, employing the method of least squares. Calculate the frequency factor and the entropy of activation.

2. Using collision theory, calculate the rate constant at 300°K for the decomposition of hydrogen iodide, assuming a collision diameter of 3.5 A and an activation energy of 44 kcal. To what entropy of activation does the result correspond?

3. Using the values given on page 90, calculate the rate at 400°C of the reaction between hydrogen and iodine, both present at ½ atm pressure.

4. Using the entropy values given in Table 17, calculate the rate at 500°C of the hydrogen-iodine reaction when both reactants are present at ½ atm pressure.

5. The frequency factor for the gas-phase dissociation of the dimer of cyclopentadiene is 1.3×10^{13} sec^{-1}, and the activation energy is 35.0 kcal. Calculate (*a*) the entropy of activation, (*b*) the rate constant at 100°C, and (*c*) the rate at 100°C and 1 atm pressure.

6. Calculate the frequency factor for the hypothetical gas-phase combination of two hydrogen atoms, assuming the interatomic separation in the activated state to be 0.74 A. Assume the transmission coefficient to be unity.

7. Using the following rate constants for the nitric oxide–oxygen reaction:

T, °K	$k \times 10^{-9}$, *cc*^{2} *mole*$^{-2}$ *sec*$^{-1}$
80	86.0
143	16.2
228	5.3
300	3.3

and assuming the activation energy to be zero, determine to the nearest half power the temperature dependence of the frequency factor.

8. The following are the specific rates of the termolecular reaction between nitric oxide and chlorine:

T, °K	$k \times 10^{-6}$, *cc*^{2} *mole*$^{-2}$ *sec*$^{-1}$
273	5.5
355	27.2
451	182
566	1,130

[1] K. H. Geib and P. Harteck, *Z. physik. Chem., Bodenstein-Festband*, 849 (1931).

Assuming that the frequency factor is inversely proportional to T^3, determine the energy of activation.

9. From the data given on page 104 for the rearrangement of pinene, verify that at least eight degrees of freedom must be assumed. Take $\sigma = 10^{-7}$ cm.

10. The rate constant for the gaseous racemization of 2,2′-diamino-6,6′-dimethyldiphenyl is given as

$$k = 2.35 \times 10^{10} e^{-45{,}100/RT} \quad \text{sec}^{-1}$$

If 20 degrees of vibrational freedom contribute, at what pressure will the first-order coefficient begin to fall off? Take $\sigma = 10^{-7}$ cm.

CHAPTER 5

REACTIONS IN SOLUTION

When a chemical reaction takes place in solution, the solvent is usually in such great excess that its concentration cannot change appreciably as the reaction proceeds, and the rate expression accordingly need not involve it. In some cases, moreover, the stoichiometric equation for the reaction does not involve the solvent, which may then merely provide a physical environment for the reaction. In other instances there is reason to believe that the solvent enters into the chemical change and may or may not be regenerated at the end of the process; in these cases the solvent would be said to exert a chemical effect on the reaction, this being superimposed on its physical effect. Since the physical forces are much less well understood than the purely chemical ones, no satisfactory treatment of solvent effects has been given. In the first part of the present chapter will be presented some of the more significant experimental results which may throw some light on the problem, and the various theories that have been put forward will be outlined.[1]

Valuable evidence as to the influence of the solvent on the rates of reactions in solution has come from two types of investigation. In the first, studies have been made both in solution and in the gas phase; only a few reactions have been studied in this way, largely because a great many reactions which occur in solvents, in particular ionic reactions, will not take place homogeneously in the gas phase. Accordingly much of the information on the influence of the solvent has had to come from the second type of investigation, which is less definite and more difficult to interpret: this comprises the work that has been done on reactions in different solvents.

Comparison between gas-phase and solution reactions

In the present section will be considered those reactions which have been studied comprehensively in the gas phase and in at least one solvent.

[1] For reviews of solvent effects, see E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, New York, 1947; K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940); R. P. Bell, "Handbuch der Katalyse," Vol. II, 319, J. Springer, Berlin, 1940 (reprinted by J. W. Edwards, Ann Arbor, Michigan, 1944); S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," Chap. VIII, McGraw-Hill Book Company, Inc., New York, 1941.

These reactions comprise both simple and complex processes, of which the former will be considered first.

Isomerization of Pinene. The gas-phase isomerization of pinene to give *dl*-limonene was considered in the last chapter; the reaction in petrolatum solution has also been investigated.[1] In both cases the reaction is an elementary homogeneous reaction of the first order. The rate is about 50 per cent greater in solution, and the activation energy in solution is 41.2 as compared with 43.7 kcal in the gas phase. However no significance is to be attached to the difference in activation energy, as the value in solution is based on limited data.

Racemization of 2,2′-diamino-6,6′-dimethyldiphenyl. This reaction in the gas phase was considered on page 108; the kinetics have also been investigated in molten diphenyl as solvent.[2] The rate in solution is about 3.5 times that in the gas phase, and the activation energy is given as 45.1 kcal in both cases.

Para-Ortho Hydrogen Conversion, Catalyzed by Oxygen. The influence of oxygen on the conversion of *p*-hydrogen into an equilibrium mixture of the para and ortho forms is not a chemical effect but is a magnetic one brought about by the paramagnetic character of the oxygen. The reaction has been investigated in the gas phase and in solution,[3] and the rates were found to be the same at 20°C within the experimental error. The measurements were made at only one temperature, so that no activation energy is available; however, it is probable that the value is zero in each case.

Reversible Dimerization of Cyclopentadiene. The dimerization of cyclopentadiene and the reverse dissociation of the dimer have been studied in the gas phase, in the pure liquid state, and in the solvents carbon tetrachloride, carbon disulfide, benzene, and paraffin.[4] The values of $\log_{10} A$ and E for both reactions are given in Table 22. It is seen that with the exception of the dimerization in paraffin solution the values are identical within the experimental error; in paraffin the activation energy and the frequency factor seem to be appreciably higher.

The above examples constitute the only elementary reactions which have been studied both in the gas phase and in solution. The remaining reactions will comprise the only complex reactions for which this has been done.

[1] D. F. Smith, *J. Am. Chem. Soc.*, **49**, 43 (1927).

[2] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, **58**, 1043 (1936).

[3] L. Farkas and H. Sachsse, *Z. physik. Chem.*, **B, 23**, 1, 19 (1933).

[4] B. S. Khambata and A. Wassermann, *Nature*, **137**, 496 (1936); **138**, 368 (1936); A. Wassermann, *J. Chem. Soc.*, 1028 (1936); G. A. Benford, B. S. Khambata, and A. Wassermann, *Nature*, **139**, 669 (1937); A. Wassermann, *Trans. Faraday Soc.*, **34**, 128 (1938).

TABLE 22. VALUES OF $\log_{10} A$ AND E FOR THE DIMERIZATION OF CYCLOPENTADIENE AND THE REVERSE DISSOCIATION

Medium	Dimerization		Dissociation	
	$\log_{10} A$	E, kcal	$\log_{10} A$	E, kcal
Gas phase	6.1	16.7	13.1	35.0
Pure liquid	5.7	16.0	13.0	34.5
Carbon tetrachloride	5.9	16.2		
Carbon disulfide	5.7	17.7		
Benzene	7.1	16.4		
Paraffin	8.1	17 4	13.0	34 2

TABLE 23. VALUES OF k, $\log_{10} A$, AND E FOR THE DECOMPOSITION OF NITROGEN PENTOXIDE IN VARIOUS SOLVENTS

Solvent	$k \times 10^5$ (at 25°C)	$\log_{10} A$	E, kcal
(Gas phase)*	3 38	13 6	24 7
Carbon tetrachloride†	4 09	13 8	25.5
Carbon tetrachloride‡	4 69	13.6	24 2
Chloroform†	3 72	13.6	24 5
Chloroform‡	5 54	13 7	24 6
Ethylene dichloride‡	4.79	13.6	24.4
Ethylidine dichloride‡	6 56	14.2	24.9
Pentachloroethane‡	4 30	14.0	25 0
Nitromethane‡	3.13	13.5	24 5
Bromine‡	4 27	13 3	24 0
Nitrogen tetroxide‡	7 05	14 2	25.0
Nitric acid‡	0 147	14 8	28.3
Propylene dichloride‡	0.510	14 6	27.0

* F Daniels and E. H. Johnston, *J Am Chem. Soc.*, **43**, 53 (1921).
† R. H Lueck, *ibid.*, **44**, 757 (1922).
‡ H. Eyring and F. Daniels, *ibid.*, **52**, 1473 (1930).

Decomposition of Nitrogen Pentoxide. The gas-phase decomposition of nitrogen pentoxide will be seen in Chap. 8 to be a complex reaction, and a mechanism will be given which is consistent with the first-order kinetics and other features of the reaction. The reaction has also been studied in a wide variety of solvents[1] and again follows the first-order law. The specific rates, activation energies, and values of $\log_{10} A$ are given in Table 23. In all except the last two solvents the results indicate only small deviations from those found in the gas phase; the velocity variations are slightly

[1] R. H. Lueck, *J. Am. Chem. Soc.*, **44**, 757 (1922); H. Eyring and F. Daniels, *ibid.*, **52**, 1473 (1930).

greater than the experimental error, but the variations in A and in E are not significant. In nitric acid and propylene dichloride, on the other hand, there is a considerable decrease in velocity, an increase in the activation energy, and perhaps a significant increase in the value of the frequency factor.

Decomposition of Chlorine Monoxide. This reaction has been studied in the gas phase and also in carbon tetrachloride solution.[1] The reaction is complex, and it has not been possible to evaluate the velocity constants for the various stages; therefore the best that can be done is to compare the over-all rates, and this was done by comparing the times for a certain percentage of the reaction to take place. This was carried out at five temperatures between 60 and 80°C, and the times were found to be the same, at a given temperature, in solution and in the gas phase. It can therefore be concluded that the values of the rate, of A, and of E, are not much different in the two media.

Decomposition of Ozone Catalyzed by Chlorine. The decomposition of pure ozone has been found to be approximately of the second order in the gas phase (*cf.* p. 224) and of the first order in carbon tetrachloride solution.[2] Consequently the rates cannot be compared, but it is to be noted that this change of order indicates that the rates of some of the elementary processes occurring are different in the gas phase and in the solvent. The kinetics of the chlorine-catalyzed reaction are the same in the gas phase and in carbon tetrachloride solution.[3] The reaction was not studied in the same temperature range in the two media, but as far as can be told from extrapolation of the results in solution, the rates, frequency factors, and activation energies are the same.

Decomposition of Ethylene Diiodide. The decomposition of ethylene diiodide has been studied in carbon tetrachloride solution[4] as well as in the gas phase; the data are not very accurate, but no significant difference between the values of k, A, and E in the two media could be detected.

The hydrolysis of carbonyl sulfide by water has been studied in the gas phase, in aqueous solution, and in alcohol solution,[5] but the reaction is too complex to permit a comparison between the results in the various media.

[1] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **123**, 2730 (1923); C. N. Hinshelwood and J. Hughes, *ibid.*, **125**, 1841 (1924); J. J. Beaver and G. Steiger, *Z. physik. Chem.*, **B, 12**, 93 (1931); E. A. Moelwyn-Hughes and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 131**, 177 (1931).

[2] E. J. Bowen, E. A. Moelwyn-Hughes, and C. N. Hinshelwood, *ibid.*, **A, 134**, 212 (1931).

[3] *Ibid.*

[4] M. Polissar, *J. Am. Chem. Soc.*, **52**, 956 (1930).

[5] H. W. Thompson, C. F. Kearton, and S. A. Lamb, *J. Chem. Soc.*, 1033 (1935).

Comparison between different solvents

It is apparent from the results quoted above that in most cases there are no great differences between the kinetics of reactions occurring in solution and in the gas phase. However it would be unwise to conclude from this that the influence of the solvent is in general not important, as the similarity between the rates to some extent depends upon the ability of the reaction to occur in the gas phase as well as in solution. When reactions which do not occur in the gas phase are considered, it is found that the influence of the solvent, as judged by comparing the kinetics in different solvents, is very much more marked.

In considering such reactions, it is of interest to compare the values of A obtained in solution with those expected on the basis of simple collision theory or the theory of absolute reaction rates. It has been seen that collision theory gives a value of 10^9 to 10^{11} for the frequency factor† and that this value is also obtained for second-order reactions involving relatively simple molecules by the theory of absolute rates. When complex molecules react in a bimolecular manner, the latter theory predicts that the frequency factor should be much less than that given above. As will be seen in the present section, a number of reactions in solution have been found to have very low frequency factors and are accordingly spoken of as "slow" reactions; well-known examples are the formation of quaternary ammonium salts and the benzoylation of amines. To exactly what extent these low frequency factors are due to specific solvent influences is difficult to ascertain in view of the failure of the reactions to proceed in the gas phase. However it is important to note that the dimerization of cyclopentadiene has a very low frequency factor in the gas phase as well as in solution (*cf.* Table 22), so that in this instance, at least, the low frequency factor cannot be attributed to a solvent influence; the decrease in entropy as the two molecules become one is clearly the cause.

In general, it is found that reactions between an ion and a neutral molecule have a "normal" frequency factor, *i.e.*, 10^9 to 10^{11}, even when the neutral molecule is of some complexity; the rates of such reactions would therefore agree with their hypothetical rates in the gas phase as predicted by either of the theories. Reactions between ions of opposite sign have high frequency factors and those between ions of the same sign low ones. This is due to the electrostatic forces and will be considered quantitatively in a later section of this chapter.

The results obtained with one or two reactions in various solvents will now be discussed briefly.

† Unless otherwise stated, frequency factors for second-order reactions are in the units liters per mole per second.

Formation of Quaternary Ammonium Salts. The reaction between triethylamine and ethyl iodide was studied in 22 different solvents by Menschutkin,[1] who found variations in the velocity of about a thousand-fold. He measured no activation energies, but this was done by Grimm,

TABLE 24. FORMATION OF QUATERNARY AMMONIUM SALTS IN VARIOUS SOLVENTS

Solvent	Ethyl iodide and triethylamine			Pyridine and Methyl Iodide	
	$k \times 10^5$ (at 100°C)	E, kcal	$\log_{10} A$	E, kcal	$\log_{10} A$
Hexane	0.5	16.0	4.0		
Toluene	25.3	13.0	4.0	14.5	5.5
Benzene	39.8	11.4	3 3	14 2	5.4
Bromobenzene	166.0	12.5	4 6	13 7	5.7
Acetone	265 0	11.9	4 4	14 0	6.5
Benzonitrile	1,125.0	11 9	5.0	13.7	6.5
Nitrobenzene	1,383.0	11 6	4 9	13 7	6 6

Ruf, and Wolff,[2] some of whose results are included in Table 24. The reaction between pyridine and methyl iodide has also been investigated,[3] and some of the results are given in the table. It is seen that in both reactions the variation in the rate is largely determined by the activation energy, the

TABLE 25. BENZOYLATION OF *m*-NITROANILINE IN VARIOUS SOLVENTS

Solvent	E, kcal	$\log_{10} A$
Carbon tetrachloride	13 6	5.5
Isopropyl ether	10.9	4.4
Benzene	10.3	4.2
Chlorobenzene	11.4	4.8
Nitrobenzene	9.4	5 0
Benzonitrile	10.1	6 4

value of $\log_{10} A$ being comparatively constant. The reaction is seen to be a "slow" one; this is probably largely due to entropy effects.

Benzoylation of Amines. A similar variation in rate and activation energy with change of solvent was found with the benzoylation of *m*-

[1] N. Menschutkin, *Z. physik. Chem.*, **6**, 41 (1890).

[2] H. G. Grimm, H. Ruf, and H. Wolff, *ibid.*, **B, 13**, 301 (1931).

[3] N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936); R. A. Fairclough and C. N. Hinshelwood, *ibid.*, 538, 1573 (1937).

nitroaniline,[1] some of the results for which are given in Table 25. Again the variation in A is somewhat less important than that in E.

Addition of Cyclopentadiene to Benzoquinone. The addition of cyclopentadiene to benzoquinone is a simple reaction which has been studied in a variety of solvents;[2] some of the results are included in Table 26. The

TABLE 26. REACTION BETWEEN CYCLOPENTADIENE AND BENZOQUINONE

Solvent	E, kcal	$\log_{10} A$
Ethyl alcohol	12.7	7.0
Carbon tetrachloride	9.2	4.5
Benzene	11.5	6 3
Nitrobenzene	8 8	5 0

main variations are again in the energy of activation, but the changes in $\log_{10} A$ are here greater than those cited previously.

Decomposition of Trinitrobenzoic Acid. The thermal decomposition of trinitrobenzoic acid is an example of a first-order decomposition that has been studied in a variety of solvents;[3] some results are given in Table

TABLE 27. DECOMPOSITION OF TRINITROBENZOIC ACID

Solvent	$9 + \log_{10} k$ (at 70°C)	E, kcal	$\log_{10} A$
Toluene	0.21	31 6	12.0
Nitrobenzene	0.6	35.0	14.6
Anisole	2.29	30.7	13.5
Acetophenone	2.76	25 5	10 5
Water	3.52	30 0	14 3

27. It is seen that a thousandfold variation in the rate is observed with the solvents used but that the values of E and $\log_{10} A$ are rather scattered.

The examples of reactions studied in different solvents could be continued, but the reactions quoted are sufficient to illustrate the general type of behavior that is observed.

Factors determining reaction rates in solution

Rate-determining Step in Solution. The reaction between two molecules in solution can be thought of as occurring in three well-defined stages:

[1] Pickles and Hinshelwood, *loc. cit.*

[2] A. Wassermann, *Ber.*, **66**, 1932 (1933); *Nature*, **137**, 497 (1936); *Trans. Faraday Soc.*, **34**, 128 (1938); R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 236 (1938).

[3] Moelwyn-Hughes and Hinshelwood, *op. cit.*, 186.

(1) the diffusion of the molecules to one another, (2) the actual chemical transformation, and (3) diffusion of the products away from one another. Diffusion in a liquid, like many other physical processes, has an activation energy, but the magnitude of this is generally not greater than 5 kcal. Chemical reactions which have activation energies of more than this, as do most, thus cannot involve diffusion as the slow step, which must therefore be step (2), the purely chemical process. This conclusion is supported by the fact that the rates of these reactions do not depend upon the viscosity of the solvent, as they would if diffusion were important, diffusion and viscosity being very closely related. Most of the discussion in the present book will be devoted to such reactions in which step (2) is slow and rate determining.

On the other hand, there are some processes occurring in solution in which the diffusion is rate controlling; these are certain reactions which occur very rapidly. Ionic recombinations are of this type; the rates of such reactions are too rapid to be measured conveniently, but it would no doubt be found that diffusion was rate controlling. The quenching of fluorescence in solution also involves diffusion as the slow step.[1] Certain heterogeneous reactions between solids and liquids are also of this type.

Since the chemical interaction between the molecules is of primary importance in determining the rate in most cases, a study of rates in different solvents will be concerned largely with the influence of the solvent on this step. This problem will be considered in terms of the theory of absolute reaction rates, which offers the most constructive approach to the problem.

Theory of Absolute Reaction Rates.[2] The application of the theory of absolute reaction rates to reactions in solution is simple in principle but is difficult to carry out quantitatively, owing to our imperfect knowledge of the liquid state. As with gas reactions, the rate can be expressed in terms of partition functions for the reacting species and the activated state, but they should contain terms for the influence of the solvent environment. However, since there is so much uncertainty about partition functions in solution, it is better to treat rates in solution in a less fundamental manner, by using activity coefficients.

It has been seen in Chap. 3 that the rate of a reaction may be expressed as the product of the frequency $\mathbf{k}T/\mathbf{h}$ and the concentration $[X^{\ddagger}]$ of the

[1] *Cf.* R. W. Roughton and G. K. Rollefson, *J. Am. Chem. Soc.*, **61**, 2634 (1939); **62**, 2264 (1940); V. K. LaMer and M. E. Kamner, *ibid.*, **57**, 2662 (1935); P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); J. Q. Umberger and V. K. LaMer, *J. Am. Chem. Soc.*, **67**, 1099 (1945).

[2] *Cf.* W. F. K. Wynne-Jones and H. Eyring, *J. Chem. Phys.*, **3**, 493 (1935); A. E. Stearn and H. Eyring, *ibid.*, **5**, 113 (1937); K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

activated complex, *i.e.*,

$$v = \frac{\mathbf{k}T}{\mathbf{h}} [X^{\ddagger}] \tag{1}$$

the transmission coefficient being assumed to be unity. For the reaction

$$A + B \rightleftharpoons X^{\ddagger} \rightarrow \text{products}$$

the concentration $[X^{\ddagger}]$ may be expressed as

$$[X^{\ddagger}] = K^*[A][B] \frac{\alpha_A \alpha_B}{\alpha_{\ddagger}} \tag{2}$$

where the α are the activity coefficients, previously neglected since in the gas phase they are close to unity. Substituting this expression in Eq. (1), the equation for the rate is seen to be

$$v = [A][B] \frac{\mathbf{k}T}{\mathbf{h}} K^* \frac{\alpha_A \alpha_B}{\alpha_{\ddagger}} \tag{3}$$

and the specific rate is

$$k = \frac{\mathbf{k}T}{\mathbf{h}} K^* \frac{\alpha_A \alpha_B}{\alpha_{\ddagger}} \tag{4}$$

For an ideal gaseous system the activity coefficients are unity, so that the specific rate reduces to

$$k_g = \frac{\mathbf{k}T}{\mathbf{h}} K^* \tag{5}$$

The specific rate in solution can therefore be related to that in the gas phase by the equation

$$k = k_g \frac{\alpha_A \alpha_B}{\alpha_{\ddagger}} \tag{6}$$

This equation can be used for relating the rate constant in solution not only to that in the gas phase but also to that in very dilute solution, where the substances behave ideally; this will be considered later.

If the rates in solution and in the gas phase are to be equal, the activity-coefficient factor $\alpha_A \alpha_B / \alpha_{\ddagger}$ must be equal to unity. This may easily arise for a unimolecular reaction, for which the appropriate factor is $\alpha_A / \alpha_{\ddagger}$; if the reactant and the activated complex have similar structures, as is often the case, α_A and $\alpha_{\ddagger}$ will not differ greatly, and the rate of reaction in solution will be similar to that in the gas phase. It has been seen that this similarity in rates is approximately true for the decomposition of nitrogen pentoxide in a number of solvents (see Table 23, p. 113). The abnormally slow rate of decomposition in nitric acid and propylene dichloride, and the

correspondingly high energies of activation, may be due to the formation of a complex between the reactant and the solvent; such compound formation decreases α_A and consequently the rate of reaction. Other unimolecular reactions taking place at about the same rate in solution as in the gas phase include the isomerization of pinene, the racemization of 2,2′-diamino-6,6′-dimethyldiphenyl, and the decomposition of chlorine monoxide.

The situation with regard to bimolecular reactions in solution is best considered in terms of empirical results for entropies and energies of solution.[1] It has been found that heats and entropies of solution are related in a linear manner by the equation

$$T\ \Delta S_0 = \rho\ \Delta H_0 + \sigma \tag{7}$$

where ρ and σ are constants. If the specific reaction rates in solution and in the gas phase are written in the forms

$$k_s = \frac{\mathbf{k}T}{\mathbf{h}}\, e^{\Delta S_s^*/R} e^{-\Delta H_s^\ddagger/RT} \tag{8}$$

and

$$k_g = \frac{\mathbf{k}T}{\mathbf{h}}\, e^{\Delta S_g^*/R} e^{-\Delta H_g^\ddagger/RT} \tag{9}$$

the ratio is given by

$$\frac{k_s}{k_g} = e^{\Delta S^*/R} e^{-\Delta H^\ddagger/RT} \tag{10}$$

where $\Delta S^* = \Delta S_s^* - \Delta S_g^*$ and $\Delta H^\ddagger = \Delta H_s^\ddagger - \Delta H_g^\ddagger$. The physical significance of ΔS^* is that it is the entropy of solution of the activated complex minus the sum of the entropies of solution of A and B,

$$\Delta S^* = \Delta S_0^* - (\Delta S_{0A} + \Delta S_{0B}) \tag{11}$$

Substitution of the entropies of solution given by Eq. (7) gives

$$\Delta S^* = \left(\frac{\rho_\ddagger\, \Delta H_0^\ddagger}{T} + \frac{\sigma_\ddagger}{T}\right) - \left(\frac{\rho_A\, \Delta H_{0A}}{T} + \frac{\sigma_A}{T}\right) - \left(\frac{\rho_B\, \Delta H_{0B}}{T} + \frac{\sigma_B}{T}\right) \tag{12}$$

which may be abbreviated to

$$\Delta S^* = \frac{\Sigma\rho\ \Delta H}{T} + \frac{\Sigma\sigma}{T} \tag{13}$$

Substitution of this expression for ΔS^* into Eq. (10) gives

$$\frac{k_s}{k_g} = e^{\Sigma\sigma/RT} e^{-(\Delta H^\ddagger - \Sigma\rho\ \Delta H)/RT} \tag{14}$$

[1] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936); R. P. Bell, *ibid.*, **33**, 496 (1937); J. A. V. Butler, *ibid.*, 171, 229 (1937); I. M. Barklay and J. A. V. Butler, *ibid.*, **34**, 1445 (1938).

The ratio of frequency factors is therefore given by $e^{\Sigma\sigma/RT}$, while the difference in activation energies is equal to $\Delta H^{\ddagger} - \Sigma\rho\ \Delta H$. For many gases the value of σ lies within the range -470 to -840 cal at 25°C; taking the value of -650 cal, it is seen that the ratio of frequency factors for a bimolecular reaction is[1]

$$\frac{A_s}{A_g} = e^{650/RT} \tag{15}$$

which has the value of 2 to 3 at ordinary temperatures. If therefore the heats of activation are the same in solution as in the gas phase, such a ratio will be found between the rates; this condition will hold only provided that the reactants and activated complex are not appreciably solvated in solution.

It may therefore be concluded that, provided processes of an unusual nature do not occur, the rate of a bimolecular reaction should be of the same order in solution as in the gas phase. This has been seen to be true in a number of instances.

Influence of Internal Pressure. The application of the theory of solutions to reaction rates has revealed some interesting regularities concerning the relationship between rate and internal pressure. The activity coefficient α, which appears in Eq. (6), is proportional to the more usual activity coefficient γ, which relates the behavior of a solute to its behavior in an ideal solution, so that the rate of reaction can be written as

$$\frac{k_s}{k_0} = \frac{\gamma_A\gamma_B}{\gamma_{\ddagger}} \tag{16}$$

where k_0 is now the rate in the ideal solution. For a regular solution, *i.e.*, one in which the molecular distribution is entirely random in spite of the nonideality, the activity coefficient γ_1 of a solute can be expressed in the form[2]

$$RT \ln \gamma_1 = v_1 \left(\frac{N_2 v_2}{N_1 v_1 + N_2 v_2}\right)^2 \left[\left(\frac{E_1}{v_1}\right)^{1/2} - \left(\frac{E_2}{v_2}\right)^{1/2}\right]^2 \tag{17}$$

where N_1 and N_2 are the mole fractions of solute and solvent, v_1 and v_2 their molar volumes, and E_1 and E_2 the energies of vaporization of solute and solvent when in the form of pure liquids. If the solution is dilute, $N_1 v_1$ may be neglected in comparison with $N_2 v_2$, and the expression reduces to

$$RT \ln \gamma_1 = v_1 \left[\left(\frac{E_1}{v_1}\right)^{1/2} - \left(\frac{E_2}{v_2}\right)^{1/2}\right]^2 \tag{18}$$

[1] *Cf.* M. G. Evans and M. Polanyi, *ibid.*, **31**, 875 (1935); Bell, *loc. cit.*, *ibid.*, **35**, 324 (1939); *Ann. Repts. on Progress Chem. (Chem. Soc. London)*, **36**, 82 (1939).

[2] G. Scatchard, *Chem. Revs.*, **8**, 321 (1931); J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933); Laidler and Eyring, *loc. cit.*

The quantities E/v are approximately equal to a/v^2, where a is the van der Waals attraction constant, and are hence roughly equal to the internal pressure P of the liquid; thus

$$RT \ln \gamma_1 = v_1(P_1^{1/2} - P_2^{1/2})^2 = v_1\Delta \tag{19}$$

Here Δ is an abbreviation for $(P_1^{1/2} - P_2^{1/2})^2$ and is always a positive quantity. Taking logarithms of Eq. (16) and inserting the values of $\ln \gamma$ given by Eq. (19) gives

$$RT \ln k_s = RT \ln k_0 + v_A\Delta_A + v_B\Delta_B - v_\ddagger\Delta_\ddagger \tag{20}$$

For regular solutions the influence of the solvent is therefore determined by the molar volumes and the internal-pressure terms.

The molar volumes do not vary greatly; hence the internal-pressure factor is the more important. If the internal pressures of solvent, of A, B, and of the activated complex are all similar, the solvent will have little effect on the rate of reaction as compared with a solvent in which the reaction behaves ideally. If the internal pressure of the solvent is close to the values for the reactants, *i.e.*, if Δ_A and Δ_B are small, but appreciably different from that of the complex, *i.e.*, $\Delta_\ddagger$ is large, the factor $v_A\Delta_A + v_B\Delta_B - v_\ddagger\Delta_\ddagger$ will have a relatively large negative value, and in accordance with Eq. (20) the rate in this solvent will be low. If, on the other hand, the solvent has an internal pressure similar to that of the activated complex, but different from those of one or both of the reactants, the factor $v_A\Delta_A + v_B\Delta_B - v_\ddagger\Delta_\ddagger$ will be large and positive, and the reaction rate will be high. Since the activated complex has properties which approach those of the products of reaction, and which may resemble them very closely in some cases, it follows as a general rule that if the reaction is one in which the products are of higher internal pressure than the reactants, it is accelerated by solvents of high internal pressure. This rule was first stated empirically by Richardson and Soper[1] and was arrived at theoretically by Glasstone.[2]

This rule may now be applied to some of the examples quoted earlier in this chapter. In general, for bimolecular associations of the type $A + B \rightarrow C$, the activated complex may be expected to resemble C; thus for the formation of quaternary ammonium salts the complex will resemble the ionic product and consequently have a high internal pressure. It should therefore be accelerated by solvents of high internal pressure; this is confirmed by the first column of figures given in Table 28, the solvent internal pressures increasing roughly in the order given. On the other hand, solvents which favor the formation of quaternary ammonium salts tend to slow down reactions like the dissociation of sulfonium salts and esterifications

[1] M. Richardson and F. G. Soper, *J. Chem. Soc.*, 1873 (1929).

[2] S. Glasstone, *ibid.*, 723 (1936).

(*cf.* Table 28) in which the products are of lower internal pressure than the reactants. However, deviations from these rules are often found and can frequently be explained as solvation effects, the solutions no longer being regular.

Influence of Solvation. The degree of solvation of the reactants and the activated complex has a very pronounced influence on the rate of reaction. If the reactants are not appreciably solvated but the activated complex is, the activity coefficient of the complex is smaller than it is in a solvent that does not solvate it; consequently, by Eq. (2), the rate of the reaction will be greater than in a nonsolvating solvent. This explains at least in part the very high rate of formation of quaternary ammonium salts in nitrobenzene as compared with benzene (see Table 28); the activated complex probably resembles the product in being a polar substance and

TABLE 28. INFLUENCE OF SOLVENTS ON SPECIFIC RATES

Solvent	Triethylamine and ethyl iodide (at 100°C)	Acetic anhydride and ethyl alcohol (at 50°C)
Hexane	0 00018	0 0119
Chlorobenzene	0 023	0.0053
Benzene	0 0058	0.0046
Anisole	0.040	0.0029
Nitrobenzene	70 1	0 0024

hence is solvated to a considerable degree by nitrobenzene but not by benzene. On the other hand, a reaction occurring in a solvent which solvates the reactants to a greater degree than the activated complex will take place less rapidly than it would in a solvent in which the reactants are not solvated.

Reactions between ions

The Brønsted-Bjerrum Equation. In treating reactions between nonelectrolytes, it is difficult to do more than to discuss the influence of solvent qualitatively; for reactions between ions, on the other hand, a quantitative treatment is possible. This arises because the activity coefficients of ions can be expressed explicitly and fairly accurately in terms of the ionic charge, since the electrical forces exert a more powerful influence on the activity coefficients than the nonelectrical forces, which are much more difficult to evaluate.

The equation for the rate of an ionic reaction in terms of the relevant activity coefficients was first given by Brønsted,[1] whose derivation was

[1] J. N. Brønsted, *Z. physik. Chem* **102**, 169 (1922).

improved by Bjerrum.[1] Bjerrum's approach was equivalent to that of the theory of absolute reaction rates, in that the rate of reaction was assumed to be proportional to the concentration of a critical complex, which is equivalent to the activated complex of the modern theory. For the treatment of ionic reactions it is most convenient to compare the rates in a given solution with those obtained in an infinitely dilute solution; the corresponding activity coefficients, relating the behavior of a solution to the infinitely dilute solution, may be denoted by f. The equilibrium condition between the complex and the reactants may thus be expressed as

$$K^{\ddagger} = \frac{c_{\ddagger}}{c_A c_B} \frac{f_{\ddagger}}{f_A f_B} \tag{21}$$

so that

$$c_{\ddagger} = K^{\ddagger} c_A c_B \frac{f_A f_B}{f_{\ddagger}} \tag{22}$$

The rate constant is therefore of the form

$$k = k_0^s \frac{f_A f_B}{f_{\ddagger}} \tag{23}$$

where k_0^s is now the rate constant in the infinitely dilute solution. The equation is analogous to Eq. (2), which relates the rate in solution to the rate in the gas phase.

Influence of the Ionic Strength. The concept of Brønsted and Bjerrum was extended by Christiansen[2] and Scatchard,[3] of whom the latter assumed a definite model for the activated complex in an ionic reaction and derived an explicit expression for the influence on the rate of the ionic strength of the medium. If the reacting ions A and B have z_A and z_B unit charges, where z_A and z_B may be positive or negative, the activated complex will have the charge $z_A + z_B$; the reaction may therefore be represented as

$$A^{z_A} + B^{z_B} \rightarrow X^{z_A + z_B} \rightarrow \text{products}$$

In Scatchard's treatment the concentration of activated complexes $[X^{\ddagger}]$ was taken as proportional to the concentration of A ions, $[A]$, multiplied by the average concentration of B ions, $[B]_r$, at a distance r from it, where r is the distance between the two charges in the activated complex. Following the method of Debye and Hückel,[4] the concentration of B ions at a distance r from A, where the electrostatic potential is ψ_r, is given by

[1] N. Bjerrum, *ibid.*, **108**, 82 (1924).
[2] J. A. Christiansen, *ibid.*, **113**, 35 (1924).
[3] G. Scatchard, *Chem. Revs.*, **10**, 229 (1932).
[4] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923); **25**, 145 (1924).

$$[B]_r = [B]e^{-\psi_r \epsilon z_B/\mathbf{k}T} \tag{24}$$

where ϵ is the unit charge. The concentration of activated complexes is therefore given by

$$[X^\ddagger] = k[A][B]_r \tag{25}$$

$$= k[A][B]e^{-\psi_r \epsilon z_B/\mathbf{k}T} \tag{26}$$

where k is a proportionality constant. According to the Debye-Hückel theory the potential ψ_r is given by

$$\psi_r = \frac{\epsilon z_A}{D}\frac{e^{-\kappa r}}{r}\frac{e^{\alpha\kappa}}{1+\kappa a} \tag{27}$$

so that the concentration $[X^\ddagger]$ becomes

$$[X^\ddagger] = k[A][B]\exp\left(-\frac{\epsilon^2 z_A z_B}{D\mathbf{k}T}\frac{e^{-\kappa r}}{r}\frac{e^{\kappa a}}{1+\kappa a}\right) \tag{28}$$

In this expression D is the dielectric constant, a the mean distance of closest approach of the ions, and the factor κ is defined by

$$\kappa^2 = \frac{8N\pi\epsilon^2}{1{,}000D\mathbf{k}T}u \tag{29}$$

where N is Avogadro's number and u is the ionic strength of the medium, defined by

$$u = \tfrac{1}{2}\sum cz^2 \tag{30}$$

the summation being taken over all the ions. At high dilutions κ approaches zero, and Eq. (28) then becomes

$$[X^\ddagger]_0 = k'[A]_0[B]_0 e^{-\epsilon^2 z_A z_B/D\mathbf{k}Tr} \tag{31}$$

The activity coefficient is by definition equal to the concentration at low ionic strengths divided by that in the system under consideration, so that

$$\ln\frac{f_A f_B}{f_\ddagger} = \ln\frac{[A]_0[B]_0}{[X^\ddagger]_0} - \ln\frac{[A][B]}{[X^\ddagger]} \tag{32}$$

Hence, using Eqs. (28) and (31),

$$\ln\frac{f_A f_B}{f_\ddagger} = \frac{\epsilon^2 z_A z_B}{D\mathbf{k}Tr}\left(1 - \frac{e^{-\kappa r}e^{\kappa a}}{1+\kappa a}\right) \tag{33}$$

which is approximately equal to

$$\ln\frac{f_A f_B}{f_\ddagger} \approx \frac{\epsilon^2 z_A z_B}{D\mathbf{k}T}\frac{\kappa}{1+\kappa a} \tag{34}$$

To a further approximation,

$$\ln \frac{f_A f_B}{f_\ddagger} \approx \frac{\epsilon^2 z_A z_B \kappa}{DkT} \tag{35}$$

Taking logarithms of Eq. (23) and introducing Eq. (35) gives

$$\ln k = \ln k_0^s + \frac{\epsilon^2 z_A z_B \kappa}{DkT} \tag{36}$$

Elimination of κ by means of Eq. (29) then gives

$$\ln k = \ln k_0^s + \frac{2 z_A z_B N^2 \epsilon^3 (2\pi)^{1/2}}{(DRT)^{3/2}(1{,}000)^{1/2}} u^{1/2} \tag{37}$$

which may be written as

$$\log k = \log k_0^s + 2Q z_A z_B u^{1/2} \tag{38}$$

where Q is given by

$$Q = \frac{N^2 \epsilon^3 (2\pi)^{1/2}}{2.303(DRT)^{3/2}(1{,}000)^{1/2}} \tag{39}$$

and is a constant for a given solvent and temperature. The value of Q is approximately 0.51 for aqueous solutions at 25°C; Eq. (38) may therefore be written as

$$\log k = \log k_0^s + 1.02 z_A z_B u^{1/2} \tag{40}$$

The equation has been subjected to a considerable number of experimental tests, particularly by Brønsted, LaMer, and others.[1] This has usually been done by studying ionic reactions in media of varying ionic strength and plotting log k against the square root of the ionic strength; if Eq. (40) is obeyed, a straight line of slope $1.02 z_A z_B$ will be obtained. The equation has been confirmed in this manner for a considerable number of reactions having a range of values, both positive and negative, of $z_A z_B$. In Fig. 18 are plotted in this way the data collected by LaMer; the lines are plotted with the theoretical slopes, and the points are seen to lie very close to them. It is to be noted that if one of the reactants is a neutral molecule, $z_A z_B$ is zero, and the specific rate should be independent of the ionic strength; this is true for the ethyl acetate reaction (see Fig. 18) and for other reactions, although, as will be seen later, deviations are expected, and occur, at higher concentrations. Deviations are found, indeed, in all cases at higher concentrations, for Eq. (40) is only approximately valid under such condi-

[1] For reviews see V. K. LaMer, *Chem. Revs.*, **10**, 179 (1932); *J. Franklin Inst.*, **225**, 709 (1938).

tions. In media of low dielectric constant, deviations sometimes result from the formation of associated ions.[1]

In a recent paper Olson and Simonson[2] have produced evidence that the above formulation of the specific rate as a function of ionic strength is not of universal validity. Their data indicate that for reactions between ions of the same sign, the rate is influenced only by ions of signs opposite to those of the reactants; for reactions between ions of opposite sign, ions of both signs may influence the rate. Evidently a new theoretical treatment of the behavior is required.

Influence of the Dielectric Constant. In order to consider the influence of the dielectric constant of the solvent on the rate of an ionic reaction, it is necessary to define an activity coefficient β which relates the infinitely dilute solution to the ideal gas; since f relates the solution under consideration to the infinitely dilute solution, it follows that $\alpha = \beta f$. The specific rate k_0^s in the infinitely dilute solution is therefore related to that in the gas phase by

$$k_0^s = k_0 \frac{\beta_A \beta_B}{\beta_\ddagger} \qquad (41)$$

or

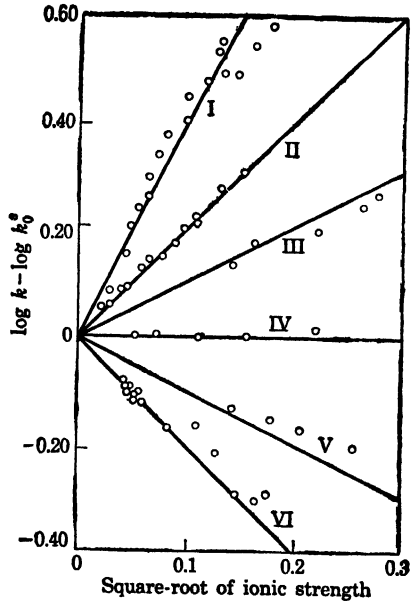


FIG. 18. Plots of log k against the square root of the ionic strength, for various types of ionic reactions. (*LaMer.*) The reactions are:

I. $Co(NH_3)_5Br^{++} + Hg^{++}$	$(z_A z_B = 4)$
II. $S_2O_8^{--} + I^-$	$(z_A z_B = 2)$
III. $NO_2NCO_2C_2H_5^- + I^-$	$(z_A z_B = 1)$
IV. $CH_3COOC_2H_5 + OH^-$	$(z_A z_B = 0)$
V. $H_2O_2 + H^+ + Br^-$	$(z_A z_B = -1)$
VI. $Co(NH_3)_5Br^{++} + OH^-$	$(z_A z_B = -2)$

$$\ln k_0^s = \ln k_0 + \ln \frac{\beta_A \beta_B}{\beta_\ddagger} \qquad (42)$$

The second term is given by

$$\ln \frac{\beta_A \beta_B}{\beta_\ddagger} = \ln \frac{[X^\ddagger]_0}{[A]_0[B]_0} - \ln \left(\frac{[X^\ddagger]_0}{[A]_0[B]_0} \right)_0 \qquad (43)$$

[1] *Cf.* A. N. Kappana, *J. Indian Chem. Soc.*, **6**, 419 (1929); D. Straup and E. J. Cohn, *J. Am. Chem. Soc.*, **57**, 1794 (1935); V. K. LaMer and M. L. Kamner, *ibid.*, 2669; S. Eagle and J. C. Warner, *ibid.*, **58**, 2335 (1936).

[2] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

where the last term, with the subscript g, refers to the ideal gas where the dielectric constant is unity. Application of the Debye-Hückel treatment in the manner indicated above, the activated complex being assumed to consist of the two reactant ions separated by the distance r, gives

$$\ln \frac{\beta_A \beta_B}{\beta_\ddagger} = \frac{\epsilon^2 z_A z_B}{\mathbf{k} T r} \left(1 - \frac{1}{D}\right) \tag{44}$$

and introduction of this into Eq. (42) gives

$$\ln k_0^s = \ln k_0 + \frac{\epsilon^2 z_A z_B}{\mathbf{k} T r} \left(1 - \frac{1}{D}\right) \tag{45}$$

This equation can be used to relate the specific rate at infinite dilution to the hypothetical specific rate in the gas phase, but its chief use is in relating rates in solutions of different dielectric constants.

A somewhat different expression has been obtained[1] on the basis of a different model for the activated complex. In the preceding treatment the activated complex is regarded as having the form of a double sphere, the original charges residing at the centers of the two spheres and separated by a distance r. Alternatively the two spheres may be regarded as merging into one single sphere having a charge equal to the algebraic sum of the charges on the two ions. The results to which the two alternative treatments lead are rather similar, and it is probable that the truth lies somewhere between the two.

In order to derive the rate expression for the case of the spherical activated complex, the procedure is to consider the free energy of transfer of an ion from the medium of unit dielectric constant to the solution of dielectric constant D. If the ion is discharged in a vacuum, the free-energy change is equal[2] to $-z^2\epsilon^2/2r$, where r is the radius of the sphere. The resulting uncharged species is then transferred to an infinitely dilute solution, during which process it experiences no change of free energy except a small one of a nonelectrostatic nature due to polarization forces; this contribution will be neglected. The species is then recharged in the medium of dielectric constant D, when the free-energy change is $\epsilon^2 z^2/2rD$. The total increase in free energy, neglecting nonelectrostatic terms, is therefore given by

$$\Delta F = -\frac{\epsilon^2 z^2}{2r} + \frac{\epsilon^2 z^2}{2rD} \tag{46}$$

$$= \frac{\epsilon^2 z^2}{2r} \left(\frac{1}{D} - 1\right) \tag{47}$$

[1] K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).
[2] M. Born, *Z. Physik.*, **1**, 45 (1920).

This quantity is related to the activity coefficient β by the expression $\Delta F = \mathbf{k}T \ln \beta$, so that for any ion i

$$\ln \beta_i = \frac{\epsilon^2 z_i^2}{2\mathbf{k}Tr_i}\left(\frac{1}{D} - 1\right) \tag{48}$$

Introducing the appropriate expressions for $\ln \beta_A$, $\ln \beta_B$, and $\ln \beta_\ddagger$ into the rate equation [Eq. (42)] gives

$$\ln k_0^s = \ln k_0 + \frac{\epsilon^2}{2\mathbf{k}T}\left(\frac{1}{D} - 1\right)\left[\frac{z_A^2}{r_A} + \frac{z_B^2}{r_B} - \frac{(z_A + z_B)^2}{r_\ddagger}\right] \tag{49}$$

This equation is to be contrasted with that due to Scatchard [Eq. (45)], but it is to be noted that it reduces to Scatchard's equation if one puts $r_A = r_B = r_\ddagger$.

Equations (45) and (49) have been submitted to a considerable amount of experimental test and have been found to represent the data fairly well. It is seen from both equations that if $\ln k_0^s$, the logarithm of the specific rate extrapolated to zero ionic strength, is plotted against $1/D$, a straight line should result, with a slope of

$$\frac{d \ln k_0^s}{d(1/D)} = -\frac{\epsilon^2 z_A z_B}{\mathbf{k}Tr} \tag{50}$$

according to Eq. (45), and a slope of the same order of magnitude according to Eq. (49). If the ions A and B are of opposite sign, it is evident that the slope of the line should be positive, while if the charges are of the same sign, it should be negative. The reaction between bromoacetate and thiosulfate ions has been studied very exhaustively from this point of view, using various aqueous solutions containing urea, glycine, and sucrose and having dielectric constants ranging from 20 to 140.[1] A plot of $\ln k_0^s$ against $1/D$ for this reaction is shown in Fig. 19, the straight line drawn through the points corresponding to a value of $r = 5.1$ A in Eq. (45), this being a reasonable value. Certain deviations from the straight line are observed at low dielectric constants, and various reasons for this have been suggested. In the first place, as Scatchard[2] has pointed out, the rate equations strictly should apply to mole-fraction and not volume concentrations, and this makes a significant difference when work is carried out in a variety of media;

[1] V. K. LaMer and R. W. Fessenden, *J. Am. Chem. Soc.*, **54**, 2351 (1932); Straup and Cohn, *loc. cit.*; LaMer and Kamner, *op. cit.*, 2662, 2669; Eagle and Warner, *loc. cit.*; V. K. LaMer, *J. Franklin Inst.*, **225**, 709 (1938); Laidler and Eyring, *loc. cit.*; G. Scatchard, *J. Chem. Phys.*, **7**, 657 (1939).

[2] Scatchard, *ibid.*

better agreement with the theoretical line is obtained if a correction for this is introduced. Another reason for deviations is that it is not correct to regard the mixed solvents as homogeneous media; at low dielectric constants in particular the water molecules will be preferentially adsorbed around the ions, and the rates will be found to correspond, as is actually the case, to those in media of higher dielectric constant.

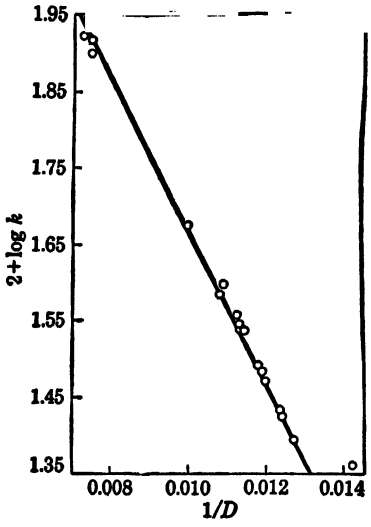


FIG. 19. Variation of the specific rate of the bromoacetate-thiosulfate reaction with the dielectric constant of the medium.

Equally good agreement with the theory has also been obtained for the reaction between bromophenol blue and hydroxyl ions in mixtures of methyl and ethyl alcohol and water;[1] the ions are again of the same sign, so that the rate is increased by increasing the dielectric constant. The opposite type of behavior is found with two reactions between ions of the opposite sign, *viz.*, the catalytic decomposition of the trimethylsulfonium ion by hydroxyl ions,[2] and the combination of ammonium and cyanate ions.[3]

Reactions between ions and neutral molecules

Influence of the Dielectric Constant.[4] If one of the reactants, such as B, is a neutral molecule, *i.e.*, if $z_B = 0$, Eq. (45) is no longer applicable, but according to Eq. (49) a straight line of slope

$$\frac{d \ln k_0^s}{d(1/D)} = \frac{\epsilon^2 z_A^2}{2kT}\left(\frac{1}{r_A} - \frac{1}{r_\ddagger}\right) \tag{51}$$

should be obtained for the plot of ln k against $1/D$. Since $r_\ddagger$, the radius of the activated complex, is usually greater than r_A, the slope will generally be positive; this means that the rate of reaction between an ion and a neutral molecule should decrease with increasing dielectric constant. Good straight lines having slopes of the predicted order of magnitude have in

[1] E. S. Amis and V. K. LaMer, *J. Chem. Phys.*, **7**, 657 (1939).

[2] J. L. Gleave, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 236 (1935).

[3] J. C. Warner and E. L. Warrick, *J. Am. Chem. Soc.*, **57**, 1491 (1935); W. J. Svirbely and A. Schramm, *ibid.*, **60**, 330 (1938); J. Lander and W. J. Svirbely, *ibid.*, 1613.

[4] Laidler and Eyring, *loc. cit.*

fact been obtained[1] for the transformations of *N*-chloroacetanilide and *N*-chloropropionanilide into the para-chloro compounds in the presence of hydrochloric acid,[2] reactions which may involve an initial attack by chloride ions. The predicted change of rate with dielectric constant is also found with the reactions between alkyl halides and hydroxyl[3] or halide ions,[4] and between water and a sulfonium cation.[5]

Influence of Ionic Strength. According to Eq. (40) a reaction between an ion and a neutral molecule should be uninfluenced by the ionic strength of the solution; however, this equation was arrived at as the result of approximations which hold only in very dilute solutions. The activity coefficient of an ion is given to a better approximation if, in addition to the Debye-Hückel term, the term bu, introduced by Hückel,[6] is added; the final equation for the ion A should therefore be written as

$$\ln f_A = -\frac{\epsilon^2 z_A^2 \kappa}{2D\mathbf{k}T} + b_A u \tag{52}$$

and a similar expression holds for the activated complex, which in this case has the same charge as A. The activity coefficient for the nonelectrolyte B should be given by the approximate expression of Debye and McAulay,[7]

$$\ln f_B = b_B u \tag{53}$$

On introducing expressions for $\ln f_A$ and $\ln f_\ddagger$ as given by Eq. (52) and for $\ln f_B$ as given by Eq. (53) into Eq. (23), it follows that

$$\ln k = \ln k_0^s + (b_A + b_B - b_\ddagger)u \tag{54}$$

The Debye-Hückel term involving κ has disappeared, since it occurs in the expressions for both A and the complex; the importance of including the b terms in this application is therefore apparent. It follows from Eq. (54) that the logarithm of the rate of a reaction of this type should vary with the first power of the ionic strength, instead of with the square root as was found with reactions between ions; the effect is, moreover, much smaller. This conclusion has received experimental support from the work

[1] *Ibid.*

[2] C. C. J. Fontein, *Rec. trav. chim.*, **47**, 635 (1928).

[3] C. A. Lobry de Bruyn and E. Steger, *ibid.*, **18**, 14, 311 (1899); E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *J. Chem. Soc.*, 225 (1936).

[4] E. D. Hughes and C. K. Ingold, *ibid.*, 1571 (1933).

[5] E. Bergmann, M. Polanyi, and A. Szabo, *Z. physik. Chem.*, B, **20**, 161 (1933); F. Juliusburger, B. Topley, and J. Weiss, *J. Chem. Phys.*, **3**, 161 (1935).

[6] E. Hückel, *Physik. Z.*, **26**, 93 (1925).

[7] P. Debye and J. McAulay, *ibid.*, **22**.

of Brønsted and Wynne-Jones on the hydrolysis of acetals by hydroxyl ions.[1]

Equation (54) can be written as

$$k = k_0 e^{bu} \tag{55}$$

where b is equal to $b_A + b_B - b_\ddagger$, and if bu is small compared with unity, as is usually the case, the exponential may be expanded and all terms beyond the first discarded; the result is

$$k = k_0(1 + bu) \tag{56}$$

A plot of k against u should therefore be a straight line under these conditions; this has been found to be the case in the hydrolysis of acetals, the hydrolysis of ethylene oxide, and the decomposition of diazoacetic ester.[2]

Summary of Results. In Table 29 the qualitative results arrived at in the preceding sections and some of the examples mentioned are summarized.

TABLE 29. INFLUENCE OF DIELECTRIC CONSTANT AND IONIC STRENGTH ON RATES OF VARIOUS TYPES OF REACTIONS

Reaction type	Effect of increasing		Examples
	Dielectric constant	Ionic strength	
Two molecules forming a polar product	Increase	No effect	$R_3N + RX$ $H_2O + RX$
Two ions:			
Same sign	Increase	Increase	$BrAc^- + S_2O_3^{--}$ $OH^- +$ bromphenol blue$^-$
Opposite sign	Decrease	Decrease	$OH^- + Me_3S^+$
Ion and neutral molecule	Small decrease	Small increase	$OH^- + RX$ $OR^- + RX$ $X^- + RX$ $Me_2BuS^+ + H_2O$

The frequency factor

It has been seen earlier that many reactions in solution have small frequency factors, which implies that they have small entropies of activation. In the case of reactions involving neutral molecules, this is usually attributable to the fact that fairly complex molecules are involved, and it has been seen that steric factors as low as 10^{-10} can be accounted for in this

[1] J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).
[2] J. N. Brønsted and C. Grove, *J. Am. Chem. Soc.*, **52**, 1394 (1930).

manner; in some instances, however, specific solvent effects, which lower the activity coefficients of the reactants or raise that of the activated complex, may be playing a part. With reactions in which one reactant is an ion, the rates usually agree within a factor of 10 with those calculated on the basis of collision theory.

In the case of reactions between two ions, an entirely different effect arises, *viz.*, that due to the electrostatic forces: these give rise to high or low frequency factors according as the charges are opposite or the same. The magnitude of this effect will now be considered with respect to the rates at zero ionic strength.

According to Eq. (45) the specific rate of an ionic reaction in a medium of dielectric constant D is related to that in the gas phase by the equation

$$\ln k_0^s = \ln k_0 + \frac{\epsilon^2 z_A z_B}{\mathbf{k}Tr}\left(1 - \frac{1}{D}\right) \tag{57}$$

If the specific rate is written in the general form

$$k_0^s = \frac{\mathbf{k}T}{\mathbf{h}} e^{-\Delta F^*/RT} \tag{58}$$

or

$$\ln k_0^s = \ln \frac{\mathbf{k}T}{\mathbf{h}} - \frac{\Delta F^*}{RT} \tag{59}$$

it follows that the free energy of activation ΔF^* is given by

$$\ln k_0 + \frac{\epsilon^2 z_A z_B}{\mathbf{k}Tr}\left(1 - \frac{1}{D}\right) = \ln \frac{\mathbf{k}T}{\mathbf{h}} - \frac{\Delta F^*}{RT} \tag{60}$$

or

$$\Delta F^* = RT\left(\ln \frac{\mathbf{k}T}{\mathbf{h}} - \ln k_0\right) - \frac{N\epsilon^2 z_A z_B}{r}\left(1 - \frac{1}{D}\right) \tag{61}$$

The last term in this expression is the contribution to the free energy of activation arising from the electrostatic terms,

$$\Delta F_D^* = -\frac{N\epsilon^2 z_A z_B}{r}\left(1 - \frac{1}{D}\right) \tag{62}$$

The entropy of activation is obtained from the free energy of activation by using the relationship

$$\Delta S^* = \left(\frac{\partial \Delta F^*}{\partial T}\right)_P \tag{63}$$

so that the electrostatic contribution to the entropy is given by

$$\Delta S_D^* = \left(\frac{\partial \Delta F_D^*}{\Delta T}\right)_P \tag{64}$$

Differentiation of the free-energy term given by Eq. (62) with respect to the temperature, allowing for the temperature dependence of D, gives

$$\Delta S_D^* = \frac{N\epsilon^2 z_A z_B}{rD^2}\left(\frac{\partial D}{\partial T}\right)_P \tag{65}$$

In an aqueous solution D is about 80 and $\partial \ln D/\partial T$ is about -0.0046, and taking r as 2×10^{-8} cm, it follows that

$$\Delta S_D^* \approx -10 z_A z_B \tag{66}$$

According to this treatment, therefore, the entropy of activation in aqueous solution should decrease by 10 units for each unit of $z_A z_B$; moreover since the frequency factor A is proportional to $e^{\Delta S^*/R}$, it follows that it should decrease by a factor of $e^{10/R}$, *i.e.*, about a hundredfold, for each unit of $z_A z_B$. That this rough rule is obeyed experimentally is shown by the results in Table 30;[1] the second column of figures gives the values of

TABLE 30. ENTROPY FACTORS FOR IONIC REACTIONS

Reaction	$z_A z_B$	Entropy factor	
		Theoretical	Experimental
$Cr(H_2O)_6^{+++} + CNS^-$	-3	10^6	10^6
$Co(NH_3)_5Br^{++} + OH^-$	-2	10^4	2×10^4
$NH_4^+ + CNO^-$	-1	10^2	0.6
$C_6H_5NClCOCH_3^+ + Cl^-$	-1	10^2	0.8
$ClO^- + ClO_2^-$	1	10^{-2}	4×10^{-5}
$C_6H_5C{:}CCOO^- + I_3^-$	1	10^{-2}	7×10^{-6}
$CH_2ClCOO^- + S_2O_3^{--}$	2	10^{-4}	6×10^{-7}
$Co(NH_3)_5Br^{++} + Hg^{++}$	4	10^{-8}	6×10^{-6}
$AsO_3^{---} + TeO_4^{--}$	6	10^{-12}	10^{-7}

$e^{\Delta S^*/R}$ calculated on the basis of this rule, while the last column gives the experimentally obtained values.

Deviations from the rule are expected if the specific rates are not extrapolated to zero ionic strength; in such cases the problem could be treated by employing the rate expression which includes the ionic-strength term.

[1] *Cf.* E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," p. 94, Oxford University Press, New York, 1947.

The magnitude of the effect is small, however, and it will not be considered here.

Influence of substituents on reaction rates

An important aspect of chemical reactions in solution arises from the fact that a great many series of homologous reactions are known and provide important information as to the effect of substituents on reaction rates. As an example may be mentioned the benzoylation of amines; the reaction between benzoyl chloride and aniline can be studied, as well as the reactions between these molecules carrying various substituents. A great deal of work has accumulated on the influence of substituents on reactions of this kind; only the purely kinetic aspects of the problem can be discussed here.

It has been seen that the specific rate of any reaction can be expressed by means of the equation

$$k = \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^*/R} e^{-\Delta H^\ddagger/RT} \tag{67}$$

where ΔS^* is the entropy of activation and $\Delta H^\ddagger$ the heat of activation, a quantity that is closely related to the experimental energy of activation. Sometimes it is found that substituents exert their effect primarily on the energy of activation, changes in the entropy of activation, or in the frequency factor, being rather incidental.[1] Among reaction types in which the entropy of activation remains constant within the experimental error, while the activation energy varies significantly, may be mentioned the benzoylation of amines,[2] the alkaline hydrolysis of benzoic esters,[3] the alcoholysis of triarylmethyl chlorides,[4] and the reaction between substituted dimethylanilines and methyl iodide.[5]

Electronic Theories of Organic Reactivity. The influence of substituents on the rates of organic reactions has been interpreted in terms of electrical effects, the developments along these lines being due to a considerable number of workers of whom J. Stieglitz, G. N. Lewis, H. J. Lucas, A. Lapworth, R. Robinson, and C. K. Ingold may be mentioned in particular. This type of treatment provided the basis for the kinetic work on this problem, and a brief account of the modern views will be given.[6]

[1] A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 1006 (1928); 2903 (1931); B. Spencer and J. Spencer, *ibid.*, 2907 (1931); C. N. Hinshelwood, K. J. Laidler, and E. W. Timm, *ibid.*, 848 (1938).

[2] E. G. Williams and C. N. Hinshelwood, *ibid.*, 1079 (1934).

[3] W. B. S. Newling and C. N. Hinshelwood, *ibid.*, 1357 (1936); D. P. Evans, J. J. Gordon, and H. B. Watson, *ibid.*, 1430 (1937).

[4] A. C. Nixon and G. E. K. Branch, *J. Am. Chem. Soc.*, **58**, 492 (1936).

[5] K. J. Laidler, *J. Chem. Soc.*, 1786 (1938).

[6] For further details reference should be made to C. K. Ingold, *Chem. Revs.*, **15**,

A substituent changes the reactivity of a parent compound by altering the availability of electrons at the seat of reaction. Certain types of reactions are favored by an increase of electron density in a certain region, and substituents which effect such an increase cause the rate to increase; as seen previously, they usually do this by decreasing the energy of activation. An example of this is seen in the reaction between pyridine and methyl iodide, which is favored by an increase in the electron density in the neighborhood of the nitrogen atom, the formation of the carbon-nitrogen bond being facilitated by this. Substituents such as methyl groups are known, from general evidence to be referred to later, to repel electrons, and their introduction into the pyridine ring thus increases the rate of reaction. This reaction is also aided by substituents which decrease the electron density in the neighborhood of the central carbon atom on the iodide.

Studies of the effects of substituents on reaction rates combined with measurements of the dipole moments of substituted molecules[1] have led to the conclusion that four different effects are involved; of these, two are permanent electrical effects which can be detected by dipole-moment measurements, while two are temporary in the sense that they are brought into play only during the act of chemical change. Of each type one is associated with a simple shift of electron densities, while the other is more complicated and occurs only in conjugated structures in which a certain type of resonance is possible. These four effects may now be described briefly.

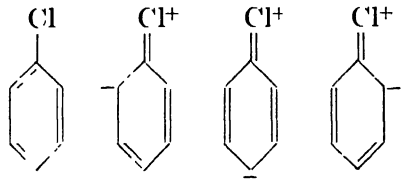
Inductive Effect. This mode of electron displacement is transmitted from atom to atom along a chain without any reorganization of the chemical bonds in the molecule; when, for example, a nitro group replaces a hydrogen atom in an organic molecule, the inductive effect consists in a shift of electrons toward the nitro group. The effect becomes progressively less as the distance from the group increases. The symbol I is frequently used to denote the inductive effect of groups; thus the nitro group is said to have a $-I$ effect since it removes electrons from the seat of reaction.

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225 (1934); R. Robinson, "Outline of an Electrochemical Theory of the Course of Organic Reactions," The Institute of Chemistry, London, 1932; W. A. Waters, "Physical Aspects of Organic Chemistry," D. Van Nostrand Company, Inc., New York, 1935; L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, 1940; A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley & Sons, Inc., New York, 1943; G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, 1941; M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, New York, 1949.

[1] L. E. Sutton, *Proc. Roy. Soc.* (*London*), **A, 133,** 668 (1931).

Mesomeric Effect. When certain types of electronic structures occur, particularly where conjugated double bonds are found, molecules are considered to exist in a resonance state between two extreme structures; thus chlorobenzene exists in a resonance state consisting mainly of the structures



As a result of this, chlorobenzene has an excess electron density in the ortho and para positions in the benzene nucleus, and accordingly the chlorine atom is said to exert a positive ($+M$) mesomeric effect. The mesomeric effect is seen to differ from the inductive effect in that a definite change in the valence bond structures is involved. Both effects are permanent.

Inductomeric Effect. In addition to the permanent inductive effect considered above, a further electronic displacement may arise during the act of chemical change, being brought into play by the change in electrical environment produced by the approach of the second molecule. The extent to which the effect is induced depends on the strength of the polarizing field of the approaching molecule. The inductomeric effect is sometimes indicated by the symbol I_d, the subscript d implying "dynamic." The inductomeric effects of different substituents correspond fairly closely to their inductive effects.

Electromeric Effect. The electromeric effect is of the same character as the mesomeric effect but is brought into play only during reaction at the demand of the attacking molecule; it is usually denoted by the symbol E.

An important difference between the permanent and the temporary effects is that the latter, being invoked at the demand of the colliding molecule, may not impede the progress of a reaction. The permanent effects may reduce reaction rates; thus the $-I$ effect of the halogens decreases the reactivity of the benzene ring with respect to aromatic substitution.

Influence of Substituents on the Energy of Activation. The ideas outlined above have been extended somewhat in a theoretical treatment of the influence of substituents on the energy of activation.[1] If the reaction

$$X + Y{-}Z \rightarrow X{-}Y + Z$$

[1] Hinshelwood, Laidler, and Timm, *loc. cit.*

is considered, the introduction of a substituent into the molecule YZ will bring about changes in the bond energies and interaction energies and will in this way influence the energy of activation and hence the rate of reaction. Suppose, for example, that X is a negative ion, or the negative end of a dipolar molecule, and that the substituent has the effect of increasing the positive charge on Y and the negative charge on Z, in the following manner:

$$X + Y^{\delta+}—Z^{\delta-} \rightarrow X—Y + Z$$

where $\delta+$ and $\delta-$ represent the changes in the effective electronic charge. The effect of these changes brought about by the introduction of the substituent is an increase in the attraction between Y and Z and a decrease in the repulsion between X and Y. The first of these, the increase in the attraction between Y and Z, will clearly tend to increase the activation energy; on the other hand, the increased attraction between X and Y will tend to lower the activation energy. The two effects therefore act in

TABLE 31. ACTIVATION ENERGIES FOR THE FORMATION OF QUATERNARY AMMONIUM SALTS

Amine	Iodide	E, kcal
Triethylamine	Methyl	9 7
Triethylamine	Ethyl	11.4
Triethylamine	Isopropyl	17.1
Pyridine	Methyl	14.3
Pyridine	Ethyl	15.8
Pyridine	Isopropyl	18.0

opposite directions. In the majority of reactions studied, it is found that the influence of a substituent is in the direction that would be predicted if only the second effect were taken into consideration; in other words, the attraction between the reacting molecules seems to be of chief importance. An example of this type of behavior is found in the formation of quaternary ammonium salts, some results for which are shown in Table 31.[1] The figures are for the reactions of the two bases triethylamine and pyridine with methyl, ethyl, and isopropyl iodides. Methyl groups exert a positive inductive, *i.e.*, electron-repelling, effect, so that the introduction of a methyl group in passing, for example, from methyl to ethyl iodide, makes the central atom more negative; its attraction for the negative reagent therefore becomes less, and the observed increase in energy of activation

[1] C. A. Winkler and C. N Hinshelwood, *J. Chem. Soc* , 1147 (1935); K. J. Laidler and C. N. Hinshelwood, *ibid.*, 858 (1938).

is to be expected. A further increase is found on passing from ethyl to isopropyl iodide.

Additional proof that the repulsion energy between the base and the iodide is of chief importance in this type of reaction comes from experiments in which the strength of the base was varied by the introduction of substituents into dimethylaniline.[1] The figures in Table 32, in which the bases are arranged in order of decreasing strength, *i.e.*, decreasing effective negative charge on the nitrogen atom, show that the increased repulsion between the base and the positive carbon atom gives rise to an increase in the energy of activation.

TABLE 32. ACTIVATION ENERGIES FOR THE REACTION BETWEEN METHYL IODIDE AND SUBSTITUTED DIMETHYLANILINES

Substituent	*E, kcal*
p-OCH_3	11.7
p-CH_3	12.3
(H)	12.8
p-Br	13.7
p-Cl	13.9

Many other reactions are known in which the influence of the repulsion energy between the two reacting molecules is of chief importance in determining the influence of substituents. One example is benzene substitution.[2] Here the influence of a substituent on the rate of reaction can be predicted from a consideration of the electrostatic interactions between the reagent and the aromatic molecule; the ease with which the carbon-hydrogen bond is broken is of minor importance. A further example is to be found in the acid-catalyzed prototropic changes of substituted acetophenones,[3] the reaction mechanism being

$$CH_3CC_6H_4X \;(\text{O}) + H^+ \rightarrow H{-}CH_2CC_6H_4X \;(\text{O}^+{-}H) \rightarrow H^+ + CH_2{=}CC_6H_4X \;(\text{OH})$$

The activation energies vary in the manner determined by the attraction between the acetophenone and the hydrogen ion, the ease with which the C-H bond is ionized being unimportant.

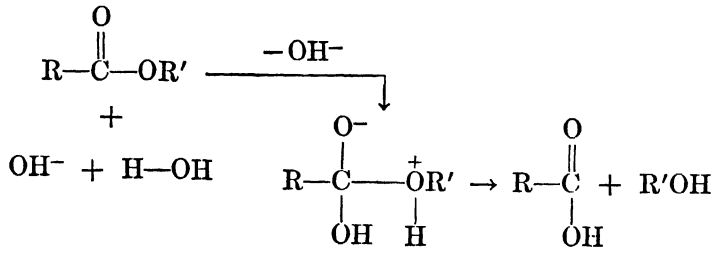
[1] Laidler, *loc. cit*; D. P. Evans, H. B. Watson, and L. Williams, *J. Chem. Soc.*, 1345 (1939).

[2] For a quantitative treatment of benzene substitution, see T. Ri and H. Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

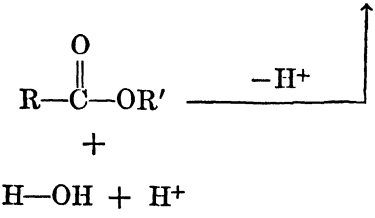
[3] D. P. Evans, V. G. Morgan, and H. B. Watson, *J. Chem. Soc.*, 1167 (1935).

A particularly interesting case is the acid- and base-catalyzed hydrolysis of esters, the accepted mechanism for which is as follows:

Alkaline:



Acid:



In agreement with this scheme, it is found[1] that the introduction of a substituent into the *R* group of the ester brings about the same type of change in the activation energy for both acid and base catalysis; the effect is attributed to the change in the effective charge on the carbonyl carbon atom, which therefore operates in the same way in both types of hydrolysis. The activation energy for the base-catalyzed reaction of a given ester is lower by 5 to 7 kcal than that for the acid-catalyzed hydrolysis; this is due to the fact that in acid hydrolysis the uncharged ion attacks the carbonyl carbon atom, so that the repulsion energy is greater than when the hydroxyl ion attacks it. In agreement with this explanation, it is found that the effect of a substituent is greater in alkaline than in acid hydrolysis.

In contrast to the reactions discussed above, a certain number of reactions are also known in which the influence of a substituent on the energy of activation seems to be determined by its influence on the bond strength of the bond that is broken—more exactly, since most of the reactions under consideration are ionic, by the substituent's influence on the ionizability of the bond. It is to be expected that this situation will be found when the repulsion between the reacting molecules is large, so that a greater degree of ionization will occur in reaching the activated state. A trend in this direction is to be seen in the values quoted in Table 31. It has been

[1] C. K. Ingold and W. S. Nathan, *ibid.*, 222 (1936); E. W. Timm and C. N. Hinshelwood, *ibid*, 862 (1938).

noted that the substitution of methyl groups, by increasing the repulsion between the reactants, increases the energy of activation; this effect is seen to be much less with the weak base pyridine than with the stronger triethylamine. This may be explained as due to the fact that with pyridine, where the repulsion between the reacting molecules is greater, the ionization of the C-I bond plays a more important role than with the stronger base.

In these reactions the repulsion energy still controls the energy of activation, but cases are known in which the ionization of the bond determines the influence of a substituent upon the energy. An example of this is to be found in the hydrolysis of triarylmethyl chlorides,[1] activation energies for which are given in Table 33. It is to be noted that a methoxy group, which aids the ionization but increases the repulsion of the reacting hydroxyl ion, decreases the energy of activation; the ionization is therefore controlling. These results are to be contrasted with those obtained for the hydrolysis of

TABLE 33. ACTIVATION ENERGIES FOR ALCOHOLYTIC REACTIONS

Triarylmethyl chlorides	E, kcal	Acyl chlorides	E, kcal
$(p\text{-}NO_2C_6H_4)_3CCl$	16.7	$p\text{-}NO_2C_6H_4COCl$	11.1
$(p\text{-}ClC_6H_4)_3CCl$	13.5	$p\text{-}ClC_6H_4COCl$	13.9
$(C_6H_5)_3CCl$	13.4	C_6H_5COCl	14.4
$(p\text{-}CH_3OC_6H_4)(C_6H_5)_2CCl$	12.5	$p\text{-}CH_3OC_6H_4COCl$	18.7

acyl chlorides[2] (*cf.* Table 33), in which reactions the substituents have the opposite effect; here the repulsion energy is apparently more important. The difference in behavior is associated with the easier ionizability of the triarylmethyl chlorides, and with the larger positive charge residing on the carbon atom of the carbonyl group in the acyl chlorides; in the former case there will therefore be more ionization and less approach of the hydroxyl ions in the activated state.

The hydrolysis and alcoholysis of alkyl halides offer an example of an intermediate type of behavior, the two effects being of about equal magnitude and canceling one another out. Some figures[3] are given in Table 34, and it will be seen that there is very little change in activation energy on changing the halide. If the repulsion-energy factor were the more important, the change from methyl through ethyl to isopropyl would increase the energy of activation; if the ionic character were dominant, the

[1] A. C. Nixon and G. E. K. Branch, *J. Am. Chem. Soc.*, **58**, 492 (1936).

[2] G. E. K. Branch and A. C. Nixon, *ibid.*, 2499.

[3] G. H. Grant and C. N. Hinshelwood, *J. Chem. Soc.*, 258 (1933); E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *ibid.*, 225 (1936); K. A. Cooper and E. D. Hughes, *ibid.*, 1138 (1937).

effect would be the opposite. Apparently the two effects approximately balance one another.

If the reactant molecule is a water molecule instead of a negative ion, the repulsion energy is larger, since the electrostatic attraction between the water molecule and the carbon atom of the halide is less than in the case of the ion. Since the effects of the repulsion energy and the bond strength approximately balance in the case of the ions, it would be anticipated that when the water molecule effects the hydrolysis, the ionizability of the bond will be more important than the repulsion energy. Changing from methyl through ethyl to isopropyl should therefore decrease the activation energy by increasing the ionizability of the bond. Experimental values are not available, but it is known that isopropyl and tertiary-butyl halides are more rapidly hydrolyzed by water than are the corresponding

TABLE 34 ACTIVATION ENERGIES FOR ALKYL HALIDE REACTIONS

Reaction	Activation energy with		
	R = CH_3	R = C_2H_5	R = $CH(CH_3)_2$
$RCl + OH^-$	....	23.0	23 0
$RBr + OH^-$	. ..	23.0	21.7
$RI + C_6H_5O^-$	22.1	22 0	22.1
$RI + C_6H_5CH_2O^-$	20.6	21.9	21 4

methyl and ethyl halides;[1] since rates are generally determined by activation energies, this can be taken as evidence that the energies actually fall in the predicted order. Another example of the same thing has been seen in the alcoholysis of the triarylmethyl chlorides.

A somewhat more extreme view than the one presented above has been put forward by Hughes and Ingold,[2] who discuss the problem in terms of two distinct mechanisms. The first, known as the S_N2 mechanism, is bimolecular and may be represented as

$$X^- + YZ \rightarrow X \quad Y.. .Z^- \rightarrow XY + Z^-$$

while in the second, denoted S_N1, the slow stage is ionization of YZ

$$YZ \rightarrow Y^+ + Z^-$$

and this is followed by rapid reaction between X^- and Y^+

$$X^- + Y^+ \rightarrow XY$$

[1] E. D. Hughes, *ibid.*, 255 (1935).

[2] E. D. Hughes and C. K. Ingold, *ibid.*, 244; E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).

The S_N2 mechanism is clearly analogous to the case discussed above in which the repulsion energy is the important factor, while in the S_N1 mechanism the ionization is rate controlling. On the Hughes-Ingold formulation, intermediate cases are interpreted as due to the occurrence of simultaneous reactions involving the two mechanisms.

Substituent Effects and Dipole Moments. In connection with the influence of substituents on rates and activation energies, a number of attempts have been made to correlate the observed effects with other properties of the reactants. In particular, relationships with the dipole moment have been sought, and the activation energies of reactions involving substituents in the meta position to the reaction center have been found empirically[1] to be related to the dipole moment μ by

$$E = E_0 - c(\mu + b\mu^2) \tag{68}$$

where E_0 is the activation energy in the absence of a substituent and b and c are constants. Alternatively it has been proposed by Jenkins[2] that the direction of operation of the dipole moment should be taken into account, and it was found that the activation energy varied linearly with the electrostatic potential produced by the substituent at the reaction center. This relationship of Jenkins is obeyed more accurately than Eq. (68), but ortho and para compounds are always found to be anomalous.[3]

Rate Constants and Equilibrium Constants. Another important type of relationship concerns the influence of substituents on the rates and equilibrium constants of related processes. This has been expressed by Hammett[4] by means of the equation

$$\log k = \log k_0 + \sigma\rho \tag{69}$$

where k can be a rate or an equilibrium constant for a reaction involving a given substituent, k_0 is that for the reaction with no substituent, and σ and ρ are constants. σ depends only upon the substituent, while ρ is a reaction constant, dependent upon the reaction and the external conditions. The value of unity is arbitrarily chosen for ρ for the ionization equilibrium of substituted benzoic acids, so that values of σ can be determined by studying

[1] W. S. Nathan and H. B. Watson, *J. Chem. Soc.*, 893 (1933); J. F. J. Dippy and H. B. Watson, *J. Soc. Chem. Ind. (London)*, **54**, 735 (1935); *J. Chem. Soc.*, 436 (1936); W. A. Waters, *Phil. Mag.*, **8**, 436 (1938).

[2] H. O. Jenkins, *J. Chem. Soc.*, 640, 1137, 1780 (1939).

[3] *Cf.* H. B. Watson, "Modern Theories of Organic Chemistry," p. 205, Oxford University Press, New York 1937; *Ann. Repts. Progress Chem. (Chem. Soc. London)*, **35**, 243 (1938).

[4] L. P. Hammett, *Chem. Revs.*, **17**, 125 (1935); *Trans. Faraday Soc.*, **34**, 156 (1938); "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, 1940.

the effect of substituents on this equilibrium. Using these values, values of σ for other reactions can then be determined. The relationship has been found to be applicable with very little error to a large number of processes and is therefore valuable for predicting rates and equilibrium constants.

PROBLEMS

1. The second-order rate constant for the reaction between pyridine and methyl iodide in benzene solution at 60°C is 1.46×10^{-4} liter mole $^{-1}$ sec^{-1}, and the activation energy is 14.3 kcal. Calculate the frequency factor and the entropy of activation.

2. The frequency factor for the dimerization of cyclopentadiene in benzene solution is 1.3×10^{7} liters mole^{-1} sec ^{1}, and the activation energy is 16.4 kcal. Calculate the rate constant of the reaction at 25°C and the rate of the reaction at a concentration of 0.1 mole per liter.

3. The frequency factor for the reaction between cyclopentadiene and benzoquinone in ethyl alcohol solution is 1.0×10^{7} liters mole^{-1} sec^{-1}, and the activation energy is 12.7 kcal. Calculate the rate of the reaction at 50°C if the two substances are present at concentrations of 0.05 mole per liter.

4. The following rate constants were obtained[1] for reactions between substituted dimethylanilines and methyl iodide in nitrobenzene solution:

Amine	$k \times 10^5$, liters mole^{-1} sec^{-1}				
	15.0°C	24.8°C	40.1°C	60.0°C	80.1°C
Dimethyl-*p*-anisidine	34.7	71.9	183	560	
Dimethyl-*p*-toluidine		28.4	79 6	253	759
Dimethylaniline		8.39	21.0	77.2	238
p-Chlorodimethylaniline	0.926	2.11	5 97	25.6	
p-Bromodimethylaniline	0.824	1.80	5.55	21 3	

Show that the influence of the substituent is mainly on the energy of activation.

[1] K. J. Laidler, *J. Chem. Soc.*, 1786 (1938).

CHAPTER 6

REACTIONS ON SURFACES AND IN THE SOLID STATE

The rates of a great many chemical reactions are found to be influenced by solid surfaces. As has been seen in Chap. 2, this fact is frequently a serious complication to the study of homogeneous gas reactions, in that an appreciable amount of reaction may occur on the surface of the reaction vessel and must be allowed for if the rate of the homogeneous reaction is required. In experiments of this kind it has been seen that the amount of surface reaction can be determined by determining reaction rates under conditions in which the area of the surface is varied over as wide a range as possible.

In addition to investigations in which there is incidental catalysis by the walls of the vessel, a great many experiments have been made on the kinetics of reactions occurring on surfaces which are deliberately introduced into the system. As a result of this work, it has been found that many processes can be made to occur very much more rapidly by the introduction of a suitable surface upon which the reaction proceeds; the solid material is then said to catalyze the reaction. In particular, a number of processes which do not occur homogeneously at an appreciable rate can be made to occur on surfaces. As a result of this fact, the subject of catalysis by solid surfaces is of very great technical importance. The majority of investigations of surface reactions have, in fact, been carried out with the object of finding a suitable substance to catalyze a technical gas reaction and have not been carried out under conditions suitable for an elucidation of the fundamental processes concerned. In the present chapter, primary attention will be devoted to a consideration of investigations of a fundamental nature, the essential criteria of such being that they include specification of the surface used, in particular its smoothness and area, and that absolute rates and activation energies of the reaction be measured accurately.

The most important result that has emerged from such investigations is that catalysis by surfaces involves specific chemical interaction between the surface and the reacting gas molecules, which must become adsorbed on the surface before reaction can occur. This view was first proposed in 1825 by Faraday, who studied the nature of adsorption on surfaces, and considered that reaction occurred in adsorbed films. The original idea was that the main effect of the catalysis was to cause the molecules to be

present in much higher concentrations than in the main body of the gas. This concept is, however, shown to be false by the fact that in certain cases different surfaces give rise to different products of reaction; *e.g.*, ethyl alcohol decomposes primarily into ethylene and water on an alumina catalyst, and mainly into acetaldehyde and hydrogen on copper. This result, along with many others, clearly indicates that specific chemical forces are involved at surfaces. In view of the importance of adsorption forces in connection with surface catalysis, some discussion will now be devoted to modern views on this subject.

Adsorption[1]

It is now generally accepted that two main types of adsorption may be clearly distinguished. In the first type the forces are of a physical nature and the adsorption is relatively weak; the forces correspond to those assumed in the van der Waals equation of state of gases and are consequently known as van der Waals forces. These play only a very unimportant part in connection with surface reactions (except for certain atomic processes), since they are not sufficiently strong to influence appreciably the reactivity of the molecules adsorbed. The second type of adsorption is considerably stronger; according to Langmuir's original concept of it,[2] the adsorbed molecules are held to the surface by valence forces of the same type as those occurring between bound atoms in molecules. As an example Langmuir cited the adsorption of oxygen on tungsten, in which case the tungsten-oxygen bonds at the surface are supposed to be of essentially the same character as those occurring in tungsten oxide. It follows that the heat evolved in this type of adsorption, which is commonly known as chemisorption, should be of the same order as that found with chemical reactions, and, in agreement with this idea, values of 10 to 100 kcal have been observed. By contrast the heat changes found with van der Waals adsorption are usually less than 5 kcal per mole.

An important consequence of this concept of chemisorption, regarded by Langmuir as an essential part of his theory, is that after a surface has become covered with a single layer of adsorbed molecules, it is essentially saturated; additional adsorption can only occur on the layer already formed, and this usually takes place with some difficulty. This idea of the unimolecular adsorption layer is capable of direct experimental test, and a number of investigations have shown that a definite adsorption limit occurs,

[1] For reviews see J. K. Roberts, "Some Aspects of Adsorption," Cambridge University Press, New York, 1939; S. Brunauer, "Physical Adsorption," Princeton University Press, Princeton, N. J., 1943; A. R. Miller, "The Adsorption of Gases on Solids," Cambridge University Press, New York, 1949.

[2] I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).

beyond which further molecules cannot be adsorbed readily. When the surface area is known, this limit is found to correspond to the existence of a unimolecular layer.[1] This result is good evidence for the theory that chemical forces are involved in chemisorption.

It was suggested by Taylor[2] that chemisorption is frequently associated with an appreciable activation energy and may therefore be a relatively slow process; for this reason it is now frequently referred to as activated adsorption. The energies of activation are often of the order of 20 kcal, and consequently the adsorption is extremely slow at low temperatures; under these conditions, van der Waals adsorption, which requires no activation energy, will predominate. Not only is the idea of activated adsorption consistent with the Langmuir concept of the nature of this type of adsorption, but also it successfully explains a number of phenomena associated with sorption. For instance, measured heats of adsorption are frequently small at low temperatures and considerably higher at higher ones. This is due to the fact that the van der Waals adsorption is the most important at the lower temperatures, whereas chemisorption, with its higher heat, predominates at higher ones. Curious relationships are frequently found[3] between the total amount of gas adsorbed and the temperature; at very low temperatures the amount decreases with increasing temperature and then rises as the temperature rises further, but at still higher temperatures the amount of adsorption again decreases with temperature (see Fig. 20). At the lower temperatures the adsorption is entirely of the van der Waals type, and the amount decreases with temperature in the manner of an ordinary dissociation. As the temperature is raised, however, the rate of chemisorption increases, so that there is an increase in the amount chemisorbed and hence in the total amount of adsorption. At still higher temperatures there is the normal decrease in the extent of chemisorption.

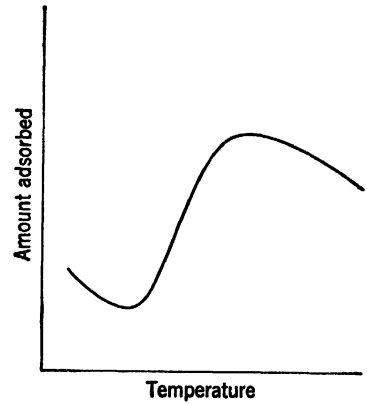


FIG. 20. Dependence of the total amount of adsorption on the temperature.

So far it has been tacitly assumed that surfaces are smooth and that

[1] I. Langmuir, *ibid.*, **40**, 1361 (1918); F. A. Paneth and W. Vorwerk, *Z. physik. Chem.*, **101**, 445, 480 (1922).

[2] H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 578 (1931); *Chem. Revs.*, **9**, 1 (1931).

[3] See, for example, A. W. Gauger and H. S. Taylor, *J. Am. Chem. Soc.*, **45**, 920 (1923).

adsorbed molecules are arranged on them in simple layers. However Taylor[1] has pointed out that even polished surfaces are not absolutely smooth from the molecular standpoint. They consist of atoms of varying degrees of unsaturation; certain atoms will be present at peaks on the surface and, owing to their high affinity, adsorption will take place preferentially in such positions. Atoms occurring along the edges of crystals will also be more adsorptive than those of plane surfaces. According to this concept, therefore, adsorption will occur not uniformly over the surface but predominantly on certain "active points," or "active centers." A number of different types of evidence have been put forward in favor of this point of view; *e.g.*, it has been found that certain substances adsorbed on a surface "poison" the surface for one reaction but not for another. Presumably the two reactions occur on different sets of active centers, only one of which is affected by the poison.

When a surface is extremely irregular, as in the case of charcoal, which contains macroscopic pores running right through the material, the situation is even more complex. Here a good deal of the adsorption which occurs is of the van der Waals type, which may give rise to extensive condensation within the pores. The ease of adsorption by such materials seems to be approximately proportional to the ease with which the gas can be liquefied. This type of adsorption does not appear to play any significant part in connection with the catalysis of reactions involving stable molecules, but it may be important in the catalysis of atomic and free-radical combinations and similar processes.

The Adsorption Isotherm. Since chemical reaction on surfaces almost always involves chemisorption of the reacting molecules, it is necessary to have a theoretical expression relating the amount of adsorption to the partial pressure of the gas in equilibrium with the adsorbed layer on the surface; this is known as the "adsorption isotherm." The theory was worked out in a simple manner for the case of a smooth surface by Langmuir,[2] and can be extended to rough surfaces in a qualitative manner. Consider a gas at pressure p in equilibrium with unit area of the surface of a solid. The fraction of the surface which is covered by adsorbed gas may be denoted by θ, so that the fraction uncovered is $1 - \theta$. At a given temperature the rate of condensation v_c on the surface is proportional to the pressure of the gas (since the number of molecules striking unit surface is proportional to the pressure) and to the fraction of the surface uncovered, since only molecules striking the uncovered part of the surface have a chance of becoming adsorbed (assuming only a monomolecular layer to be possible).

[1] H. S. Taylor, *Proc. Roy. Soc.* (*London*), **A, 108,** 105 (1925); *J. Phys. Chem.*, **30,** 145 (1926).

[2] I. Langmuir, *J. Am. Chem. Soc.*, **38,** 2221 (1916); **40,** 1361 (1918).

This can be expressed as

$$v_c = k_1 p(1 - \theta) \tag{1}$$

where k_1 is a constant. The rate of evaporation, v_e, depends only on the amount of gas adsorbed and is therefore proportional to θ,

$$v_e = k_{-1}\theta \tag{2}$$

At equilibrium the rates of condensation and evaporation are equal, so that

$$k_1 p(1 - \theta) = k_{-1}\theta \tag{3}$$

Rearranging, it is found that the fraction covered is given by

$$\theta = \frac{k_1 p}{k_{-1} + k_1 p} \tag{4}$$

In two special cases, which frequently occur in practice, this relationship simplifies somewhat. If the surface is only very sparsely covered by adsorbed molecules, the term $1 - \theta$ in Eq. (3) is practically equal to unity, so that

$$k_1 p = k_{-1}\theta \tag{5}$$

or

$$\theta = \frac{k_1}{k_{-1}} p \tag{6}$$

For this case of slight adsorption, the amount of gas adsorbed is directly proportional to the pressure.

In the second case the surface is nearly saturated; θ therefore approximates to unity. Equation (3) may therefore be written as

$$k_1 p(1 - \theta) = k_{-1} \tag{7}$$

so that

$$1 - \theta = \frac{k_{-1}}{k_1 p} \tag{8}$$

This means that the fraction of surface uncovered is in this case inversely proportional to the pressure of the gas. These two special cases, expressed by Eqs. (6) and (8), will be found to have important applications in the study of chemical reactions on surfaces.

In the case of an irregular surface, on which adsorption occurs only on certain active centers, the fraction of surface covered must be taken as applying not to all the surface atoms but only to the active centers. The surface would therefore be said to be completely covered when all the active centers were covered, even though the remaining surface atoms were bare.

For certain purposes it is convenient to formulate the rates of adsorption and desorption, and the adsorption isotherm, in a somewhat different manner, making use of the concentrations of surface atoms instead of the fractions covered and uncovered.[1] Suppose that N_g is the total number of molecules in the gas phase, which is of volume V; the concentration in the gas phase is therefore N_g/V molecules per cubic centimeter. If, after adsorption equilibrium has been attained, the number of adsorption sites that are uncovered is N_s, and if the area of the surface is S sq cm, the concentration of adsorption centers is N_s/S sites per square centimeter. Similarly, if the number of molecules adsorbed on the surface is N_a, the concentration of molecules adsorbed is N_a/S. Thus,

Concentration in gas phase $c_g = N_g/V$ molecules per cubic centimeter

Concentration of adsorption centers $c_s = N_s/S$ sites per square centimeter

Concentration of adsorbed molecules $c_a = N_a/S$ molecules per square centimeter

The process of adsorption can be envisaged as a chemical reaction between a gas molecule and a site, and its rate is therefore proportional to the product of the concentration in the gas phase and the concentration of sites,

$$v_a = k_1' c_g c_s \tag{9}$$

The desorption process may be considered to be the unimolecular decomposition of a complex consisting of a surface site and an adsorbed molecule, and the rate is therefore given by

$$v_d = k_{-1}' c_a \tag{10}$$

The equilibrium condition is given by equating these two rates,

$$k_1' c_g c_s = k'_{-1} c_a \tag{11}$$

or

$$\frac{c_a}{c_g c_s} = \frac{k_1'}{k_{-1}'} = K \tag{12}$$

where K, equal to k_1'/k_{-1}', is an equilibrium constant for the system. This relationship can readily be put into the form of Eq. (4) by making use of the fact that c_g is proportional to p, c_a to θ, and c_s to $1 - \theta$.

Adsorption with Dissociation. In certain cases, particularly when the adsorbed gas is hydrogen, there is reason to believe that the process of adsorption is accompanied by the dissociation of the molecule, the adsorbed

[1] K. J. Laidler, S. Glasstone, and H. Eyring, *J. Chem. Phys.*, **6**, 659 (1940); see also G. E. Kimball, *ibid.*, **6**, 447 (1938); M. Temkin, *Acta Physicochim. U.R.S.S.*, **6**, 141 (1938).

species therefore being the atoms. It is found, for example, that when a tungsten filament is heated in the presence of hydrogen gas, hydrogen atoms are produced at the surface and travel to the walls of the reaction vessel.[1] This suggests that the adsorbed hydrogen is in the atomic form, a conclusion that has received support from quantum-mechanical calculations.[2] The reason that dissociation is favored is that the resulting atoms are capable of forming very much stronger bonds with the surface atoms than would be the case if molecules were present; at the expense of breaking one bond, therefore, two adsorption bonds can be formed.

In this case the processes of adsorption and desorption may be represented as

$$G_2 + 2S \rightleftharpoons 2G\text{—}S$$

where the gas molecule is represented as G_2 and the adsorption complex as G—S. If, after equilibrium is established, the concentration of sites is c_s, while that of adsorbed molecules is c_a, the adsorption equilibrium can be written as

$$\frac{c_a^2}{c_g c_s^2} = K \tag{13}$$

so that

$$\frac{c_a}{c_s} = c_g^{1/2} K^{1/2} \tag{14}$$

In this case the concentration of adsorbed molecules is proportional to the square root of the concentration of the gas, rather than, as previously, to its first power. Since c_a/c_s is equal to $\theta/(1 - \theta)$ this equation may be written as

$$\frac{\theta}{1 - \theta} = c_g^{1/2} K^{1/2} \tag{15}$$

$$= ap^{1/2} \tag{16}$$

where a is a new constant. This rearranges to

$$\theta = \frac{ap^{1/2}}{1 + ap^{1/2}} \tag{17}$$

At low pressures, where the surface is sparsely covered,

$$\theta = ap^{1/2} \tag{18}$$

i.e., the fraction covered is proportional to the square root of the pressure.

[1] I. Langmuir, *J. Am. Chem. Soc.*, **34**, 1310 (1912); **37**, 417 (1915).

[2] A. Sherman and H. Eyring, *ibid*, **54**, 2661 (1932).

Chemical reactions on surfaces

Mechanisms of Surface Reactions. A reaction occurring on a surface may usually be regarded as involving five consecutive steps, as follows:

1. Diffusion of the reacting molecules to the surface
2. Adsorption of the gases on the surface
3. Reaction on the surface
4. Desorption of the products
5. Diffusion of the desorbed products into the main body of the gas

At one time it was fairly generally believed that one of the diffusion processes, (1) or (5), was the slowest process, and, therefore, determined the over-all rate. More detailed investigations of surface reactions showed, however, that this could not be the case, except perhaps in certain technical processes. This is evident from the fact that heterogeneous processes nearly always involve appreciable activation energies, whereas diffusion in the gaseous state involves no activation energy; the diffusion process is, therefore, much more rapid than the over-all process and cannot constitute its slow step. Langmuir[1] presented the same type of argument in a somewhat different form when he showed that in order for diffusion to be the slow step it would be necessary to postulate a very thick diffusion layer on the surface, and one that would be visible. Since diffusion is slower in solution than in the gas phase it may sometimes be the rate-determining step in the case of solid-liquid reactions.

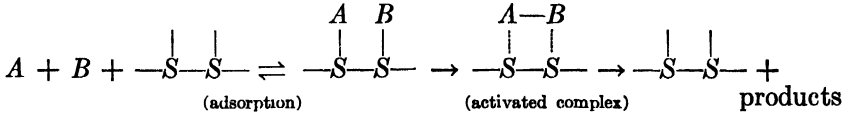
The processes of adsorption or desorption are much more likely to be the slow steps in heterogeneous reactions, since both may involve appreciable energies of activation. The activation energies for desorption are particularly high, and it is likely that in very many reactions the desorption of the products is the rate-determining step. In practice, however, it is not always convenient to separate steps (3) and (4) because one usually does not know the rate of desorption of the products; it is usual, therefore, to regard the reaction on the surface, giving the *gaseous* products, as a single step. This concept is in fact the basis of the usual modern treatment of surface reactions, due to Langmuir[2] and Hinshelwood.[3] This treatment involves, first, obtaining an expression for the concentrations of reactant molecules on the surface, and then expressing the rate of formation of gaseous products in terms of these surface concentrations; the rate is then expressible in terms of the concentrations of the gaseous reactants. If there is a single reactant, the surface process is a simple unimolecular change; if there are two, A and B, reaction can only occur if they become

[1] I. Langmuir, *ibid.*, **38**, 1145 (1916).

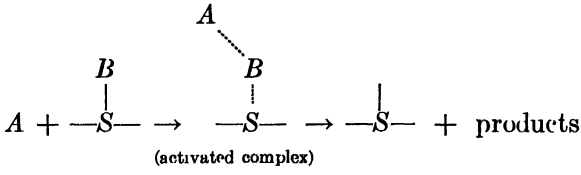
[2] I. Langmuir, *Trans. Faraday Soc.*, **17**, 621 (1921).

[3] C. N. Hinshelwood, "Kinetics of Chemical Change," p. 145, Oxford University Press, New York, 1926; p. 187, 1940.

adsorbed on neighboring surface sites, and the probability of this happening is proportional to the individual concentrations of adsorbed A and adsorbed B. The Langmuir-Hinshelwood mechanism for a reaction between A and B may be formulated as follows:



The essential feature of the mechanisms considered above is that the processes of adsorption and reaction are quite distinct. There are some reactions, however, which do not occur in this way, but in which a reactant molecule reacts with an adsorbed molecule without itself becoming adsorbed; for reaction between two molecules A and B we may represent such a process as follows:



This type of mechanism was first propounded by Rideal[1], and is applicable to the para-ortho hydrogen conversion on surfaces, and to the recombination of atoms and radicals at surfaces. It has also been suggested that the mechanism is applicable to the reaction between ethylene and hydrogen on various surfaces, and to certain reactions involving exchange between hydrogen and deuterium; however, this has not been well established. Some of these reactions will be considered later; first, the general laws applicable to the Langmuir-Hinshelwood type of mechanisms will be developed.

Unimolecular Reactions. If the reaction involves one molecule of the reactant A the activated complex of the surface-catalyzed reaction consists of an adsorbed molecule which has acquired the energy and entropy necessary for dissociation into the products or for isomerization. The equilibrium between reactants and activated complex may therefore be represented by

$$A + S \rightleftharpoons A—S \rightarrow \text{products}$$

and the equilibrium constant is

$$\frac{c_\ddagger}{c_0 c_s} = K^\ddagger \tag{19}$$

[1] E. K. Rideal, *Proc. Camb. Phil. Soc.*, **35**, 130 (1939); *Chem. and Ind.*, **62**, 335 (1943).

The significance of c_g and c_s is the same as previously, and $c_\ddagger$ ($= N_\ddagger/S$) is the concentration of the activated complexes on the surface. Since the rate is proportional to $c_\ddagger$, it follows from Eq. (19) that it is proportional to $c_g c_s$,

$$v = kc_g c_s \tag{20}$$

It is to be noted that this expression is of the same form as that for the rate of adsorption [Eq. (9)], although the activated states are different in the two cases. Two special cases of this rate law may now be considered.

Case I. Sparsely Covered Surface. If the surface is sparsely covered by adsorbed molecules, the concentration c_s of bare adsorption sites on the surface is practically independent of the concentration in the gas phase. Under these circumstances the rate of reaction therefore takes the form

$$v = k'c_g \tag{21}$$

where k', equal to kc_s, is a new constant. The reaction is therefore of the first order. An alternative but equivalent way of arriving at this result is by using the adsorption isotherm [Eq. (6)], according to which the concentration of adsorbed molecules is, for a sparsely covered surface, directly proportional to the gas pressure. The over-all rate, being proportional to the rate of reaction of the adsorbed reactant, is therefore proportional to the concentration or pressure of the reactant in the gas phase.

A great many examples of this behavior have been found; *e.g.*, the decompositions of arsine,[1] phosphine,[2] and formic acid[3] on a number of different surfaces are found to be of the first order. Other reactions of this class are the decompositions of nitrous oxide on a gold surface[4] and of hydrogen iodide on platinum.[5] Since in the latter reactions the total surface area was known, a quantitative application of the theory of absolute reaction rates has been possible, and the calculated values were found to be in satisfactory agreement with the experimental ones.[6]

Case II. Fully Covered Surface. If the surface is almost completely covered by adsorbed molecules, the concentration of the latter is practically independent of the concentration in the gas phase; the rate, which is propor-

[1] J. H. van't Hoff, "Etudes de dynamique chimique," F. Muller and Company, Amsterdam, p. 83, 1884.

[2] J. H. van't Hoff and D. M. Kooij, *Z. physik. Chem.*, **12**, 155 (1893); M. Trautz and D. S. Bhandarkar, *Z. anorg. Chem.*, **106**, 95 (1919); C. N. Hinshelwood and B. Topley, *J. Chem. Soc.*, **125**, 393 (1924).

[3] C. N. Hinshelwood and B. Topley, *ibid.*, **123**, 1014 (1923).

[4] C. N. Hinshelwood and C. R. Prichard, *Proc. Roy Soc.* (*London*), A, **108**, 211 (1925).

[5] C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 2896 (1925).

[6] Laidler, Glasstone, and Eyring, *loc. cit.*

tional to the concentration of adsorbed molecules, is therefore independent of the gas concentration. In the rate expression (20) the value of c_s is no longer constant, and this quantity may be eliminated by substituting for $c_g c_s$ using Eq. (12). This gives

$$v = \frac{k}{K} c_a \tag{22}$$

The concentration c_a may now be taken as constant, so that the rate of reaction is independent of c_g. This type of behavior is described by saying that the reaction is of zero order.

The first example of this type of behavior to be discovered was the decomposition of ammonia on tungsten,[1] which was considered in Chap. 2. Some of the results are shown in Fig. 10 (p. 54), in which is plotted the amount decomposed against the time for various initial pressures. The slope of the curve represents the rate, which is seen to be initially the same for the three initial pressures shown. At later times there is a falling off of the rate, presumably owing to the fact that at lower pressures the surface is no longer almost completely covered.

Approximately zero-order kinetics have also been found for the decomposition of ammonia on molybdenum,[2] osmium,[3] and nickel,[4] and of hydrogen iodide on gold.[5] Zero-order kinetics are also frequently found in liquid systems, particularly in enzyme-catalyzed reactions; examples of this will be found in Chap. 10.

Behavior between the two extremes of first-order and zero-order kinetics is often found, and the kinetic laws must now be expressed in their more general form. The rate of reaction is given by Eq. (20).

$$v = kc_g c_s \tag{23}$$

where c_s is a function of the gas concentration c_g. The adsorption isotherm

$$\frac{c_a}{c_g c_s} = K \tag{24}$$

can be expressed as

$$\frac{L - c_s}{c_g c_s} = K \tag{25}$$

[1] C. N. Hinshelwood and R. E. Burk, *J. Chem. Soc.*, **127**, 1051 (1925). *Cf.* C. H. Kunsman, *J. Am. Chem. Soc.*, **50**, 2100 (1928); C. H. Kunsman, E. S. Lamar, and W. E. Deming, *Phil. Mag.*, **10**, 1015 (1930).

[2] R. E. Burk, *Proc. Natl. Acad. Sci. U. S.*, **13**, 67 (1927); *loc. cit.*

[3] E. A. Arnold and R. E. Burk, *J. Am. Chem. Soc.*, **54**, 23 (1932).

[4] Kunsman, *loc. cit.*

[5] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 1552 (1925).

where L, equal to $c_s + c_a$, is the total concentration of sites when the surface is bare. Elimination of c_s between Eqs. (23) and (25) gives

$$v = \frac{kLc_g}{1 + Kc_g} \tag{26}$$

which may be written as

$$v = \frac{ap}{1 + bp} \tag{27}$$

where a and b are constants and p the pressure of the gas. This expression could also have been obtained directly from Eq. (4), the rate of reaction being proportional to θ.

According to this rate expression, the rate increases with the pressure less rapidly than in direct proportion to the pressure. As an approximation, the rate may be expressed in the form

$$\frac{dp}{dt} = kp^n \tag{28}$$

where the exponent n is a constant which is less than unity. Usually the experimental data fit Eqs. (27) and (28) about equally well.

The decomposition of antimony hydride (stibine) on an antimony surface[1] was fitted to an equation of the second type and will equally well fit Eq. (27). It may therefore be concluded that this reaction is one in which the surface coverage is intermediate in extent.

Bimolecular Reactions. In a surface reaction between two molecules, which may be of the same type or different, it is usually necessary for the molecules to be adsorbed on neighboring sites in order for reaction to occur The reaction may therefore be envisaged as occuring between one molecule of each of the reactants A and B (or $2A$) and a dual surface site which consists of two single sites,

$$A + B + S_2 \rightarrow ABS_2 \rightarrow \text{products}$$

In order to express the rate of reaction, it is necessary to express the concentration of dual sites in terms of the concentration of available single sites (c_s). If the fraction of surface covered by reactant A is θ and that covered by B is θ', the number of bare sites adjacent to a given site is, on the average, $s(1 - \theta - \theta')$, where s is the number of neighboring sites when the surface is bare. Each of the c_s bare single sites is surrounded by $s(1 - \theta - \theta')$ bare sites, so that if the total number of dual sites were counted by considering each bare site, the result would be $c_s s(1 - \theta - \theta')$.

[1] A. Stock and M. Bodenstein, *Ber.*, **40**, 570 (1907).

However this procedure counts each pair twice, and the number of dual sites is really $\frac{1}{2}c_s s(1 - \theta - \theta')$. The fractions θ and θ' may be expressed in terms of the concentrations c_a and c_a' of adsorbed molecules of A and B,

$$\theta = \frac{c_a}{c_a + c_a' + c_s} \tag{29}$$

and

$$\theta' = \frac{c_a'}{c_a + c_a' + c_s} \tag{30}$$

The concentration of bare dual sites is therefore

$$c_{s_2} = \frac{\frac{1}{2}sc_s^2}{c_a + c_a' + c_s} \tag{31}$$

$$= \frac{\frac{1}{2}sc_s^2}{L} \tag{32}$$

where $L = c_a + c_a' + c_s$ is the total number of single sites per square centimeter of bare surface.

Considering the reaction on the surface as one involving A, B, and S_2, the rate can be expressed as

$$v = kc_g c_g' c_{s_2} \tag{33}$$

where c_g and c_g' represent the concentrations of A and B in the gas phase. Substitution of (32) for c_{s_2} gives

$$v = \frac{\frac{1}{2}sk}{L} c_g c_g' c_s^2 \tag{34}$$

A number of special cases of this general equation may now be considered.

Case I. Sparsely Covered Surface. If the sum of c_a and c_a' is small compared with c_s, c_s is practically equal to L, so that Eq. (34) reduces to

$$v = \tfrac{1}{2}skc_g c_g' L \tag{35}$$

thus the rate is directly proportional to the two gas concentrations. A number of reactions obey this law; examples are the reaction between nitric oxide and oxygen on glass[1] and the reaction between ethylene and hydrogen on copper under certain conditions of temperature.[2] Cases of reactions of this type involving only one reactant, for which the rate equation becomes

$$v = \tfrac{1}{2}skc_g^2 L \tag{36}$$

[1] M. Temkin and W. Pyzhow, *Acta Physicochim. U.R.S.S.*, **2**, 473 (1935).

[2] U. Grassi, *Nuovo Cimento*, (6) **11**, 147 (1916); R. N. Pease, *J. Am. Chem. Soc.*, **45**, 2235 (1923).

are rare; one example is the decomposition of acetaldehyde on various surfaces.[1]

Case II. One Reactant More Strongly Adsorbed Than the Other. If the reactant A is considerably more strongly adsorbed than B, c_a' may be neglected in comparison with c_a, so that L may be put equal to $c_a + c_s$. Equation (34) therefore becomes

$$v = \frac{\frac{1}{2}sk}{L} c_g c_g' (L - c_a)^2 \tag{37}$$

The adsorption isotherm $c_a = Kc_g c_s$ for the reactant A may also be written as

$$c_a = Kc_g(L - c_a) \tag{38}$$

whence

$$L - c_a = \frac{L}{1 + Kc_g} \tag{39}$$

Introduction of this expression into Eq. (37) gives

$$v = \frac{1}{2} skL \frac{c_g c_g'}{(1 + Kc_g)^2} \tag{40}$$

According to this expression the rate of the reaction is directly proportional to the concentration of the reactant which is more weakly adsorbed but is not directly proportional to that of the more strongly adsorbed substance, except approximately at very low concentrations when Kc_g can be neglected in comparison with unity. When the concentration of A is increased, the term in the denominator becomes more and more important, and finally the rate may decrease as the concentration of A increases. Such a maximum in the rate has been observed in the reaction between hydrogen and carbon dioxide on platinum.[2]

Case III. One Reactant Very Strongly Adsorbed. The limiting case of the above behavior is of special interest; this is when the reactant A is so strongly adsorbed that it occupies most of the available surface. The fraction c_a/c_s, which is equal to Kc_g, is then much greater than unity, so that Eq. (40) approximates to

$$v = \frac{1}{2} s \frac{k}{K^2} L \frac{c_g'}{c_g} \tag{41}$$

Under these circumstances the rate is inversely proportional to the concentration of the strongly adsorbed reactant A.

[1] P. C. Allen and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), A, **121**, 141 (1928).
[2] C. N. Hinshelwood and C. R Prichard, *J. Chem. Soc.*, **127**, 806 (1925).

Several examples of this type of behavior have been found. Under certain circumstances the rate of the reaction between carbon monoxide and oxygen on the surface of quartz[1] and of platinum[2] is directly proportional to the concentration of oxygen and inversely proportional to the concentration of carbon monoxide, which is therefore strongly adsorbed. Another case is the reaction between hydrogen and oxygen on platinum,[3] in which, over a certain temperature range, the rate is proportional to $[O_2]/[H_2]$, indicating that the hydrogen is strongly adsorbed. The reaction between ethylene and hydrogen on copper[4] sometimes follows a similar law.

Case IV. Intermediate Behavior. In a large number of cases the kinetics do not fall into any of the classes considered above, but show intermediate behavior, indicating that one or both of the reactants are more than sparsely adsorbed on the surface but do not completely cover it. Thus on a different type of quartz from that used by Bodenstein and Ohlmer, the rate of the reaction between oxygen and carbon monoxide was found by Benton and Williams[5] to be proportional to $[O_2][CO]^{1/2}$. This indicates that the oxygen is sparsely adsorbed, but that the adsorption of the carbon monoxide is of an intermediate character. On a silver surface, hydrogen and oxygen react at a rate which is proportional to the hydrogen pressure but independent of that of oxygen,[6] indicating intermediate adsorption of the oxygen.

The kinetics of the reaction $CO_2 + H_2 \rightarrow CO + H_2O$ on the surface of platinum at 1000°C show somewhat complex behavior.[7] The rate was found to be directly proportional to the pressure of hydrogen over almost the entire range investigated but was directly proportional to the carbon dioxide pressure only at very small pressures. At higher pressures of carbon dioxide the rate was inversely proportional to the pressure of this gas. This behavior indicates that at low pressures of carbon dioxide the gas is only weakly adsorbed, but that at the higher pressures it is strongly adsorbed and displaces the hydrogen from the surface.

Retardation of Surface Reactions by Poisons. Nonreacting substances which are adsorbed on a catalytic surface reduce the number of surface sites available for reaction and therefore reduce the rate of reaction. The product of a reaction is frequently adsorbed in this way, sometimes strongly, and therefore inhibits the reaction, at the same time influencing

[1] M. Bodenstein and F. Ohlmer, *Z. physik Chem.*, **53**, 166 (1905).
[2] I. Langmuir, *Trans. Faraday Soc*, **17,2** 61 (1922).
[3] Bodenstein and Ohlmer, *loc. cit.*
[4] R. N Pease, *J. Am. Chem. Soc.*, **45**, 1196 (1923).
[5] A. F. Benton and T. L. Williams, *J. Phys Chem.*, **30**, 1487 (1926).
[6] A. F. Benton and J. C. Elgin, *J. Am. Chem. Soc.*, **48**, 3027 (1926).
[7] Hinshelwood and Prichard, *loc. cit.*

the kinetic laws. Various special cases of this behavior will now be considered.

Case I. Unimolecular Reactions. If a unimolecular reaction proceeds on a sparsely covered surface, so that in the absence of a poison it would exhibit first-order kinetics, the free surface area in the presence of the poison can be calculated using the adsorption isotherm

$$c_{ap} = K_p c_s c_{gp} \tag{42}$$

Here c_{ap} is the concentration of the adsorbed poison, c_{gp} that of the poison in the gas phase, and the K_p the equilibrium constant for the adsorption of the poison. Since by hypothesis very few molecules of the reacting gas are on the surface, L is approximately equal to $c_{ap} + c_s$, so that on elimination of c_{ap} the isotherm rearranges to

$$c_s = \frac{L}{1 + K_p c_{gp}} \tag{43}$$

The rate of the reaction, equal to $kc_g c_s$, therefore becomes

$$v = \frac{kLc_g}{1 + K_p c_{gp}} \tag{44}$$

which may be written in terms of pressures as

$$v = \frac{k'p}{1 + Bp_p} \tag{45}$$

where p is the pressure of the reacting gas and p_p that of the poison. If the poison is very strongly adsorbed, Bp_p is large compared with unity so that the rate is

$$v = k'' \frac{p}{p_p} \tag{46}$$

If the poison is a product of the reaction, Eq. (45) may be expressed in a special form. If a is the original concentration of the reactant and x is the amount transformed after time t, then p is proportional to $a - x$ and p_p to x. The rate equation therefore becomes

$$\frac{dx}{dt} = \frac{k(a - x)}{1 + bx} \tag{47}$$

where k and b are new constants. This equation integrates to

$$k = \frac{1 + ab}{t} \ln \frac{a}{a - x} - \frac{bx}{t} \tag{48}$$

This law has been found to be obeyed by the decomposition of nitrous oxide on the surface of platinum,[1] the reaction being poisoned by the oxygen produced. The applicability of the law was proved by showing that the quantity $(1/t) \ln [(a/(a - x)]$ was a linear function of x/t.

When the surface is strongly poisoned by the product of the reaction, Eq. (49) reduces to

$$\frac{dx}{dt} = k \frac{a - x}{x} \tag{49}$$

which integrates to

$$k = \frac{a}{t} \ln \frac{a}{a - x} - \frac{x}{t} \tag{50}$$

This law is closely followed by the decomposition of ammonia on platinum[2] at about 1000°C; this reaction is poisoned by hydrogen, which is probably adsorbed in the atomic form.

The same kinetic laws as the above are obtained if the reaction takes place on a pair of surface sites, provided that the poison is adsorbed atomically and therefore occupies two sites. This situation appears to exist more frequently than that considered above and probably occurs in the two examples mentioned.

Case II. Bimolecular Reactions. If a reaction involves two molecules, which may be the same or different, the general equation [Eq. (34)] is still applicable, but L is now equal to $c_s + c_a + c_a' + c_{ap}$. If the reactant molecules are only weakly adsorbed, but the poison is more strongly adsorbed, c_a and c_a' may be neglected so that L is equal to $c_s + c_{ap}$. On substituting the value $K_p c_s c_{gp}$ for c_{ap}, as previously, one obtains

$$L = c_s + K_p c_s c_{gp} \tag{51}$$

and introduction of this into Eq. (34) gives for the rate

$$v = \frac{1}{2} sk \frac{c_g c_g' c_s}{1 + K_p c_{gp}} \tag{52}$$

Elimination of c_s using Eq. (51) then gives

$$v = \frac{1}{2} sk \frac{L c_g c_g'}{(1 + K_p c_{gp})^2} \tag{53}$$

which may be written as

$$v = \frac{k' p_A p_B}{(1 + b p_p)^2} \tag{54}$$

[1] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 327 (1925).

[2] C. N. Hinshelwood and R. E. Burk, *ibid.*, 1105; G. M. Schwab and H. Schmidt, *Z. physik. Chem.*, B, **3**, 337 (1929).

If the two molecules are the same, the rate is

$$v = \frac{k' p_A^2}{(1 + b p_p)^2} \tag{55}$$

If the poison is strongly adsorbed, unity may be neglected in comparison with bp_p, so that the rate is proportional to p_A^2/p_p^2. It is important to note that a poison adsorbed molecularly retards a bimolecular reaction according to the square of the pressure and not to the first power. However, if, as is often the case, the poison is a diatomic molecule which is adsorbed with dissociation into atoms it can be shown by similar arguments that the rate is given by an expression of the form

$$v = k \frac{p_A^2}{p_p} \tag{56}$$

Behavior of the type represented by this equation has been found for the decomposition of nitric oxide on platinum and on a rhodium-platinum surface,[1] the reaction being in both cases retarded by the product, oxygen, which is adsorbed in the atomic form. No simple cases are known in which two different reacting molecules are involved, but the reaction between sulfur dioxide and oxygen on platinum[2] shows retardation by the product, sulfur trioxide. The rate is stated to be inversely proportional to the sulfur trioxide pressure, a result that indicates an intermediate degree of adsorption.

Interaction between a Gas Molecule and an Adsorbed Molecule. It was mentioned earlier that there are certain reactions to which the Langmuir-Hinshelwood mechanism, involving adsorption of the reacting molecules, may not be applicable. These may occur by interaction between a gas-phase molecule and an adsorbed molecule, or perhaps between a gaseous molecule and the surface itself. Some reactions to which such a mechanism may apply will now be considered.

Para-Ortho Hydrogen Conversion. On various surfaces *p*-hydrogen becomes converted into an equilibrium mixture of the ortho and para forms. On paramagnetic substances this change involves a physical twisting of the spins of the nuclei, a process that will not be discussed here. On the surfaces of the transition metals, in particular, the reaction is of a chemical nature in that the breaking and remaking of chemical bonds take place; that this is so is indicated by the fact that the exchange reaction between hydrogen and deuterium,

$$H_2 + D_2 = 2HD$$

will also occur on these catalysts.

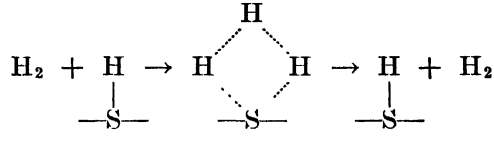
[1] P. W. Bachman and G. B. Taylor, *J. Phys. Chem.*, **33**, 447 (1929); *cf.* G. E. Green and C. N. Hinshelwood, *J. Chem. Soc.*, 1709 (1926).

[2] M. Bodenstein and C. G. Fink, *Z. physik. Chem.*, **60**, 1 (1907).

The conversion by the chemical mechanism has been studied in great detail.[1] The order of the reaction varies with the degree of surface coverage, being the first for a sparsely-covered layer and zero for a fully-covered one. The first mechanism proposed[2] involved the adsorption (with dissociation) of the hydrogen molecules on the surface, followed by recombination,

$$p\text{-}H_2 + 2S \rightleftharpoons 2SH \rightleftharpoons 2S + o\text{-}H_2$$

That this cannot occur, at any rate on a tungsten surface, was, however, shown by Roberts,[3] whose experiments indicated that at ordinary temperatures hydrogen atoms form a firmly bound layer and do not recombine at an appreciable rate. To account for this fact Rideal[4] proposed that the mechanism is an interaction between chemisorbed hydrogen atoms and hydrogen molecules held in a van der Waals layer. Since these molecules are only weakly held this may be regarded as interaction between an adsorbed atom and a gaseous molecule, and the mechanism may be written as



(activated complex)

Support for this mechanism is provided by the fact that a quantitative treatment[5] gives good agreement between observed and calculated rates.

Surface Combination of Atoms and Radicals. All atom and radical recombinations on surfaces have been found[6] to follow a first-order law over a wide range of temperatures and pressures. This fact excludes the possibility that the mechanism involves reaction between atoms adsorbed on neighboring sites, since this would give rise to a second-order law. Another obvious mechanism is that the over-all reaction is controlled by the adsorption of the radicals (a first-order process), the subsequent reaction and desorption being rapid. This explains the first-order kinetics, but is inconsistent with the observation that on some of the surfaces for

[1] See in particular K. F. Bonhoeffer, A. Farkas, and K. W. Rummel, *Z. physik. Chem.*, B, **21**, 225 (1933); A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, London, 1935; D. D. Eley and E. K. Rideal, *Proc. Roy. Soc.* (*London*), A, **178**, 429 (1941).

[2] Bonhoeffer, Farkas, and Rummel, *loc. cit.*

[3] J. K. Roberts, *Trans. Faraday Soc.*, **35**, 941 (1939).

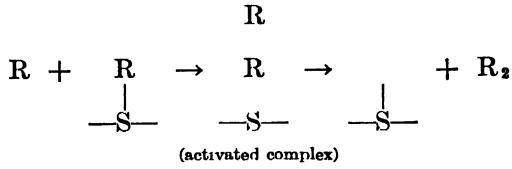
[4] E. K. Rideal, *Proc. Cambridge Phil. Soc.*, **35**, 130 (1939); Eley and Rideal, *loc. cit.*

[5] D. D. Eley, *Trans. Faraday Soc.*, **44**, 216 (1948).

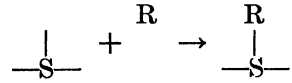
[6] For a review see L. von Müffling, in G. M. Schwab's "Handbuch der Katalyse", J. Springer, Berlin, Vol. VI, p. 94. 1943; see also W. V. Smith, *J. Chem. Phys.*, **11**, 110 (1943).

which these kinetics are obtained (*e.g.*, tungsten[1] and glass[2]) the recombination of adsorbed radicals is very slow. To avoid this difficulty it has been proposed[3] that the mechanism involves interaction between a gaseous radical and a surface-adsorbed radical:

(1)

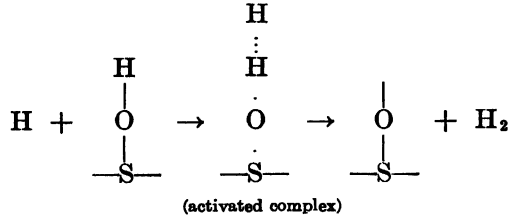


(2)



The observed first-order kinetics requires the fraction of surface covered by radicals to be independent of the gas-phase concentration, *i.e.*, the surface must be fully covered; this condition is very frequently satisfied in atomic and radical adsorption.[4] It is clear that the mechanism proposed is of the same type as that suggested by Ridcal for the para-ortho hydrogen conversion.

One interesting phenomenon in connection with the combination of hydrogen atoms on glass surfaces is the well-marked poisoning effect of water.[5] It has been seen earlier that the poisoning of surfaces is commonly due to the necessity for the desorption of a molecule of poison before the reaction can occur, a process that requires energy and, therefore, involves an increase in the activation energy of the over-all process. An examination of the data for the water-vapor poisoning of glass surfaces in the hydrogen-atom combination has indicated, on the other hand, that a water molecule is not desorbed, since there is no corresponding increase of activation energy. Instead it appears that at higher temperatures the reaction occurs on a film of adsorbed hydroxyl radicals,



[1] J. K. Roberts, *Trans. Faraday Soc.*, **35**, 941 (1939).
[2] M. C. Johnson, *Trans. Faraday Soc.*, **28**, 162 (1932).
[3] K. E. Shuler and K. J. Laidler, *J. Chem. Phys.*, **17**, 1212 (1949); *cf.* K. J. Laidler, *J. Phys. & Colloid Chem.*, **53**, 712 (1949).
[4] I. Langmuir, *J. Chem. Soc.*, 511 (1940).
[5] R. W. Wood, *Proc. Roy. Soc.* (*London*), **97**, 455 (1920).

At lower temperatures a different effect is important; here there is apparently a marked decrease in the number of effective surface sites, and the process may involve interaction between gaseous atoms and a small number of atoms attached to the surface by van der Waals forces.

Hydrogenation of Ethylene. The kinetics of the reaction between hydrogen and ethylene have been very extensively investigated on a wide variety of catalysts.[1] It is found that in the range of temperatures from 100 to 150°C the reaction is of the first order with respect to hydrogen and of zero order with respect to ethylene; however, at higher ethylene concentrations the rate decreases. The ethylene is more strongly adsorbed, so that the fraction of the surface covered by ethylene is proportional to $ap_{C_2H_4}/(1 + ap_{C_2H_4})$, and the fraction not covered to $1/(1 + ap_{C_2H_4})$, a being a constant. The hydrogen only sparsely covers the surface, so that the hydrogen coverage is proportional both to p_{H_2} and to the fraction not covered by ethylene, *i.e.*, to

$$\frac{p_{H_2}}{1 + ap_{C_2H_4}}$$

If the reaction involves interaction between *adsorbed* hydrogen and ethylene, *i.e.*, if the Langmuir-Hinshelwood mechanism is applicable, the rate is proportional to the product of the two surface concentrations, or to

$$\frac{p_{H_2}p_{C_2H_4}}{(1 + ap_{C_2H_4})^2}$$

This correctly interprets the first-order kinetics with respect to hydrogen, the zero-order kinetics at intermediate ethylene concentrations (where the rate goes through a maximum), and the decrease in rate at high ethylene concentrations. Moreover a calculation of the absolute rate in the neighborhood of the maximum gives good agreement with the experimental values.[2]

Two Rideal mechanisms are possible for this reaction: In the first gaseous hydrogen interacts with adsorbed ethylene, while in the second gaseous ethylene reacts with adsorbed hydrogen. The first is excluded by the fact that adsorbed ethylene does not react sufficiently rapidly with hydrogen. Both mechanisms lead to the conclusion that the rate should be proportional to

$$\frac{p_{H_2}p_{C_2H_4}}{1 + ap_{C_2H_4}}$$

[1] For a discussion with references see D. D. Eley in "Advances in Catalysis," p. 157, Academic Press, New York; *Quart. Revs.*, **3**, 209 (1949).

[2] K. J. Laidler, Discussion on Heterogeneous Catalysis, *Trans. Faraday Soc.*, 1950, in press.

and the second mechanism has been advocated by Beeck.[1] However, this mechanism is incapable of explaining the falling off of the rate at high ethylene concentrations, and, on the whole, the Langmuir-Hinshelwood mechanism seems to offer a better interpretation of the data.

In general, we may expect that Langmuir-Hinshelwood mechanisms will apply in most cases. This is so because the activation energy involved in the formation of an adsorbed product molecule will be less when both reactant molecules are adsorbed than when only one is adsorbed. The condition leading to a Rideal type of mechanism is strong adsorption of the product, so that its removal from the surface constitutes the slow step. This is the case in the para-ortho-hydrogen conversion and the combination of atoms, since the products, *i.e.*, hydrogen molecules, are only slowly desorbed. This condition does not hold in the hydrogenation of ethylene, since ethane is very weakly adsorbed on the surfaces used. Mechanisms of the Rideal type have also been proposed for various types of hydrogen-deuterium exchange reactions, but there is still considerable doubt as to their applicability.

Absolute Rates of Surface Reactions. So far attention has been confined to the question of the influence of the concentration of the reacting substances on the rate, without regard to the absolute rates of the reactions. The treatment of this latter problem involves, as with all reactions, two types of consideration. The first is a calculation by quantum-mechanical methods of the energy of activation; the second is the evaluation of the partition functions for the initial and activated states. The first problem is a very difficult one; approximate methods have to be used, and good agreement with experiment cannot be achieved. In addition to the usual complications of such calculations, there is the difficulty that very little is known about the nature of the surfaces that are involved in catalysis. However, by making use of the experimental activation energies and theoretical partition functions, it has been possible to calculate absolute rates of surface reactions which are in satisfactory agreement with the experimental ones.[2] This procedure has been applied to a number of reactions of different kinds and will now be explained with reference to a unimolecular process on a sparsely covered surface.

According to the postulates of the theory of absolute reaction rates, the activated complexes in any reaction are approximately in equilibrium with the reactants, which are in this case the gas molecules and the adsorption sites; the equilibrium equation is therefore Eq. (19), *viz.*,

$$\frac{c_{\ddagger}}{c_g c_s} = K^{\ddagger} \tag{57}$$

[1] O. Beeck, *Rev. Modern Phys.*, **17**, 61 (1945).

[2] K. J. Laidler, S. Glasstone, and H. Eyring, *J. Chem. Phys.*, **8**, 667 (1940); *cf.* B. Topley, *Nature*, **128**, 115 (1931); R. E. Burk, *J. Am. Chem. Soc.*, **56**, 1279 (1934).

The concentrations may, as on page 150, be expressed in terms of numbers of molecules, so that the equilibrium constant is

$$K^{\ddagger} = \frac{c_{\ddagger}}{c_g c_s} = \frac{N_{\ddagger}/S}{(N_g/V)(N_s/S)} \tag{58}$$

$$= \frac{N_{\ddagger}}{(N_g/V)N_s} \tag{59}$$

Hence

$$K^{\ddagger} = \frac{f^{\ddagger}}{(f_g/V)f_s} \tag{60}$$

where the f's are the complete partition functions of the species indicated. Writing the partition function for unit volume of gas as F_g, *i.e.*,

$$F_g = \frac{f_g}{V} \tag{61}$$

it follows from Eqs. (57) and (60) that

$$\frac{c_{\ddagger}}{c_g c_s} = \frac{f^{\ddagger}}{F_g f_s} \tag{62}$$

so that

$$c_{\ddagger} = c_g c_s \frac{f^{\ddagger}}{F_g f_s} \tag{63}$$

According to the theory of absolute reaction rates, the rate is given by

$$v = c_g c_s \frac{\mathbf{k}T}{\mathbf{h}} \frac{f_{\ddagger}}{F_g f_s} \tag{64}$$

where $f_{\ddagger}$ differs from $f^{\ddagger}$ by the removal of the contribution of the degree of vibrational freedom in the reaction coordinate. If the zero-point energy is extracted from the partition functions (*cf.* p. 67), the rate expression becomes

$$v = c_g c_s \frac{\mathbf{k}T}{\mathbf{h}} \frac{f_{\ddagger}}{F_g f_s} e^{-\epsilon_0/\mathbf{k}T} \tag{65}$$

where ϵ_0 is the energy of activation at the absolute zero; the partition functions in this equation are evaluated from the corresponding zero-point levels.

Since the adsorbed molecule constituting the activated complex has very little motion, it is a sufficiently good approximation to take its partition function as unity; this will be in error only by a small factor representing the small amount of vibration and rotation possible, since the translational term, usually the most important, is here absent; however,

the symmetry factor σ (p. 65) should be included. The adsorption sites are atoms in the surface and have vibrational energy only; the partition function f_s may also taken as unity. For F_g it is sufficient to consider only the translational and rotational factors, the vibrational being of little importance. When these approximations are made, the rate expression becomes

$$v = c_g c_s \frac{\mathbf{k}T}{\mathbf{h}} \frac{1/\sigma_\ddagger}{\dfrac{(2\pi m \mathbf{k}T)^{3/2}}{\mathbf{h}^3} \dfrac{8\pi^2 I \mathbf{k}T}{\sigma \mathbf{h}^2}} e^{-\epsilon_0/kT} \tag{66}$$

for a diatomic molecule; an expression can also be written down for a nonlinear polyatomic molecule. An analogous expression can be obtained if the reaction involves adsorption on more than one surface site. If the activation energy is known from experiment, these expressions permit an absolute calculation of the rate of reaction on a given area of surface.

TABLE 35. OBSERVED AND CALCULATED FIRST-ORDER RATE CONSTANTS

Decomposition of	Surface	Temperature, °K	Specific rate, sec^{-1}	
			Calculated	Observed
PH_3	Glass	684	2.2×10^{-8}	4.7×10^{-7}
HI	Platinum	836	1.2×10^{-3}	1.0×10^{-3}
N_2O	Gold	1211	3.4×10^{-6}	$12\ 3 \times 10^{-5}$

In this manner the specific rates for the surface decompositions of phosphine, hydrogen iodide, and nitrous oxide have been calculated. It has been seen that these reactions all show first-order kinetics, so that the surface is sparsely covered, and it was assumed that there are about 10^{15} sites per square centimeter of surface. In Table 35 the calculated rates are compared with the observed; the values are the ordinary first-order rate constants, which refer to the particular area of surface used in the experiments. The calculated and observed rates are seen to be in satisfactory agreement, especially in view of the approximations made and the uncertainty as to the true area of the surface. Owing to surface roughness, the number of sites per apparent square centimeter may be greater than 10^{15}; this would tend to make the calculated values too low in comparison with the observed.

The theory has also been applied to unimolecular reactions on covered surfaces (zero-order kinetics), to bimolecular reactions on both sparsely covered and fully covered surfaces, and to reactions retarded by poisons. In all cases the agreement with experiment was found to be satisfactory,

so that there can be little doubt as to the validity of the procedure. It may be noted that collision theory cannot be successfully adapted to the calculation of the absolute rates of surface reactions.

Comparison of Homogeneous and Heterogeneous Reactions.[1] Calculations of the kind outlined in the last section can readily be used for making a comparison between the rates of heterogeneous and homogeneous reactions between the same reactants. The reaction rate per square centimeter of surface for a second-order heterogeneous reaction between A and B may be written as

$$v_{\text{het}} = c_A c_B c_s \frac{\mathbf{k}T}{\mathbf{h}} \frac{1}{F_A F_B} e^{-E_{\text{het}}/RT} \tag{67}$$

The partition functions of the activated complex and of the reaction centers have been taken as unity. For the corresponding homogeneous process, the rate, according to the theory of absolute reaction rates, is

$$v_{\text{hom}} = c_A c_B \frac{\mathbf{k}T}{\mathbf{h}} \frac{F_\ddagger}{F_A F_B} e^{-E_{\text{hom}}/RT} \tag{68}$$

It follows, therefore, that

$$\frac{v_{\text{het}}}{v_{\text{hom}}} = \frac{c_s}{F_\ddagger} e^{\Delta E/RT} \tag{69}$$

where ΔE is equal to $E_{\text{hom}} - E_{\text{het}}$. For 1 sq cm of surface, c_s is about 10^{15}, whereas for 1 cc of gas F is frequently about 10^{27}; hence

$$\frac{v_{\text{het}}}{v_{\text{hom}}} = 10^{-12} e^{\Delta E/RT} \tag{70}$$

the heterogeneous rate being for 1 sq cm of surface and the homogeneous rate for 1 cc of reactants. It is evident that for the two rates to be comparable, either a very large surface, *viz.*, approximately 10^{12} sq cm, must be employed, or the activation energy of the heterogeneous reaction must be sufficiently less than that of the gas-phase reaction; alternatively a combination of these two factors may make the rates comparable. At a temperature of 300°K the rates will be comparable for 1 sq cm of surface if the activation energy of the surface reaction is about 16.5 kcal lower than that of the homogeneous reaction. At higher temperatures a larger difference is necessary, the difference required being proportional to the absolute temperature.

In view of this result, it is clearly necessary for a reaction which proceeds at an appreciable rate on a surface of comparatively small size to have a much smaller activation energy on the surface than in the gas phase.

[1] Laidler, Glasstone, and Eyring, *loc. cit.*

An examination of the data reveals that in a number of instances this is the case; some values are given in Table 36. It can be shown that the difference between the two activation energies is equal to the energy of adsorption of the activated complex on the surface.

TABLE 36. ACTIVATION ENERGIES FOR HETEROGENEOUS AND HOMOGENEOUS REACTIONS

Decomposition of	Surface	E_{het}, kcal	E_{hom}, kcal
HI	Au	25.0	44.00
	Pt	14.0	
N_2O	Au	29.0	58.5
	Pt	32.5	
NH_3	W	39.0	>80
	Os	47.0	
	Mo	32–42	
CH_4	Pt	55–60	~80

When a reaction takes place on a surface that is almost completely covered by a poison, the activation energy is increased by the energy of adsorption of the poison. This is true because in order for the reacting molecules to become adsorbed on the surface and form the activated complex, they are required to expend additional energy in removing a molecule of the poison from the surface.

Surface activity

Active Centers. In the above discussion of the influence of concentration and temperature on the rates of surface reactions, it has been tacitly assumed that all the surface sites are of the same character. However, as has already been mentioned, H. S. Taylor has laid stress on the improbability of a perfectly smooth surface such as would be necessary for consistency with the idea of uniformity of the sites. Some of the evidence for variations in surface activity will now be discussed.

Experiments on the retarding influence of gases on reactions frequently provide evidence of this kind. For instance, the rate of decomposition of ammonia on molybdenum[1] is retarded by nitrogen, but as the surface becomes saturated with nitrogen, the rate of the decomposition does not fall to zero. This suggests that the reaction can occur on certain adsorption sites upon which the nitrogen cannot be adsorbed. A further conclusion that can be drawn is that one type of active center can be most

[1] R. E. Burk, *Proc. Natl. Acad. Sci. U. S.*, **13**, 67 (1927).

active for the adsorption of one species and another type for the adsorption of another type of molecule. An additional example leading to the same conclusion is the fact that a platinum surface that has been poisoned by carbon dioxide with respect to reaction between it and hydrogen remains unpoisoned with respect to the decomposition of nitrous oxide.[1]

Further evidence of the same kind comes from studies on the amounts of reactants adsorbed in surface reactions. When hydrogen and carbon dioxide react on the surface of platinum, it is found that the total adsorption of hydrogen is very much greater than that of carbon dioxide, although the reaction rate varies inversely with the pressure of the latter; it is therefore evident that the reaction occurs only on certain sites upon which the carbon dioxide is much more strongly adsorbed; the hydrogen molecules adsorbed on other sites play no part in the reaction.

Another fact which is consistent with the idea of active centers is that the heat of adsorption is commonly found to decrease as the surface becomes more and more covered.[2] The explanation of this in terms of active centers is that the initial adsorption will be on the most active sites and will have the highest heats of adsorption; as adsorption proceeds. less active sites will be covered with a decreased amount of heat liberated, However, this effect has alternatively been explained in terms of the repulsive forces acting between molecules on the surface. When the first molecules become adsorbed, they will arrange themselves as far apart as possible, and the heat of adsorption will be a maximum; subsequent molecules, however, will be adsorbed close to those already on the surface, and owing to the repulsion forces, less heat will be evolved. It is probable that both factors play a part in explaining the decrease in the heat of adsorption.

Support to the idea of active centers is also given by the fact that raising the temperature of a metal results in a decreased activity for adsorption and catalysis; this is explained as due to sintering of the surface, resulting in a decrease in the number of unsaturated atoms constituting the most active centers.

Kinetics on Nonuniform Surfaces. When a reaction takes place on a surface on which there is a variation of activity the over-all rate is, of course, the sum of the rates on the various types of site. Suppose for simplicity that there are only two kinds of site; these may be imagined to be atoms projecting from the surface and having high activity, and those in a flat part of the surface, having low activity. If the concentrations of the two kinds of site are c_1 and c_2 and the activation energies are E_1

[1] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 806 (1925).

[2] J. K. Roberts, *Proc. Roy. Soc.* (*London*), **A, 152**, 445 (1935).

and E_2, and if it is assumed that both types of site are sparsely covered, the rate of reaction involving a single reactant is clearly given by

$$v = c_g \frac{\mathbf{k}T}{\mathbf{h}} \frac{1}{F_g} (c_1 e^{-E_1/RT} + c_2 e^{-E_2/RT}) \tag{71}$$

The sites of type 1 have been supposed to be the more active, which means that E_1 is less than E_2. If c_1 and c_2 are of comparable magnitude this implies that the first term in Eq. (71) is more important than the second, or that the over-all activation energy is closer to the lower value E_1 than to the higher value E_2. This result is also to be expected if there is a variety of types of site, when the over-all rate is given by

$$v = c_g \frac{\mathbf{k}T}{\mathbf{h}} \frac{1}{F_g} \sum_i c_i e^{-E_i/RT}$$

Unless the distribution of the numbers of sites is a very unusual one, it is again to be expected that the reaction will occur mainly on the most active sites, and that the energy of activation of the over-all process will approach the value which corresponds to these sites. This has been shown to be the case by Constable[1] for a particular and probable distribution of numbers of sites.

This simple conclusion, that on a nonuniform surface the kinetics will approximately correspond to the occurrence of the reaction on the most active sites, may require modification in certain cases. In the above discussion it was assumed that all types of site were sparsely covered, and that the rate was controlled by interaction between gas molecules and sites. There is also the possibility, however, that the rate-controlling step is not the same on all types of site; thus, it might be interaction between gas molecule and site on some types, and desorption of the products on others. If this is the case the reaction will not show the simple kinetics that would be expected if the surface were uniform.

It may first be demonstrated that adsorption processes themselves may show complex behavior on nonuniform surfaces.[2] Suppose that a surface consists of two types of site, and that the activation energies for chemisorption are E_1 and E_2 and the heats of adsorption ϵ_1 and ϵ_2. If gas is gradually admitted to the system at sufficiently low temperatures, and E_1 is less than E_2, the sites of type 1 will be covered more rapidly than those of type 2, and may be completely covered before the latter are more

[1] F. H. Constable, *Proc. Roy. Soc.* (*London*), **A, 108,** 355 (1925); see also E. Cremer and G. M. Schwab, *Z. physik. Chem.*, **A, 144,** 243 (1929); G. M. Schwab, *ibid.*, **B, 5,** 406 (1929).

[2] *Cf.* H. S. Taylor and S. C. Liang, *J. Am. Chem. Soc.*, **69,** 1306 (1947).

than sparsely covered. The relationship between total coverage and gas pressure will clearly be more complex than corresponds to the Langmuir isotherm for the case. Further complexities will be revealed when the temperature is raised. Suppose that this occurs when sites of type 1 are practically fully covered and those of type 2 are sparsely covered. If $E_2 + \epsilon_2$ is larger than $E_1 + \epsilon_1$, the rate of desorption from sites of type 2 will be less than that from sites of type 1, so that raising the temperature may bring about complete coverage of sites of type 2 and sparse coverage of the other sites. It is clear that the temperature coefficient of the over-all rate of adsorption would be quite meaningless in such circumstances except in relation to the two different kinds of site.

If degree of adsorption may vary with pressure and temperature in a complex manner on nonuniform surfaces, the rates of surface reactions, which depend on surface coverage, will also do so. Suppose that E_1 is the activation energy for reaction to give *adsorbed* products on sites of type 1, and E_1' is the activation energy for desorption of products; similarly let E_2 and E_2' be the corresponding quantities for reaction on sites of type 2. If E_1 is greater than E_1' the rate-controlling step on sites of type 1 is the formation of the adsorbed products. If the product is more strongly adsorbed on sites of type 2, this will have the effect of reducing the activation energy for the formation of the adsorbed products (*i.e.*, E_2 is less than E_1), but at the same time the activation energy for desorption, E_2' will be raised. The net effect may be that the desorption controls the rate on the sites of type 2. It is thus possible for the rate of the reaction to be controlled by different processes on different types of surface sites. The surfaces upon which the desorption is the slow process will be more covered than the others, and there will clearly be no simple relationship between the rate and the gas pressure or temperature.

Some special cases of this type of behavior have been treated quantitatively by Halsey.[1] With certain simplifying assumptions, which are probably approached in certain cases, it was found that a reaction which obeys the law

$$v = \frac{ap}{1 + bp} \tag{73}$$

[*cf.* Eq. (27)] on a smooth surface, may obey

$$v = \left(\frac{ap}{1 + bp}\right)^{1/2} \tag{74}$$

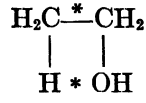
on a nonuniform one. This result is a particularly interesting one since it throws light on the fractional orders frequently found in surface reac-

[1] G. D. Halsey, *J. Chem. Phys.*, **17**, 758 (1949).

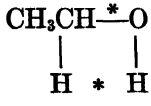
tions. The decomposition of ammonia on doubly-promoted iron catalysts is discussed by Halsey in terms of his treatment.

It should be emphasized that this type of kinetic complexity will not necessarily arise on a rough surface; in order for the rate to be controlled by different processes on the different types of sites the distribution of surface activities must be sufficiently broad. If this condition is not satisfied the reaction will occur most rapidly on the most active sites, as envisaged by Constable, and the rate will then vary with pressure and temperature in the manner found with a smooth surface. This is probably the case for most of the reactions discussed earlier in this chapter.

Variation in Interatomic Distances. Another idea that has been of great practical importance in connection with surface activity was that of Burk[1] that the adsorption of a molecule sometimes takes place on more than one site; this is often referred to as "multiple adsorption." It follows from this that adsorption must depend upon the lattice spacing at the surface, and this concept was developed by Balandin[2] in his so-called "multiplet hypothesis." Balandin postulated that catalysis frequently arises as the result of the action of more than one surface site, and considered that if two atoms become adsorbed on a single site a bond must be formed between them. For example, the dehydration of ethyl alcohol was envisaged as involving the attachment of two carbons to one site, and of a hydrogen and oxygen atom to a neighboring one, the situation being represented as follows, the asterisks denoting sites:



Since the hydrogen atoms of the methyl group and the oxygen atom are attached to the same site, there is a tendency for them to unite, so that the splitting off of water is facilitated by the catalyst. In the dehydrogenation of alcohol, on the other hand, the adsorption would be as follows



so that the splitting off of a hydrogen molecule would occur.

Balandin discussed the dehydrogenation of hydroaromatic compounds from the same point of view, the rings being adsorbed upon the octahedral faces, as represented in Fig. 21. The surface atoms *a*, *b*, and *c* are supposed to cause extension of the carbon-carbon distances, while the

[1] R. E. Burk, *J. Phys. Chem.*, **30**, 1134 (1926).

[2] A. A. Balandin, *Z. physik. Chem.*, **B, 2**, 289 (1929); **B, 3**, 167 (1929).

atoms *d*, *e*, and *f* attract pairs of hydrogen atoms and aid their combination. This picture of what occurs on a catalytic surface is undoubtedly too simple, but it has proved valuable in leading to qualitative predictions of the right kind.

The general conclusion from this kind of catalyst model—that catalytic activity depends upon interatomic spacing—is an important one and has received confirmation from many sources. Sherman and Eyring[1] have calculated activation energies for the adsorption of hydrogen on a carbon surface and found them to be very sensitive to the carbon-carbon distance in the surface layer, a distance of 3.6 A being most favorable. It is of interest that this distance is considerably larger than the normal H-H

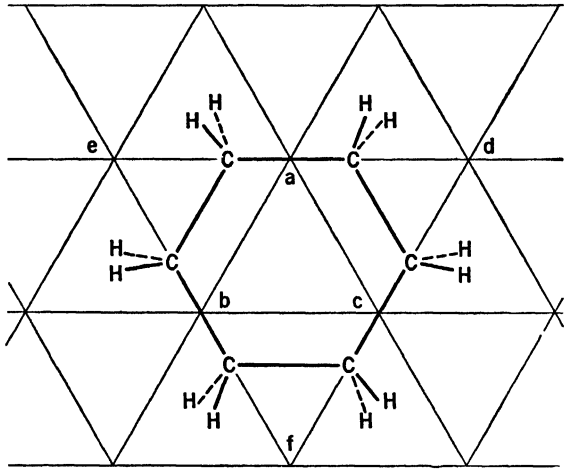


FIG. 21. Balandin's representation of the mechanism of the dehydrogenation of a hydroaromatic compound.

distance in molecular hydrogen. Similar results have been obtained from calculations of the activation energy for the adsorption of hydrogen on nickel.[2] Two different Ni-Ni distances are found in nickel, 2.49 A and 3.52 A, and calculations were made for both; the latter separation gave a much lower energy of activation, from which the conclusion can be drawn that adsorption will occur primarily on the (100) and (110) planes of nickel, since the (111) plane contains only the 2.49-A separation. However the calculated activation energies are much too high, the experimental values being approximately zero; the general conclusion that the

[1] A. Sherman and H. Eyring, *J. Am. Chem. Soc.*, **54**, 2661 (1932).

[2] G. Okamoto, J. Horiuti, and K. Hirota, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **29**, 223 (1936); *cf.* A. Sherman, C. E. Sun, and H. Eyring, *J. Chem. Phys.*, **3**, 49 (1934).

activation energies depend upon the spacing is nevertheless valid. The main reason that the calculations do not yield satisfactory results is that too simple a model was assumed for the surface.

The problem of the influence of the lattice spacing on the catalytic activity of a surface has been extensively investigated, especially by Beeck and his collaborators,[1] who have studied in particular the hydrogenation of ethylene on a nickel surface. The main conclusion is that the activity on the (110) plane is five times as great as that on a nickel film in which the crystals are oriented at random; the situation is, however, very much more complicated than the theoretical calculations would imply. Studies on the selective activities of different crystal faces have also been made by Gwathmey and his coworkers.[2]

Reactions in the solid state

It was mentioned in the preceding chapter that there are certain types of reactions in solution in which the slow step is the diffusion of the reactants towards one another, the actual chemical transformation being a more rapid step. With reactions occurring in the solid state this behavior becomes almost universal, owing to the low rates of diffusion in solids. Since a detailed discussion of diffusion processes[3] is beyond the scope of this book, only a very general and qualitative treatment of reactions in the solid state will be given here. Two types of processes will be considered: reactions between gases and solids and reactions between two solids.

Uptake of Gases by Solids.[4] When gases such as hydrogen, oxygen, and nitrogen are placed in contact with the majority of metals, with organic polymers, and with other types of solids, it is frequently found that penetration into the solid occurs. In some cases, as with the hydrogen-palladium system, purely physical adsorption occurs; in others, as with oxygen and copper, chemical reaction occurs, and a film of product (in this instance copper oxide) is formed and increases in thickness as the process continues. The kinetic laws applying to the uptake of gas take

[1] O. Beeck, A. Wheeler, and A. Smith, *Phys. Rev.*, **55**, 601 (1939); O. Beeck and A. Wheeler, *J. Chem. Phys.*, **7**, 631 (1939); A. E. Smith and O. Beeck, *Phys. Rev.*, **55**, 602 (1939); O. Beeck, A. E Smith, and A. Wheeler, *Proc. Roy. Soc. (London)*, **177**, 64 (1940). *Cf.* G. H. Twigg and E. K. Rideal, *Trans. Faraday Soc.*, **36**, 533 (1940)

[2] H. Leidheiser and A. T. Gwathmey, *J. Am. Chem. Soc.*, **70**, 1200, 1206 (1948).

[3] Diffusion has been treated using the theory of absolute reaction rates by H. Eyring in *J. Chem. Phys.*, **4**, 283 (1936); diffusion in the solid state by A. E. Stearn and H. Eyring, *J. Phys. Chem.*, **44**, 955 (1940). For a review, see S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," Chap. IX, McGraw-Hill Book Company, Inc., New York, 1941.

[4] *Cf.* R. M. Barrer, "Diffusion in and through Solids," Chaps. III, IV, Cambridge University Press, New York, 1941.

the same form whether or not chemical reaction occurs; the diffusion of the gas into the solid, on the other hand, obeys entirely different laws in the two cases.

If the diffusion process involves the gas in the molecular form, it can be shown[1] that the rate of uptake of the gas obeys the law

$$-\frac{dp}{dt} = \frac{ap}{1 + bp} \tag{75}$$

where p is the gas pressure and a and b are constants. At sufficiently low pressures, when bp is negligible compared with unity, the rate of uptake becomes approximately

$$-\frac{dp}{dt} = ap \tag{76}$$

i.e., the rate is proportional to the first power of the pressure. At high pressures, when bp is large compared with unity, the rate law becomes

$$-\frac{dp}{dt} = \frac{a}{b} \tag{77}$$

so that the rate is independent of the pressure. The physical significance of this is that the surface is almost completely covered by adsorbed molecules, the diffusion of which into the solid is rate controlling. Since for complete surface coverage the surface concentration is independent of the pressure, the rate is also pressure-independent.

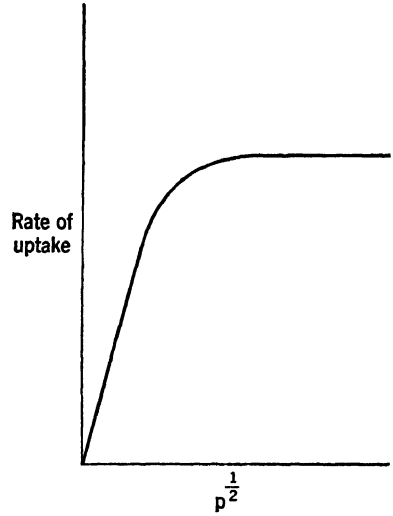


FIG. 22. The rate of uptake of oxygen by nickel as a function of the square root of the pressure.

A more common case is found when the molecule is dissociated on adsorption and diffuses in the atomic form. The general rate law then becomes

$$-\frac{dp}{dt} = \frac{ap^{\frac{1}{2}}}{1 + bp^{\frac{1}{2}}} \tag{78}$$

The rate is now proportional to the square root of the pressure at low pressures and becomes independent of the pressure at sufficiently high pressures; this is again due to the formation of an almost covered surface. An example of this type of behavior is to be found in the nickel-oxygen

[1] R. M. Barrer, *Phil. Mag*, **28**, 353 (1939); K. J. Laidler, *Bull. soc. chim. France*, **D, 16**, 171 (1949).

system;[1] the rate of uptake is plotted against the square root of the pressure in Fig. 22. The curve is seen to be linear at low pressures and to show pressure independence at high pressures. This type of behavior is very common when chemical reaction occurs, and most of the investigations on the oxidation of metals have been carried out in the region corresponding to pressure independence of the rate.

The manner in which diffusion into the solid occurs, in the case that chemical reaction occurs, is less well understood. With the oxidation of metals it is frequently found that the thickness x of the oxide film formed is related to the time t by the parabolic law

$$x^2 = kt \tag{79}$$

where k is a constant. Other laws have also been found under certain conditions. Various deductions of this law have been given,[2] using the laws of diffusion, and in particular Mott[3] has obtained explicit expressions for the constant k on the basis of various diffusion mechanisms.

Reactions between Two Solids. In general, the rate of reaction between two solid phases is equal to the rate of interdiffusion of the solids; an example is the formation of silver iodide when solid silver and solid iodine are placed together. The kinetics of such reactions have been extensively studied; the papers of Wagner[4] and Jost's book[5] should be consulted for further details.

PROBLEMS

1. Making use of the facts given on page 55 for the decomposition of ammonia on platinum, calculate the rate constant.

2. A first-order surface reaction is proceeding with a velocity v moles liter^{-1} sec^{-1} and a rate constant k sec^{-1}. What will be the rate and the rate constant if (*a*) the surface area is increased tenfold, (*b*) the gas volume is increased tenfold, (*c*) the area and the volume are both increased tenfold?

If the reaction occurs with rate v and rate constant k on the surface of a spherical vessel of radius r, what will be the rate and rate constant in a similar vessel of radius $10r$?

Define a new rate constant k' which, unlike k, is independent of the gas volume V and the area S of the catalyst surface.

3. How far are the conclusions of problem 2 valid for (*a*) a zero-order reaction, (*b*) a second-order reaction?

[1] C. Smithels and C. E. Ransley, *Proc. Roy. Soc.* (*London*), **A, 157,** 292 (1936).

[2] G. Tammann, *Nachr. Ges. Wiss. Gottingen, Math.-physik. Klasse,* 225 (1919); N. B. Pilling and R. E. Bedworth, *J. Inst. Metals,* **29,** 529 (1925).

[3] N. F. Mott, *Trans. Faraday Soc.,* **35,** 1175 (1939); **36,** 472 (1940); **43,** 429 (1947).

[4] See, for example, C. Wagner, *ibid.,* **34,** 851 (1938).

[5] W. Jost, "Diffusion und Chemikal Reaktionen in festen Stoffen," T. Steinkopff, Dresden and Leipzig, 1937.

4. Obtain an expression, in terms of partition functions, for the rate of a first-order atomic recombination on a smooth surface.[1]

5. The activation energy for the desorption of carbon monoxide from platinum is given[2] as 32.0 kcal at 600°C. The rate may be expressed as

$$v = c_a \frac{\mathbf{k}T}{\mathbf{h}} \frac{f_\ddagger}{f_a} e^{-E_0/RT}$$

where c_a, taken as 10^{15} molecules per square centimeter, is the number of adsorbed molecules per square centimeter, and $f_\ddagger$ and f_a are the partition functions for activated and adsorbed molecules, respectively. These partition functions may be assumed to be equal to one another.

Calculate E_0, the activation energy at 0°K, and then calculate the rate of desorption at 600°K, in molecules per square centimeter per second.

6. Hydrogen iodide decomposes on gold according to a zero-order law and with an activation energy of 25.0 kcal at 1000°K.[3] The mechanism required to account for the order leads to an equation identical in form with that of the preceding problem. Calculate the activation energy at 0°K and the rate at 1000°K.

***7.** Hydrogen iodide decomposes on platinum, the reaction at 826°K following a first-order law and having an activation energy of 14.0 kcal. The rate is given by Eq. (66). Calculate the activation energy at 0°K. Assuming that the number of sites is 10^{15} per square centimeter, calculate the rate of the reaction corresponding to 1 liter of gas at 1 atm pressure and a platinum surface of 1 sq. cm. The interatomic distance in hydrogen iodide is 1.604 A; the vibrational partition function may be taken as unity.

***8.** The rate of the reaction between carbon monoxide and oxygen on platinum is found under certain circumstances to be directly proportional to the oxygen pressure and inversely proportional to the carbon monoxide pressure.[4] Derive a rate equation, in terms of partition functions, which is consistent with this fact. If the activation energy is 33.3 kcal at 600°K, calculate the value at 0°K. Calculate the rate of reaction at 600°K as a function of the concentrations of oxygen and carbon monoxide (expressed in molecules per cubic centimeter) and corresponding to a volume of 1 liter and a catalyst surface area of 1 sq cm. The interatomic distances in O_2 and CO are 1.208 and 1.128 A, respectively; the vibrational partition functions may be taken as unity.

[1] *Cf.* K. J. Laidler, *J. Phys. & Colloid Chem.*, **53**, 712 (1949); K. E. Shuler and K. J. Laidler, *J. Chem. Phys.*, **17**, 1212 (1949).

[2] I. Langmuir, *Trans. Faraday Soc.*, **17**, 641 (1922).

[3] C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 806 (1925).

[4] Langmuir, *op. cit.*, 621.

CHAPTER 7

COMPLEX REACTIONS

A great many chemical processes are found, on detailed study, not to occur by a simple rearrangement of the atoms in a single stage, but to take place in a number of well-defined steps. Various kinds of evidence are available to support this conclusion in individual instances, and the present chapter is concerned with a discussion of the more significant points.

The most obvious indication of complexity is found when the kinetic law is inconsistent with the stoichiometric equation for the reaction. An example of this is the reaction between nitric oxide and hydrogen, the process being represented by the equation

$$2NO + 2H_2 = N_2 + 2H_2O$$

According to the stoichiometry this reaction might be expected to be of the fourth order, with the rate proportional to the squares of the concentrations of both nitric oxide and hydrogen. In fact, in the gas phase the rate, as has been seen in Chap. 2, is proportional to the square of the nitric oxide concentration but only to the first power of the hydrogen concentration,

$$v = k[NO]^2[H_2] \tag{1}$$

This result may be interpreted as indicating that the initial step in the reaction is actually

$$2NO + H_2 \rightarrow N_2 + H_2O_2$$

and that this process is followed by

$$H_2O_2 + H_2 \rightarrow 2H_2O$$

If it is assumed that the second reaction is rapid compared with the first, the rate of the first controls the rate and therefore gives rise to the kinetic behavior observed.

Another example of this type of complexity is found in the reaction between hydrogen and iodine monochloride,

$$2ICl + H_2 = I_2 + 2HCl$$

Instead of being of the third order, as the equation might indicate, this

reaction obeys the law[1]

$$v = k[\mathrm{ICl}][\mathrm{H_2}] \tag{2}$$

i.e., is of the second order. The mechanism suggested is that there is an initial slow process

$$\mathrm{ICl} + \mathrm{H_2} \rightarrow \mathrm{HI} + \mathrm{HCl}$$

which is rate determining, and that this is followed by the rapid process

$$\mathrm{HI} + \mathrm{ICl} \rightarrow \mathrm{HCl} + \mathrm{I_2}$$

It is because of this type of complexity that it is very frequently found that the order of a reaction is less than that which corresponds directly to the stoichiometric equation. It was seen in Chap. 4 that a reaction between three molecules is very much less probable than one between two, on account of the greater loss of entropy in the activated state; collisions between four molecules are so improbable that it is unlikely that there are any elementary reactions having a molecularity of four or more. A reaction whose stoichiometric equation involves more than three molecules usually may proceed much more effectively via a reaction of lower molecularity followed by subsequent steps.

Chain Reactions. Another type of complexity in chemical reactions consists in the formation of free atoms and radicals as intermediates. These reactions show many features which are different from those discussed above and may be recognized on the basis of showing one of more of these characteristics.

When reactions occur by a series of processes involving atoms or radicals, it is sometimes, but by no means always, found that the kinetic laws are unusually complex. A well-known example is the reaction between hydrogen and bromine, which does not obey the simple law

$$\frac{d[\mathrm{HBr}]}{dt} = k[\mathrm{H_2}][\mathrm{Br_2}] \tag{3}$$

analogous to that obeyed in the hydrogen-iodine reaction but is represented by the equation

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + \dfrac{[\mathrm{HBr}]}{k'[\mathrm{Br_2}]}} \tag{4}$$

where k and k' are constants at a given temperature. A significant feature of this law is the occurrence, in the denominator, of the concentration of the product hydrogen bromide, implying that this substance acts as an inhibitor of the reaction. It will be seen later that the existence of such

[1] W. D. Bonner, W. L. Gore, and D. M. Yost, *J. Am. Chem. Soc.*, **57**, 2723 (1935).

inhibition is unequivocal evidence in favor of an atomic or free-radical mechanism.

The reaction scheme proposed[1] to explain the kinetics obtained was

$$\begin{aligned} Br_2 &\rightarrow 2Br \\ Br + H_2 &\rightarrow HBr + H \\ H + Br_2 &\rightarrow HBr + Br \\ H + HBr &\rightarrow H_2 + Br \\ 2Br &\rightarrow Br_2 \end{aligned}$$

The way in which it interprets the kinetic results will be considered later. It is seen that hydrogen and bromine atoms are postulated as intermediates and that, since in all reactions except the last they regenerate one another, one atom of bromine may be responsible for the formation of a number of molecules of hydrogen bromide. On account of this important feature, reactions of this type are spoken of as "chain reactions."

It should be emphasized that chain reactions do not always follow complex kinetic laws: simple laws are obeyed, for example, by organic decompositions which are found to be complex on the basis of other evidence to be considered later. A particular example is the decomposition of ethane, which follows first-order kinetics.

A second piece of evidence that certain reactions proceed by a chain mechanism comes from the results of photochemical investigations, for it is found that in many cases the absorption of one quantum of light is followed by the reaction of a large number of molecules. Since on theoretical grounds a molecule is not likely to absorb more than one quantum at a time, it may be inferred that the initial act of absorption may be followed by a chain of processes which may, under favorable circumstances, bring about a considerable amount of reaction.

The original suggestion that a chemical reaction, particularly one initiated by light, may proceed by a chain process was made in 1913 by Bodenstein,[2] and a new phase in the history of kinetics may be said to have started at that time. In 1918 Nernst[3] proposed a specific scheme for the photochemical union of hydrogen and chlorine. The chains were initiated by the light absorption which dissociated chlorine molecules into atoms,

$$Cl_2 + h\nu \rightarrow 2Cl$$

each chlorine atom produced could then attack a hydrogen molecule,

$$Cl + H_2 \rightarrow HCl + H$$

[1] J. A. Christiansen, *Kgl. Danske Videnskab. Selskab Mat.-fys. Medd.*, **1**, 14 (1919); K. F. Herzfeld, *Z. Elektrochem.*, **25**, 301 (1919); *Ann. Physik*, **59**, 635 (1919); M. Polanyi, *Z. Elektrochem.*, **26**, 50 (1920).

[2] M. Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913).

[3] W. Nernst, *Z. Elektrochem.* **24**, 335 (1918).

and the resultant hydrogen atom could react with a chlorine molecule,

$$H + Cl_2 \rightarrow HCl + Cl$$

In the two last reactions two molecules of hydrogen chloride have been produced by a single chlorine atom, which has been regenerated; the process can therefore continue. If it were not for certain chain-ending processes such as $2Cl \rightarrow Cl_2$, $2H \rightarrow H_2$, and $H + Cl \rightarrow HCl$, this process could continue indefinitely. Although Nernst's general idea was correct, it is now known that his reaction scheme requires modification; this is discussed in detail later.

That reaction chains of a similar type occur in thermal reactions is evident from the strong similarity which frequently exists between thermal and photochemical reactions. With both the hydrogen-bromine and hydrogen-chlorine reactions, the rates were found to depend in a complicated fashion on the concentrations of hydrogen, halogen, and oxygen (if present) the laws being very similar in the two cases. This suggests that the main difference between the processes lies in the initial formation of the halogen atoms, the subsequent radical reactions being the same in both cases.

Various other kinds of evidence have been brought forward in favor of the participation of free-radical reactions in chemical processes. The presence of radicals in reaction systems has been detected by various means. Thus the line spectra of atoms and the band spectra of radicals have been observed in reaction mixtures, and the existence of free organic radicals in organic reactions has been proved by causing them to undergo characteristic reactions, *e.g.*, with metallic mirrors. Methods of destroying radicals in reacting systems have also been used, the result being a decrease in rate if free-radical processes are important. These and other methods of studying free-radical reactions will be discussed in detail in the present chapter.

Steady-state Treatment. The theoretical treatment of the elementary reactions which play a part in complex mechanisms follows the same lines that have been shown in the previous chapters. In order to express the over-all rate of a complex reaction in terms of the individual specific rates, a special treatment is required and will here be described.

A rigorous treatment of this problem would involve writing down the appropriate differential equations for the individual reactions, eliminating the concentrations of the intermediate atoms and free radicals, and solving the equations so obtained. However such a procedure can seldom be followed, since the resulting differential equation is always extremely complicated. As an example to illustrate this may be taken the case of a unimolecular process, which according to the Lindemann theory is formulated as occurring in two distinct stages:

$$A + A \rightleftharpoons A^* + A$$

and

$$A^* \rightarrow \text{products}$$

Denoting the specific rates by k_1, k_{-1}, and k_2, the differential equations for the rates of formation of A^* and of disappearance of A are

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^*] \tag{5}$$

and

$$-\frac{d[A]}{dt} = k_1[A]^2 - k_{-1}[A^*][A] \tag{6}$$

These equations involve $[A]$,$[A^*]$, and t and can therefore be reduced to one equation in two of the variables. The procedure will be to eliminate $[A^*]$.

From Eq. (6),

$$[A^*] = \frac{k_1[A]^2 + d[A]/dt}{k_{-1}[A]} \tag{7}$$

and differentiation gives

$$\frac{d[A^*]}{dt} = \frac{k_1}{k_{-1}}\frac{d[A]}{dt} + \frac{1}{k_{-1}[A]}\frac{d^2[A]}{dt^2} - \frac{1}{k_{-1}[A]^2}\left(\frac{d[A]}{dt}\right)^2 \tag{8}$$

Substitution of Eqs. (7) and (8) into (5) gives, after some reduction,

$$[A]\frac{d^2[A]}{dt^2} + (k_1[A]^2 + k_{-1}[A]^2 + k_2[A])\frac{d[A]}{dt} - \left(\frac{d[A]}{dt}\right)^2 + k_1k_2[A]^3 = 0 \tag{9}$$

which is the required differential equation in $[A]$ and t. This equation cannot be solved except by making certain approximations,[1] so that even in this extremely simple case of two consecutive reactions, the resulting equations are of considerable complexity. Reactions involving more than two steps lead to much greater difficulty.

As was seen on page 78, the generally accepted procedure in dealing with unimolecular reactions is to introduce the approximation that

$$\frac{d[A^*]}{dt} = 0 \tag{10}$$

Introduction of this into Eq. (5) leads at once to an expression for $[A^*]$, which can be inserted into Eq. (6) to give the rate expression. The justification for this procedure is that the value of $[A^*]$ is always small in comparison with $[A]$ (since A^* is an excited molecule); consequently its rate of change is small, except perhaps at the very beginning of reaction when its steady concentration is being built up.

[1] R. H. Fowler, "Statistical Mechanics," p. 711, Cambridge University Press, New York, 1936.

Precisely the same procedure is applied to complex reactions and is justified in the same way. Intermediates such as atoms and free radicals, the concentrations of which are necessarily low, are assumed to have a constant concentration during the course of reaction. In this way simple expressions for their concentrations may be obtained, and hence an equation for the over-all rate can be derived. The first application of this treatment to a complex reaction was made by Christiansen,[1] Herzfeld,[2] and Polanyi,[3] in 1919, the reaction treated being the hydrogen-bromine reaction. The steady-state treatment has been criticized by Skrabal,[4] but his objections have been answered by Bodenstein.[5]

The treatment of the hydrogen-bromine reaction proceeds as follows: The reaction scheme proposed is

(1) $\mathrm{Br_2} \rightarrow 2\mathrm{Br}$

(2) $\mathrm{Br} + \mathrm{H_2} \rightarrow \mathrm{HBr} + \mathrm{H}$

(3) $\mathrm{H} + \mathrm{Br_2} \rightarrow \mathrm{HBr} + \mathrm{Br}$

(4) $\mathrm{H} + \mathrm{HBr} \rightarrow \mathrm{H_2} + \mathrm{Br}$

(5) $\mathrm{Br} + \mathrm{Br} \rightarrow \mathrm{Br_2}$

the chain carriers, *i.e.*, the species participating in the reaction chain, being the hydrogen and bromine atoms. The steady-state equations for these atoms are, in terms of the specific rates k_1 to k_5 for the five processes listed above,

$$\frac{d[\mathrm{Br}]}{dt} = 2k_1[\mathrm{Br_2}] - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{H}][\mathrm{HBr}] - 2k_5[\mathrm{Br}]^2 = 0 \quad (11)$$

and

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] = 0 \quad (12)$$

These are simultaneous equations in [H] and [Br] and can be solved to give expressions for these concentrations. Addition of Eq. (11) to (12) gives rise to

$$[\mathrm{Br}] = \left(\frac{k_1}{k_5}\right)^{1/2}[\mathrm{Br_2}]^{1/2} \quad (13)$$

and insertion of this into either (11) or (12) gives

$$[\mathrm{H}] = \frac{k_2(k_1/k_5)^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]} \quad (14)$$

[1] Christiansen, *loc. cit.*
[2] K. F. Herzfeld, *loc. cit.*
[3] Polanyi, *loc. cit.*
[4] A. Skrabal, *Ann. Physik*, **82**, 138 (1927).
[5] M. Bodenstein, *ibid.*

The equation for the rate of formation of HBr is

$$\frac{d[\mathrm{HBr}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] - k_4[\mathrm{H}][\mathrm{HBr}] \tag{15}$$

and introduction of the expressions for [H] and [Br] gives, after some rearrangement,

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{1/2}[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + \dfrac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \tag{16}$$

This equation is seen to have the same form as the one obtained experimentally [Eq. (4)], a fact which gives considerable support to the mechanism proposed. Further evidence comes from studies of the rates of the individual processes and will be considered in the next chapter.

Detection and estimation of atoms and radicals in reaction systems

In only a few cases can much information concerning the specific rates of elementary processes be obtained from the kinetics of the over-all processes. The hydrogen-bromine reaction is, in fact, one of the few reactions for which this can be done; as will be seen in detail in the following chapter, the values of the five constants k_1 to k_5 can be determined by comparing the above expression with the empirical expression for the rate and making use of certain additional information. In almost all other cases of thermal reactions, however, the situation is too complicated to allow an empirical kinetic expression to be deduced on the basis of an assumed mechanism, so that other methods have to be employed in order for the individual processes to be investigated. One procedure which gives some information of this type involves making detailed analyses of the reaction mixture at various stages, but unfortunately chemical methods of analysis are usually difficult to carry out. In any case these methods are applicable only to stable molecules and do not give much information as to the detailed mechanism of the process. Methods of detecting and estimating the concentrations of the intermediate atoms and free radicals are therefore required, and a number of different systems have been developed. These include (1) spectroscopic methods, (2) the removal of metallic mirrors, a procedure particularly applicable to organic free radicals, (3) the para-ortho hydrogen conversion, (4) methods involving gas-phase reactions of the radicals, (5) methods using the mass spectrograph. These procedures will now be discussed in some detail.

Spectroscopic Methods. Spectroscopic methods of detecting and estimating atoms and radicals include the study of both absorption and emission spectra and depend on the fact that the wave lengths absorbed or

emitted are characteristic of each compound; moreover the intensities of the lines or bands can give a measure of the concentrations of the species present. Recently, absorption spectra in particular have been used in studies of this kind, and both the ultraviolet and infrared regions have been the subject of much investigation, the experimental techniques for the former being much easier. Emission spectra are especially useful when the reaction is accompanied by a flame (*cf.* Chap. 11) but give no indication of the concentrations of unexcited molecules or radicals. These methods have been applied particularly to atoms such as H and Cl and to radicals such as OH, CH, C_2, SO, and HCO; the spectra of more complicated radicals are usually too difficult to analyze satisfactorily owing to the overlapping of a large number of bands.

Indirect spectroscopic methods are also used occasionally, the general principle being the identification of reaction products which almost cer-

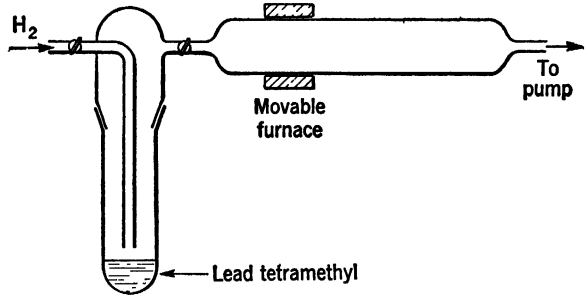


FIG. 23. Apparatus used by Paneth and Hofeditz for the detection of free organic radicals.

tainly arise from a particular atom or radical. For example, Gaydon[1] has shown that oxygen atoms can be detected by the introduction of nitric oxide into a reaction mixture, the result being the emission of a yellow-green radiation having a characteristic spectrum, which is ascribed to excited NO_2 produced in the reaction

$$O + NO \rightarrow NO_2^*$$

This method has been applied successfully to a number of oxidation systems, with significant results.

Removal of Mirrors. The technique for detecting free radicals by causing them to remove metallic mirrors deposited on surfaces is due to Paneth and Hofeditz,[2] whose apparatus is shown schematically in Fig. 23.

[1] A. G. Gaydon, *Proc. Roy. Soc.* (*London*), **A, 183,** 111 (1944); *Trans. Faraday Soc.*, **42,** 292 (1946); *cf.* W. H. Rodebush, *J. Phys. Chem.*, **41,** 283 (1937).

[2] F. Paneth and W. Hofeditz, *Ber.*, **B, 62,** 1335 (1929); *cf.* F. Paneth and W. Lautsch, *Ber.*, **B, 64,** 2702 (1931).

A stream of pure hydrogen was passed at a pressure of 1 to 2 mm through a cooled vessel in which it was saturated with lead tetramethyl, after which it was passed through a hard-glass tube one part of which was heated. The heating caused decomposition of the lead tetramethyl by the reaction

$$Pb(CH_3)_4 \rightarrow Pb + 4CH_3$$

and the lead was deposited as a mirror on the surface of the tube. It was then found that if the tube were heated upstream of the mirror instead of at the mirror, the mirror gradually disappeared, while a second mirror was deposited at the position of the second heating. This was interpreted as due to the fact that the free radicals produced in the hot tube reacted with the lead by the reverse of the reaction above. It was found that the phenomenon could not be explained as due to thermal effects causing sublimation and condensation of the mirror, since the effect was not obtained in the absence of lead tetramethyl in the hydrogen. Moreover, cooling of the tube between the position of heating and the mirror caused no change. It was found that mirror removal could be effected by heating the tube at distances up to 30 cm from the mirror, although the rate of removal was less the greater the distance. This is because the radicals have more chance to recombine as the distance becomes greater. Mirrors of zinc and antimony were also removed in the same manner.

The existence of the methyl radical in the gas phase in these experiments was shown by passing the gas over a zinc mirror and collecting the material formed; this was demonstrated by its melting point, boiling point, and other properties to be zinc dimethyl. The ethyl radical was identified in a similar manner.

Paneth's technique for the detection of free radicals by the removal of metallic mirrors was greatly simplified by Rice, Johnston, and Evering,[1] who used condensable gases as carriers in place of the hydrogen or helium used by Paneth; these gases could be frozen out with liquid air after they had passed over the mirror, and high-speed pumps were therefore rendered unnecessary. Water vapor, organic vapors, and carbon dioxide were employed, and as mirrors Rice and his coworkers showed that in addition to lead, zinc, and antimony, a wide variety of substances could be used. Examples are the alkali metals, mercury, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium.

Paneth and Hahnfeld[2] found that tellurium offered the advantage of giving results which were much more reproducible than those obtained with the other materials, and that this was because the tellurium mirrors are not affected by oxygen. In a comparison of the different kinds of mirrors

[1] F. O. Rice, W. R Johnston, and B. L. Evering, *J. Am. Chem. Soc.*, **54**, 3559 (1932).
[2] F. Paneth and K. Hahnfeld, *unpublished.*

Rice and Glasebrook[1] discovered specificities with respect to the radicals with which reaction occurs; thus tellurium, antimony, selenium, and arsenic are attacked by the methylene radical, while zinc, cadmium, bismuth, thallium, and lead are not, although they are attacked by alkyl radicals. The activity of lead mirrors was found to be lessened by heating, or by cooling to 0°C, the reason apparently being that adsorption of impurities takes place. The activity of antimony mirrors on the other hand is hardly affected by the temperature. Zinc sulfide screens have also been used to detect free radicals;[2] these glow when recombination occurs.

The Paneth-Rice technique has been modified by the use of radioactive materials. Leighton and Mortensen[3] used a lead mirror containing radium D, E, and F and followed the disappearance of the mirror by the loss of β-ray activity as measured by an electroscope. The volatile products were collected and detected by their β-ray activity. A similar procedure was employed by Burton, Ricci, and Davis,[4] who used a radium-D mirror.

In addition to organic free radicals, hydrogen atoms have been detected by the mirror-removal method. Pearson, Robinson, and Stoddart[5] found that atomic hydrogen removes arsenic, antimony, selenium, tellurium, germanium, and tin mirrors, but not lead. Burton[6] has made use of these facts to detect hydrogen atoms in photochemical processes; the reaction mixture was first passed over a lead mirror, which removes all the alkyl radicals, and then over an antimony mirror, which removes the hydrogen atoms.

With the object of identifying and estimating the free radicals present in various reaction systems, a considerable amount of work has been done on the products which are formed by the removal of mirrors. The early work of Paneth and Hofeditz has been referred to, and since that time Rice and his coworkers have identified the products using a variety of mirrors and reaction systems. Rice, Johnston, and Evering[7] have developed a technique for carrying out the analysis when the products are formed continuously and hence in larger concentrations. The radicals in the reaction system were brought into contact with a cooled surface on which mercury was condensed continuously, and the mercury alkyls were condensed in a liquid-air trap containing a saturated solution of mercuric

[1] F. O. Rice and A. L. Glasebrook, *J. Am. Chem. Soc.*, **55**, 4329 (1933); **56**, 2381, 2472 (1934).

[2] P. N. Kohanenko, *Acta Physicochim. U.R.S S.*, **9**, 93 (1938).

[3] P. A. Leighton and R. A. Mortensen, *J. Am Chem. Soc.*, **58**, 488 (1936).

[4] M. Burton, J. E. Ricci, and T. W. Davis, *ibid.*, **62**, 265 (1940).

[5] T. G. Pearson, P. L. Robinson, and E. M Stoddart, *Proc. Roy. Soc.* (*London*), **A, 142**, 275 (1933).

[6] M. Burton, *J. Am. Chem. Soc.*, **58**, 692, 1645 (1936).

[7] Rice, Johnston, and Evering, *loc. cit.*

bromide. In this way alkyl mercuric bromides were formed and could be separated from the mercuric bromide by sublimation. The various alkyl mercuric bromides were then separated from one another by fractional sublimation. In this way it was shown that methyl radicals are present in organic decompositions, but that ethyl radicals are not, these being too unstable to exist at the temperatures involved.

Reaction with Nitric Oxide. Another method which has been widely employed for the detection of free radicals in reaction systems involves the use of nitric oxide. It was found by Staveley and Hinshelwood[1] that small amounts of this substance would in many cases bring about considerable reductions in the rates of organic reactions, the relationship between rate and nitric oxide concentration frequently being of the type shown in Fig. 24. The effect of the nitric oxide is to react with, and in some manner destroy, free radicals in the systems, a conclusion that is supported by the fact that extremely small amounts of nitric oxide (1 to 2 mm) are usually sufficient to bring about inhibition to the limiting rate.

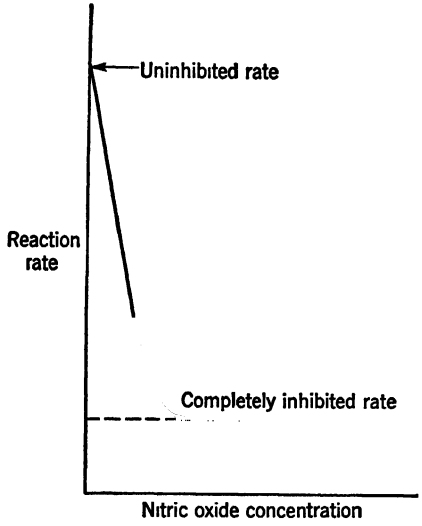


FIG. 24. Typical curve showing the influence of nitric oxide on the rate of an organic reaction.

From the fact that no further reduction in rate is found after a few millimeters of nitric oxide have been added it is natural to conclude that all the radicals have been removed. Hinshelwood and his coworkers have, in fact, maintained this view. According to them the completely inhibited reaction is one in which free radicals play no part, *i.e.*, a molecular reaction. This conclusion is supported by a comparison[2] between the inhibition of the propionaldehyde and diethyl ether decompositions by nitric oxide and by propylene; it was found that the limiting values to which the rates were reduced were the same, suggesting that the radicals are completely removed by both inhibitors.

On the other hand, some recent work[3] on the ethane and acetaldehyde decompositions, using mixtures of normal and deuterated compounds, has

[1] L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 154,** 335 (1936); *J. Chem. Soc.*, 1568 (1937); L. A. K. Staveley, *Proc. Roy. Soc.* (*London*) **A, 162,** 557 (1937).

[2] J. R. E. Smith and C. N. Hinshelwood, *ibid.*, **A, 180,** 237 (1942).

[3] L. A. Wall and W. J. Moore, *J. Phys. and Colloid Chem.*, to be published.

indicated that appreciable free-radical reaction is still occurring under the conditions of complete inhibition. Some of the results of this work do indicate that a molecular mechanism occurs in these two reactions, but apparently it does not correspond to the entire inhibited reaction.

Other Gas-phase Reactions. Rice and Polly[1] found that methyl and ethyl nitrites have an effect similar to that of nitric oxide in the removal of radicals. There appears to be some reaction between the nitrite and the free radical, but in addition there is reaction involving the nitric oxide formed by the thermal decomposition of the nitrite. Rice and Polly also used propylene in the same way, while Eshevskaya[2] used isobutene, butadiene, isoprene, and other unsaturated substances, which presumably act by forming addition compounds with the radicals.

Para-Ortho Hydrogen Conversion. It was seen in Chapter 2 that free hydrogen atoms bring about the conversion of *p*- into *o*-hydrogen. This reaction has been used to determine the concentration of hydrogen atoms in a given reaction mixture; the procedure is simply to study the rate of the conversion when a known amount of the *p*-hydrogen is introduced. The method was employed by Farkas and Sachsse[3] to determine the concentration of hydrogen atoms produced from hydrogen molecules by excited (^3P) mercury atoms. There are several limitations to the method; *e.g.*, difficulties arise if paramagnetic substances are present, since these catalyze the conversion and hence would give too high a value for the hydrogen-atom concentration. Since free radicals are themselves paramagnetic, the method cannot be used with great certainty when they are present. However Patat and Sachsse[4] have used the method for the determination of the hydrogen-atom concentration during the decomposition of ethane, assuming that the organic free radicals have a negligible effect compared with that of the hydrogen atoms. This method gives an upper limit to the hydrogen-atom concentration and was used to check a mechanism proposed for the reaction. The value obtained, although an upper limit, was found to be 1,000 times smaller than that predicted.

The conversion of *p*- to *o*-hydrogen has similarly been used to measure the concentration of deuterium atoms,[5] and the technique has been extended[6] to a study of the rate of reaction between deuterium atoms and methane, by causing them to react with *o*-deuterium at the same time.

[1] F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

[2] M. P. Eshevskaya, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 2162 (1939).

[3] L. Farkas and H Sachsse, *Z. physik. Chem.*, **B, 27**, 111 (1935).

[4] F. Patat and H. Sachsse, *Z. Elektrochem*, **41**, 493 (1935); *Nachr. Ges. Wiss. Gottingen*, **III, 1**, 41 (1935); H. Sachsse, *Z. physik. Chem.*, **B, 31**, 79, 87 (1935); F. Patat, *ibid.*, **B, 32**, 274, 294 (1936).

[5] A. Farkas, L. Farkas, and P. Harteck, *Proc. Roy. Soc.* (*London*), **A, 144**, 481 (1934); A. Farkas and L. Farkas, *ibid.*, **A, 152**, 124 (1935).

[6] A. Farkas and H. W. Melville, *ibid.*, **A, 157**, 625 (1936).

The exchange reactions $H + D_2 \rightarrow HD + D$ and $D + H_2 \rightarrow HD + H$ have been used in a similar manner for measuring H and D concentrations.[1]

Use of the Mass Spectrometer. The mass spectrometer has recently been used, particularly by Eltenton,[2] for detecting and estimating the concentrations of organic free radicals. The method is to introduce the reaction mixture into the ionization chamber of the instrument and to bombard it with electrons of about 10 volts energy. This energy is sufficient to convert the radicals into positive ions but not sufficient to produce fresh radicals by dissociating molecules. This method has been used to distinguish methyl, methylene, and ethyl radicals in organic decompositions. An alternative procedure[3] involves bombarding the radicals with slow electrons of 1 to 3 volts energy. These methods have not yet been used very extensively but are undoubtedly of the greatest value.

Other Physical Methods. Other physical properties that have been measured in a study of free radicals in reacting systems include (1) thermal conductivity, (2) heats of recombination of radicals at surfaces, and (3) diffusion. Since these methods are very limited in their applicability and have not been used to any extent, they will not be discussed here.

Production of free atoms and radicals

In the previous sections have been described some of the more important methods for detecting and estimating atoms and radicals in reaction systems. These methods give valuable information as to reaction mechanisms but in the majority of cases must be supplemented by more direct studies on the elementary reactions which constitute stages in the over-all processes. In order to make such studies, it is important to be able to cause elementary processes to occur to the exclusion of other reactions. It is difficult to achieve this, since side reactions nearly always occur; in some cases data have been obtained, but there is often some uncertainty in their interpretation.

If such a procedure is employed, and it is known that a certain reaction is occurring to the exclusion of all others, the specific rate can be determined, provided that one knows the initial concentrations of the reactants and either the rate of disappearance of a reactant or the rate of appearance of a product. For the determination of the activation energy the rate should also be known at more than one temperature; however in many cases the activation energy is obtained from the rate at only one temperature by making an assumption as to the magnitude of the frequency factor.

Since an important part of an investigation of this type is the production

[1] N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, **5**, 203 (1937).
[2] G. C. Eltenton, *ibid.*, **10**, 403 (1942).
[3] G. E. Tuxen. *Z. physik*, **103**, 463 (1936).

of the necessary atoms or free radicals to undergo reaction, the rest of this section will be devoted to a consideration of methods for this production.[1] The methods may be classified as (1) thermal, (2) photochemical, (3) radiochemical, and (4) electrical.

Thermal Methods. Appreciable concentrations of atoms and free radicals may, particularly at elevated temperatures, exist in thermal equilibrium with molecules which may therefore be introduced directly into a reaction system. The method is not, however, used very frequently, since at the temperatures necessary to produce an appreciable concentration of the active substance, the situation is usually complicated by the occurrence of side reactions.

The method is best used with certain molecules which are readily dissociated, such as iodine. Sodium is also appreciably dissociated, even at room temperature, and the reactions of atomic sodium can be investigated simply using sodium vapor; the work of Polanyi and his collaborators on certain inorganic reactions involving atomic sodium will be considered on page 226.

A more useful method of producing atoms or radicals by thermal methods involves passing the substance producing them through a heated tube, this procedure differing from the previous one in that the reacting substances, on reaching the reaction system, are no longer in equilibrium with the substance from which they are produced. This method is more commonly employed; thus in the study of the thermal decomposition of ethane (*cf.* p. 248) it is found that methyl radicals are produced initially from the ethane and react with ethane molecules. The rate of this reaction has been measured by the introduction of free radicals using the heated-tube method.

Since substances which decompose thermally to give free radicals frequently increase the rates of reactions, they are known as sensitizers. Certain metal alkyls decompose thermally to give organic free radicals and therefore act as sensitizers in many organic reactions. Sensitized reactions of this type were first investigated by Taylor and Jones,[2] who studied the influence of mercury and lead methyls on the polymerization of ethylene in the presence of hydrogen. The metal alkyls decompose into alkyl radicals and the metal, *e.g.*,

$$Hg(CH_3)_2 \rightarrow Hg + 2CH_3$$

and the radicals react with ethylene to form addition products, which may

[1] For further details see E. W. R. Steacie and D. J. Le Roy, *Chem. Revs.*, **31**, 227 (1942); E. W. R. Steacie, "Atomic and Free Radical Reactions," Chap. II, Reinhold Publishing Corporation, New York, 1946; "Free Radical Mechanisms," Chap. II, *ibid.*

[2] H. S. Taylor and W. H. Jones, *J. Am. Chem. Soc.*, **52**, 1111 (1930).

polymerize further:

$$CH_3 + C_2H_4 \rightarrow C_3H_7$$

In addition to the metal alkyls, ethylene oxide and azomethane have also been used as sensitizers. With sensitizers of this type both methods, *i.e.*, equilibrium and nonequilibrium, have been used. When these methods are employed, it is usual to determine the reaction rates by studying the rate of formation of the products obtained.

Active species are also produced thermally in reaction systems by the use of heated filaments, a method first used by Langmuir,[1] who worked mainly with hydrogen and oxygen. By measuring the heat loss from such filaments, he demonstrated the formation of the atoms; at sufficiently low pressures these were able to reach the walls of the vessel and in the case of hydrogen atoms, for example, could be detected by their reducing action on metallic oxides and in other ways. The method was applied by Storch[2] to the production of methyl radicals from methane and has been used by Belchetz and Rideal[3] in the study of various kinds of elementary reactions. The gas was streamed at high velocity and low pressure over a heated platinum or carbon filament, and the radicals formed were caused to come into contact with a target which was cooled by water. Mirrors were deposited on the target, and their removal constituted evidence of the participation of radicals in the reactions. From the study of the formation of the radicals, the rates and activation energies of the radical-forming processes were inferred; however the processes considered in this work are almost certainly not homogeneous ones but are catalyzed on the surface.

Photolytic Methods. In a large number of investigations, reaction systems have been photolyzed with the production of atoms and free radicals, which undergo subsequent reactions. If the molecules absorbing the radiation take part themselves in the main reaction, the reaction is said to be a photochemical one. In other cases the absorbing molecules do not themselves participate directly in the reaction but pass on their energy to other molecules that do; the absorbing substance is then said to be a photosensitizer. The more important features associated with the absorption of radiation, usually known as the primary photochemical process, will now be discussed briefly.[4]

[1] I. Langmuir, *ibid.*, **34**, 1310 (1912); **37**, 417 (1915); A. E. Freeman, *ibid.*, **35**, 927 (1913); I. Langmuir and G. M. J. Mackay, *ibid.*, **36**, 1708 (1914).

[2] H. H. Storch, *ibid.*, **54**, 4188 (1932).

[3] L. Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934); L. Belchetz and E. K. Rideal, *J. Am. Chem. Soc.*, **57**, 1168, 2466 (1935). See in addition E. L. Tollefson and D. J. Le Roy, *J. Chem. Phys.*, **11**, 1057 (1948); A. J. B. Robertson, *Proc. Roy. Soc.* (*London*), **A, 199**, 394 (1949).

[4] For detailed treatments, see W. A. Noyes and P. A. Leighton, "The Photo-

Dissociation of a molecule into atoms and free radicals can be effected only by radiation which is absorbed by the system; all the radiation which is absorbed is, however, by no means able to cause dissociation. It is found that there are certain ranges of wave length which correspond to absorption and that certain narrower ranges within these correspond to the formation of atoms and free radicals.

Radiation is absorbed by a molecule in quanta or photons of energy $\mathbf{h}\nu$, where **h** is Planck's constant and ν is the frequency. If it were necessary for n quanta to be absorbed by a molecule in order for reaction to be initiated, it can easily be shown that the rate of the resulting reaction would be proportional to the nth power of the intensity of the radiation. In fact, it is found experimentally that the rate is never proportional to more than the first power of the intensity, indicating that if the light is effective at all, only one quantum is required to be absorbed: this is Einstein's law of photochemical equivalence. Its validity is readily appreciated on theoretical grounds, since after a molecule has absorbed one quantum, it would be very unlikely to remain in its excited state long enough to absorb a second quantum.

In photochemical reactions it is frequently found, however, that a number of molecules are transformed chemically for every photon of light absorbed. In such a case it can be inferred that a chain reaction is occurring, the atoms or free radicals produced in each act of absorption being responsible for the reaction of many reactant molecules. The number of such molecules transformed by each photon absorbed is known as the "quantum yield" of the reaction.

Since, for most of the wave lengths employed in photochemical work, the energy of the photon is considerably larger than the average thermal energy of the molecules, there will be little variation in the effectiveness of a photon from molecule to molecule in the reacting system. It is therefore to be expected that on changing the frequency, there will be a fairly sharp transition from a region in which no reaction occurs to one in which a considerable amount of reaction occurs. Many examples of such "photochemical thresholds" have in fact been observed; reaction occurs on the lower wave length, *i.e.*, higher frequency, side of the threshold.

The photolysis of molecules is frequently a very convenient way of producing free atoms and radicals in a reaction system. Atomic chlorine, bromine, iodine, and oxygen have often been produced in this way. With hydrogen, on the other hand, the wave lengths required are very short, and the experimental difficulties are correspondingly great.

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chemistry of Gases," Reinhold Publishing Corporation, New York, 1941; G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, 1939, E. J. Bowen, "The Chemical Aspects of Light," Oxford University Press, New York. 1946.

Ketones, metal alkyls, alkyl halides, azomethane, and a variety of other substances have been used as sources of alkyl radicals by photochemical reactions. Acetone, for example, absorbs radiation in the neighborhood of 2800 A to give CH_3CO and CH_3, and at higher temperatures the acetyl radical decomposes into CH_3 and CO; the over-all process is therefore

$$CH_3COCH_3 + h\nu \rightarrow 2CH_3 + CO$$

This method has been much used in the study of the reactions of methyl radicals, particularly by Pearson and his collaborators.[1] H. S. Taylor and his coworkers[2] have frequently employed the photolysis of the mercury alkyls as a source of free radicals; thus the photolysis of mercury dimethyl gives rise to two methyl radicals,

$$Hg(CH_3)_2 + h\nu \rightarrow Hg + 2CH_3$$

and the reactions of these with a variety of organic molecules have been investigated. Alkyl halides when photolyzed give rise to the alkyl radical and the halogen atom, but the yield is low unless the reverse reaction can be prevented. Azomethane gives rise to nitrogen and two methyl radicals,

$$CH_3NNCH_3 + h\nu \rightarrow N_2 + 2CH_3$$

Photosensitization. Photosensitization has recently been used very extensively for the production of atoms and free radicals in reaction systems. The importance of the method lies in the fact that definite amounts of light energy can conveniently be transferred to certain molecules that do not absorb at the appropriate wave length. For example, the production of hydrogen atoms from a hydrogen molecule requires 103.2 kcal of energy per mole, and this corresponds to a wave length of 2776 A. However the lowest excited state of hydrogen, the repulsive $^3\Sigma$ state, requires considerably more energy than this, the corresponding wave length being 849 A. Working with such wave lengths as this is difficult, so that alternative methods are valuable. Mercury has been very widely used as a sensitizer for this and other processes; mercury vapor is normally in a 6^1S_0 state and is raised to the 6^3P_1 level by illumination with the mercury resonance line at 2537 A, which corresponds to an energy of 112 kcal. On collision with a hydrogen molecule, dissociation into atoms may occur, the process actually being very efficient. The experimental technique is very simple; the mercury vapor is mixed with the hydrogen, and the mixture illuminated

[1] T. G. Pearson, *J. Chem. Soc.*, 1718 (1934); T. G. Pearson and R. H. Purcell, *ibid.*, 1151 (1935); 253 (1936); H. H. Glazebrook and T. G. Pearson, *ibid.*, 1777 (1936); 567 (1937).

[2] J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6**, 359 (1938); W. J. Moore and H. S. Taylor, *ibid.*, **8**, 396, 466 (1940); J. O. Smith and H. S. Taylor, *ibid.*, **7**, 390 (1939); H. S. Taylor and J. O. Smith, *ibid.*, **8**, 543 (1940).

with the appropriate wave length. Many bonds having strengths of less than 112 kcal can be split in this way.

Photosensitization was first discovered by Cario and Franck,[1] who demonstrated the formation of hydrogen atoms from the molecules and excited mercury, detecting them by their chemical reactivity. They described a collision between the excited mercury atom and the molecule as a "*Stoss zweiter Art*" ("collision of the second kind"). Later Taylor and his coworkers[2] used the method to investigate the reactions of atomic hydrogen, which they caused to react with carbon monoxide, nitrous oxide, hydrocarbons, and other substances.

The mechanism of the reaction between excited mercury and hydrogen has been the subject of some investigation. The reaction is sometimes written in two stages,

$$\text{(1)} \qquad \text{Hg}(^3P_1) + \text{H}_2 \rightarrow \text{HgH} + \text{H}$$

$$\text{(2)} \qquad \text{HgH} \rightarrow \text{Hg}(^1S_0) + \text{H}$$

and it is clear that the first reaction is more exothermic than the process

$$\text{(3)} \qquad \text{Hg}(^3P_1) + \text{H}_2 \rightarrow 2\text{H} + \text{Hg}(^1S_0)$$

by the dissociation energy of HgH, which is 8.5 kcal. The presence of HgH in these systems was investigated spectroscopically by Olsen,[3] who found that it was not present in the normal state, but only in an excited state, presumably having been produced by secondary processes. It is therefore concluded that either the process (3) occurs in one stage,[4] or the HgH produced in reaction (1) is so excited vibrationally that it dissociates at once.[5] It may be mentioned here that the purely quenching type of process,

$$\text{Hg}(^3P_1) + \text{H}_2 \rightarrow \text{Hg}(^1S_0) + \text{H}_2$$

in which electronic energy is converted into translational, rotational, and vibrational energy, cannot occur (*cf.* p. 387).

Excited mercury has also been caused to react directly with other molecules, such as the hydrocarbons. With the saturated hydrocarbons the only primary process which takes place is

$$\text{Hg}(^3P_1) + \text{HR} \rightarrow \text{H} + \text{R} + \text{Hg}(^1S_0)$$

[1] G. Cario and J. Franck, *Z. Physik*, **11**, 161 (1922).

[2] H. S. Taylor and J. R. Bates, *Proc. Natl. Acad. Sci. U. S.*, **12**, 714 (1926); H. S Taylor and D. G. Hill, *J. Am Chem. Soc.*, **51**, 2927 (1929); *Z. physik. Chem.*, **B, 2**, 449 (1929); H. S. Taylor and A. L. Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

[3] L. O. Olsen, *J Chem. Phys*, **6**, 307 (1938).

[4] *Cf.* J. Franck and H. Sponer, *Nach. Ges. Wiss.* Gottingen, 241 (1928); H. Beutler and E. Rabinowitch, *Z. physik. Chem*, **B, 8**, 403 (1930).

[5] K. J. Laidler, *J. Chem. Phys.*, **10**. 43 (1942).

where R is a free radical, such as ethyl in the case of ethane. With unsaturated hydrocarbons the same type of process may occur, but in addition an excited molecule can be formed and undergo subsequent reaction; the details of some of these processes will be discussed later.

Work has also been done using mercury in its singlet-excited (6^1P_1) state, which corresponds to a wave length of 1849 A and an energy of 153.9 kcal per mole. Zinc and cadmium, in both singlet- and triplet-excited states, have been used in photosensitization experiments, particularly by Steacie and his coworkers.[1] The amounts of energy liberated in each case are given in Table 37, the values with and without the formation of the hydride being included. By using these and other excited states, the energy available for transfer to the reacting molecule can be varied over a

TABLE 37. AMOUNTS OF ENERGY LIBERATED BY EXCITED ATOMS

Metal	Line, A	Transition	Energy of excited atom, kcal	Total energy available if hydride is formed, kcal
Mercury	2537	6^3P_1-6^1S_0	112.2	120.7
	1849	6^1P_1-6^1S_0	153.9	162 4
Cadmium	3261	5^3P_1-5^1S_0	87.3	102.8
	2288	5^1P_1-5^1S_0	124.4	139.9
Zinc	3076	4^3P_1-4^1S_0	92.5	115.6
	2139	4^1P_1-4^1S_0	133.4	156.5

convenient range. In some cases there is ambiguity as to whether the hydride is formed or not, although it appears that when the reacting molecule requires the additional energy, the hydride will be formed in order to make it available. This may be illustrated by comparing the reactions of triplet mercury and cadmium. Triplet mercury has sufficient energy to split the H-H bond without hydride formation, and, as has been seen, the hydride is not formed as a final product. With triplet cadmium, on the other hand, the energy available is only just about sufficient if the hydride is formed. The fact that the reaction proceeds readily therefore requires that the hydride be a final product, and this has been found spectroscopically to be the case by Bender.[2] The over-all process is therefore

$$Cd(^3P_1) + H_2 \rightarrow CdH + H$$

[1] For reviews see E. W. R Steacie, "Atomic and Free Radical Reactions"; "Free Radical Mechanisms"; *Research*, **1**, 541 (1948).

[2] P. Bender, *Phys. Rev.*, **36**, 1535 (1930); *cf.* Olsen, *loc. cit.*

and other reactions proceed in the same way. Thus Steacie and Le Roy[1] have detected CdH in the cadmium-photosensitized reactions of propane.

A number of photosensitized processes will be discussed in Chap. 9.

Radiochemical Methods.[2] With the development of the field of nuclear physics and chemistry, there has come considerable interest in the study of chemical reactions which are induced by nuclear and other types of radiation. These radiations bring about initial ionization in substances through which they pass, and a radiochemical process may conveniently be defined as one induced by radiation which brings about ionization in the system in which it is absorbed; this distinguishes the processes from photochemical ones, in which no ionization occurs. An important phase of radiochemistry began in 1935, largely owing to the development of particle-accelerating machines, which increased the number of different types of radiation and increased the energies that could be attained with them. An additional reason for the enhanced interest at about that time was the realization[3] that the chemically active species produced by the radiations were not the ions produced in the initial step but were atoms and free radicals formed in a subsequent stage. The field was therefore brought into close relationship with photochemistry and allied subjects which had been studied for some time.

The most important radiations which are used to produce ions, and hence atoms and free radicals, are α and β rays (helium nuclei and electrons, respectively), beams of positive ions such as protons and deuterons, and X and γ rays. Of these, all except the X and γ rays are beams of charged particles, the energy of which is dissipated in the medium in which the particle is absorbed. In the case of the absorption of a photon of X rays or γ rays, an electron is ejected and again brings about ionization by transferring energy. At low energies, below about 10 kev (wave length greater than 1.5 A), an electron is emitted which has practically all the energy of the incident photon, whereas at higher energies Compton scattering is more important, in which case the electron has appreciably less energy than the incident photon. With photons of very high energy (wave length less than 10^{-2} A), more complicated processes occur ("pair production"), but the net result is the production of an electron. In the case of every type of radiation, therefore, the medium acquires energy from a charged particle, which may be an electron or an atomic nucleus.

The charged particle loses its energy in a series of inelastic collisions with the molecules of the medium through which it passes; the amount of energy

[1] E. W. R. Steacie and D. J. Le Roy, *J. Chem. Phys.*, **12**, 34 (1944).

[2] For reviews, see G. Glockler and S. C. Lind, "The Electrochemistry of Gases and Other Dielectrics," John Wiley & Sons, Inc., New York, 1939; F. S. Dainton, *Research*, **1**, 486 (1948).

[3] H. Eyring, J. O. Hirschfelder, and H. S. Taylor, *J. Chem. Phys.*, **4**, 479, 570 (1937)

transferred depends, among other things, on the energy levels available. In some instances the energy transferred causes the ejection of an electron from the molecule, which becomes a positive ion; an ion pair is then said to be produced. In other cases the molecule, upon suffering collision with a charged particle, becomes excited to a higher energy level; the resulting excited molecule may then be deactivated by collision with other molecules, may radiate (light emission is always observed when particle beams traverse gases), or may dissociate into free radicals or atoms. The formation of atoms and free radicals in this way has been confirmed by specific chemical tests, by physical methods, and by the occurrence of secondary chemical reactions that are closely similar to those brought about by photochemical means and known to involve radicals. Such radiochemical reactions are often discussed in terms of their "ionic yields," defined as the ratio of the number of molecules changed chemically to the number of ion pairs formed. Such ionic yields are always considerably greater than the quantum yields for the corresponding photochemical process, indicating that the absorption of energy required to create one ion pair also results in the dissociation of several molecules.

Some examples of the formation of atoms and free radicals by absorption of radiations of this type may be mentioned briefly. When water vapor is subjected to fast electrons, hydrogen atoms and hydroxyl radicals, the latter in both ground and excited states, have been detected experimentally. In addition, the ions H_2O^+, H_3O^+, H^+, and OH^+ have been found. In the radiolysis of hydrogen iodide by β particles, it is found that hydrogen and iodine atoms are produced, and in the α radiolysis of hydrogen, the formation of hydrogen atoms is indicated by their catalysis of the para-ortho hydrogen conversion. Methyl and other radicals are found with hydrocarbons, sometimes being produced from positive ions by reactions such as

$$C_nH_{2n+2}^+ \rightarrow CH_3 + C_{n-1}H_{2n-1}^+$$

Discharge-tube Methods. Atoms and free radicals are produced in electrical discharges in gases and may be used to give rise to chemical reaction. However, not much information has come from work in which the reacting substances are subjected to a discharge, because a large variety of atoms and radicals are formed and the processes taking place are therefore very complicated. Of more importance is the technique by which the products from a discharge through a single gas, such as hydrogen atoms in the case of hydrogen gas, are carried into the reaction system. An application of this procedure has been described in Chap. 2.

Wood[1] first demonstrated in 1920 that hydrogen atoms produced by a

[1] R. W. Wood, *Proc. Roy. Soc. (London)*, **A, 97,** 455 (1920); **A, 102,** 1 (1922); *Phil. Mag.*, **42,** 729 (1921); **44,** 538 (1922).

glow discharge in hydrogen could be pumped out of the system and transported for a considerable distance before they recombined. He found that it was necessary for the walls of the tube to be poisoned, *e.g.*, by a film of water or phosphoric acid, in order for the recombination of the atoms on the walls to be inhibited.

Bonhoeffer[1] made modifications of Wood's apparatus and carried out a number of investigations of the reactions of atomic hydrogen. A suitable piece of apparatus for work of this kind is shown in Fig. 7 on page 47. The glow discharge is produced by an emf of several thousand volts across the electrodes, and a very rapid stream of hydrogen at low pressure (0.2 to 0.5 mm) is passed through. In this way an appreciable concentration of atoms is produced in the reaction vessel, into which the other reactants are introduced. To prevent recombination of atoms, the walls of the discharge tube and reaction vessel are poisoned by a film of water vapor, or better by coating with such materials as potassium chloride or syrupy phosphoric acid.

A great many reactions of hydrogen atoms have been investigated by the Wood-Bonhoeffer method. In addition to the reaction

$$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$$

which was discussed in Chap. 2, a number of organic reactions have been studied, some of which will be mentioned in Chap. 9. It is not usual to determine activation energies by employing this method over a range of temperatures, since the measurements of the atom concentrations are not sufficiently accurate to give reliable temperature coefficients. Instead the work is done at one temperature and the activation energy estimated on the basis of collision theory, a steric factor of 0.1 being employed. This procedure is probably sufficiently reliable in most cases.

Complex reactions in solution

The previous discussion of complex reactions in the present chapter is applicable primarily to reactions in the gas phase, although, as will be seen, a number of reactions in solution involve free radicals as intermediates. However, in the case of solution reactions, an additional possibility remains: the reaction may proceed by an ionic mechanism. In the gas phase the formation of ions is much less probable than the formation of free radicals; in solution, on the other hand, "homolysis" of a bond, with the formation of free atoms or radicals, is not usually favored over "heterolysis," in which ions are formed. This is particularly the case in solvents of high dielectric constant. In general, it can be said that water, the alcohols,

[1] K. F. Bonhoeffer, *Z. physik. Chem* , **113**, 119, 492 (1924); **116**, 391 (1925); *Z. Elektrochem.*, **31**, 521 (1925); *Ergeb. exakt. Naturwiss.*, **6**, 201 (1927). *Cf.* H. S. Taylor and A. L. Marshall, *Nature*, **112**, 937 (1923).

nitrobenzene, pyridine, acetone, and some other solvents favor the ionization of bonds, but that such solvents as ether, benzene, chloroform and carbon tetrachloride make free-radical mechanisms more probable.

Ionic Mechanisms in Solution. Ionic reactions in solution generally have quite different characteristics from free-radical reactions. This arises from the fact that except in the case of inorganic salts, which are extensively ionized in suitable solvents such as water, the separation of charges is usually not complete, and the ions are therefore not free. Ionic reactions therefore do not in general proceed by well-defined reaction steps but rather by a smooth transition accompanied by a shift of electrons. This has not been generally realized, and in fact ionic reactions involving organic molecules are frequently envisaged as involving complete ionization. Thus the hydrolysis of an alkyl halide is often written as

$$RX \rightarrow R^+ + X^-$$
$$R^+ + H_2O \rightarrow ROH + H^+$$

Actually there may not be complete ionization of the bond, and the reaction should then be envisaged as involving only partial ionization, followed by gradual formation of the carbon-oxygen bond and elimination of the halide ion.

Since organic reactions of this type do not proceed by well-defined steps, they are not true complex reactions; they have in fact been treated as elementary processes in Chap. 4. An example of a complex reaction involving ions will be considered in Chap. 11.

Free-radical Mechanisms in Solution. Free radicals are usually produced in solution by the thermal and photolytic methods. Whereas in the gas phase free radicals produced by such methods can usually migrate away from one another before they recombine, in solution such diffusion is much more difficult; "primary recombination" of radicals is therefore probable and tends to lower the initial yield of radicals.[1]

However, once a radical has succeeded in diffusing away from its partner, the "cage" of solvent molecules surrounding it will hinder its recombination with other radicals. There is now the possibility of displacement reactions with solvent molecules, which generally take place readily; radicals are found to dehydrogenate alcohols, hydrocarbons, and other molecules and to remove halogen atoms from solvents such as carbon tetrachloride. In aqueous solution hydroxyl radicals are generally released.

Reactions involving free radicals in solution are, on this account, in general not specific reactions of the radicals produced initially but are more characteristic of the solvent. For example, free-radical reactions in aqueous solution are usually reactions involving the hydroxyl radical. By

[1] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

choosing the appropriate solvent, however, this difficulty can generally be avoided; hydroxyl radicals, for example, regenerate themselves in water by the reaction

$$HO + H_2O \rightarrow H_2O + OH$$

while chlorine atoms persist in carbon tetrachloride solution owing to the reversible change

$$Cl + CCl_4 \rightleftharpoons Cl_2 + CCl_3$$

CHAPTER 8

SOME COMPLEX INORGANIC REACTIONS

In the present and succeeding chapters will be considered the mechanisms that have been proposed for some complex reactions occurring in the gas phase and in solution. A number of inorganic processes will be considered in the present chapter, while some organic reactions, particularly decompositions, will be discussed in Chap. 9; the separation of the two types is somewhat arbitrary but may be justified by the fact that different types of free atoms and radicals are involved. In succeeding chapters will be treated, from essentially the same point of view, some special types of processes, *viz.*, catalyzed reactions, oxidations, and polymerizations.

Reaction between hydrogen and bromine

The formation of hydrogen bromide from hydrogen and bromine is the reaction whose mechanism is best understood. The thermal reaction was first studied by Bodenstein and Lind[1] over the temperature range from 205 to 302°C, and at pressures of the order of 1 atm. They found empirically that their results could be fitted to the equation

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{1 + \dfrac{[\mathrm{HBr}]}{m[\mathrm{Br_2}]}} \tag{1}$$

where k and m are constants, the latter having the value of about 10. This equation shows that hydrogen bromide inhibits the reaction, and it was found that iodine exerted an even more powerful inhibition; water, air, and carbon tetrachloride on the other hand had no inhibiting action.

Bodenstein and Lind suggested that the appearance of the bromine concentration as a square root probably indicated that bromine atoms play an important part in the reaction; however, the results were not properly explained until 1919, when Christiansen, Herzfeld, and Polanyi independently proposed the mechanism

(1) $\mathrm{Br_2} \rightarrow 2\mathrm{Br}$

(2) $\mathrm{Br} + \mathrm{H_2} \rightarrow \mathrm{HBr} + \mathrm{H}$

(3) $\mathrm{H} + \mathrm{Br_2} \rightarrow \mathrm{HBr} + \mathrm{Br}$

(4) $\mathrm{H} + \mathrm{HBr} \rightarrow \mathrm{H_2} + \mathrm{Br}$

(5) $\mathrm{Br} + \mathrm{Br} \rightarrow \mathrm{Br_2}$

[1] M. Bodenstein and S. C. Lind, *Z. physik. Chem.*, **57**, 168 (1907).

It was shown on page 185 that the use of the steady-state treatment gives rise to the kinetic law

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2(k_1/k_5)^{\frac{1}{2}}[\mathrm{H_2}][\mathrm{Br_2}]^{\frac{1}{2}}}{1 + \dfrac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \qquad (2)$$

This is of the same form as the empirical equation [Eq. (1)], with $k = 2k_2(k_1/k_5)^{\frac{1}{2}}$ and $m = k_3/k_4$.

The inhibition by hydrogen bromide is seen to be accounted for by reaction (4), in which hydrogen atoms are removed by reaction with hydrogen bromide. It was originally thought[1] that the inhibition by iodine could analogously be explained by the reaction

$$\mathrm{H} + \mathrm{I_2} \rightarrow \mathrm{HI} + \mathrm{I}$$

The hydrogen atoms so reacting would be lost to the reaction since the step

$$\mathrm{I} + \mathrm{H_2} \rightarrow \mathrm{HI} + \mathrm{H}$$

is much too endothermic to take place readily. However Müller[2] later found that at least part of the effect of the iodine was to reduce the concentration of bromine by forming IBr.

The individual rate constants k_1 to k_5 for the elementary reactions occurring have all been evaluated, and the methods by which this has been done will now be indicated. The experimentally determined constant k is equal to $k_2(k_1/k_5)^{\frac{1}{2}}$, and the ratio k_1/k_5 is the equilibrium constant for the dissociation of bromine into atoms, the value for which has been determined by Bodenstein and Cramer;[3] the rate constant k_2 can therefore be calculated. According to Jost[4] the best value for it is given by

$$\log k_2 = 12.30 + 0.5 \log T - \frac{17{,}600}{2.303RT} \qquad (3)$$

The activation energy is thus 17.6 kcal, and since the reaction is endothermic to the extent of 16.4 kcal, it follows that the activation energy for the reverse reaction, which is reaction (4), is equal to 1.2 kcal.

The value of m, equal to k_3/k_4, is found experimentally to be independent of the temperature; the two reactions (3) and (4) therefore have the same activation energy, so that the activation energy of (3) is also about 1.2 kcal. Since the value of m is about 10, reaction (3) proceeds about 10 times as fast as (4), in spite of the activation energies being the same. The

[1] M. Bodenstein and W. Müller, *Z. Elektrochem.*, **30**, 416 (1924).
[2] W. Müller, *Z. physik. Chem.*, **123**, 1 (1926).
[3] M. Bodenstein and F. Cramer, *Z. Elektrochem.*, **22**, 327 (1916).
[4] W. Jost, *Z. physik. Chem.*, **B, 3**, 95 (1929).

difference in rates must be accounted for in terms of frequency factors, that for (4) being one-tenth of that for (3).

The evaluation of the rates of reactions (1) and (5) involves a comparison of the kinetics of the thermal reaction with those of the corresponding photochemical reaction. Bodenstein and Lutkemeyer[1] found that the photochemical reaction proceeds according to the empirical equation

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{k'[\mathrm{H_2}]I^{\frac{1}{2}}}{1 + \dfrac{[\mathrm{HBr}]}{m'[\mathrm{Br_2}]}} \tag{4}$$

where k' and m' are constants and I is the intensity of the light absorbed. The similarity between this equation and that for the thermal reaction suggests that the mechanisms are very similar, the essential difference being that in the light reaction the bromine atoms are produced by the absorption of a quantum by a bromine molecule:

$$\mathrm{Br_2} + \mathbf{h}\nu \rightarrow 2\mathrm{Br}$$

This process is followed by the same series of reactions as before, *i.e.*, reactions (2) to (5). The steady-state equation for bromine atoms is, according to this scheme,[2]

$$\frac{d[\mathrm{Br}]}{dt} = 2I - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_4[\mathrm{H}][\mathrm{HBr}] - 2k_5[\mathrm{Br}]^2 = 0 \tag{5}$$

while Eq. (12) on page 185 still holds for the concentration of hydrogen atoms. The solution of these equations gives, for the rate of formation of hydrogen bromide,

$$\frac{d[\mathrm{HBr}]}{dt} = \frac{2k_2(1/k_5)^{\frac{1}{2}}[\mathrm{H_2}]I^{\frac{1}{2}}}{1 + \dfrac{k_4[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \tag{6}$$

which is of the same form as Eq. (4) with $k' = k_2(2/k_5)^{\frac{1}{2}}$ and $m' = k_3/k_4$.

Under the conditions employed by Bodenstein and Lutkemeyer, the rate of the photochemical reaction was found to be about 300 times that of the thermal reaction at the same temperature, which means that in the photochemical reaction the stationary concentration of bromine atoms is about 300 times that in the dark reaction, all other stages in the two reactions being identical. Since the concentration of bromine atoms in the thermal reaction is known from the thermal dissociation constant of molecu-

[1] M. Bodenstein and H. Lutkemeyer, *ibid.*, **114**, 208 (1924).

[2] In Eq. (5), and in similar steady-state expressions for photochemical reactions, I must be expressed in the units mole-quanta per unit volume per second; a mole-quantum, sometimes known as an *einstein*, is N photons or quanta of light absorbed

lar bromine, the concentration of bromine atoms in the photochemical reaction is also known, *i.e.*, is about 300 times as great.

In both reactions the rate of production of bromine atoms is equal to that of their removal. The rate of formation of bromine atoms in the photochemical reaction can be calculated using Einstein's law of photochemical equivalence (p. 195), according to which one molecule of bromine is dissociated for each quantum of light absorbed. The number of bromine atoms combining in unit time in the photochemical reaction is therefore known, and since the stationary concentration is known, the specific rate can be calculated. In this way it was found that assuming the combination of bromine atoms to be a simple two-body process, and taking reasonable values for the atomic diameters, the recombination occurs in 1 out of every 800 collisions. On theoretical grounds it is known that in fact the recombination must involve three-body collisions, and the factor of $\frac{1}{800}$ corresponds to the necessity for the presence of a third body. In agreement with this, it was found that there was a variation of the rate of combination with the total pressure.

From the rate of reaction (5) and the equilibrium constant, the rate of (1) can be calculated. It is found[1] that the rate of the thermal dissociation can be expressed very approximately by a first-order rate constant k_1 given by

$$k_1 = 10^{13} e^{-45{,}200/RT} \tag{7}$$

the activation energy of 45.2 kcal being equal to the heat of dissociation of bromine. The order is not exactly the first, however, the first-order "constant" k_1 showing some variation with the total pressure. Just as the atom recombination involves a third body, so does the dissociation require the presence of a second body; if this is represented by M, the mechanism may be represented as

(1) $$\mathrm{Br_2} + M \rightleftharpoons M + \mathrm{Br_2^*}$$

(2) $$\mathrm{Br_2^*} \rightarrow 2\mathrm{Br}$$

If the rate constants for the forward and reverse reactions (1) are k_1' and k_{-1}', and that of (2) is k_0', the steady-state equation for $\mathrm{Br_2^*}$ is

$$k_1'[\mathrm{Br_2}][M] - k_{-1}'[M][\mathrm{Br_2^*}] - k_0'[\mathrm{Br_2^*}] = 0 \tag{8}$$

whence

$$[\mathrm{Br_2^*}] = \frac{k_1'[\mathrm{Br_2}][M]}{k_{-1}'[M] + k_0'} \tag{9}$$

The over-all rate of dissociation is thus equal to

$$-\frac{d[\mathrm{Br_2}]}{dt} = \frac{k_0'k_1'[\mathrm{Br_2}][M]}{k_{-1}'[M] + k_0'} \tag{10}$$

[1] Jost, *loc. cit.*

so that the first-order rate coefficient, defined by

$$-\frac{d[\mathrm{Br}_2]}{dt} = k_1[\mathrm{Br}_2] \tag{11}$$

is equal to

$$k_1 = \frac{k_0' k_1' [M]}{k_{-1}'[M] + k_0'} \tag{12}$$

which in general varies with the total pressure. It is truly constant only if k_0' is extremely small compared with $k_{-1}'[M]$, which will be the case at higher pressures. Under these conditions the collisions between Br_2 and M are sufficient to maintain a stationary concentration of excited bromine molecules, and the rate-controlling step is the dissociation of bromine molecules. At very low pressures on the other hand, $k_0' > k_{-1}'[M]$, and the reaction will become of the second order. Complications also arise as a result of the possibility of dissociation and recombination on the walls of the reaction vessel.

Reaction between hydrogen and chlorine

The reaction between hydrogen and chlorine shows some points of resemblance to that between hydrogen and bromine but is considerably more complicated, owing to the larger number of elementary processes that play a significant part in it. Both the thermal and photochemical reactions have been the subject of much study, particularly the photochemical reaction, the details of which are now fairly well understood. This reaction will therefore be considered first.

The Photochemical Reaction. A striking feature of the photochemical reaction between hydrogen and chlorine is the extremely large quantum yield that is obtained under suitable conditions, values as high as 10^6 having been reported.[1] This is in marked contrast to the situation with hydrogen and bromine, where the quantum yield is usually less than unity. The reason for this difference is that the chain-propagating reactions are more rapid with chlorine than with bromine, as will be discussed in more detail later.

It has been established beyond question that the initial step in the photochemical reaction is the dissociation of a chlorine molecule into atoms. It is known from the spectral evidence that chlorine is dissociated by wave lengths of less than 4785 A, and it is at such wave lengths that most of the absorption takes place. More direct evidence was given by Jost and Schweizer,[2] who exposed chlorine to radiation immediately before mixing

[1] M. Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913).

[2] W. Jost and H. Schweizer, *ibid.*, **B, 13**, 373 (1931).

it with hydrogen, the radiation being prevented from reaching the hydrogen; reaction was found to take place.

A large number of investigations have been carried out with the object of determining the dependence of the rate of reaction on the concentrations of reacting molecules. Many of the earlier conclusions are now known to be in error owing to the existence of certain complications that were not at once elucidated. There may, for example, be a long induction period during which no reaction occurs; this was shown by Burgess and Chapman[1] to be due to the presence of certain nitrogenous impurities such as ammonia and organic compounds. Later Griffiths and Norrish[2] found that the real inhibitor is nitrogen trichloride, which is formed from the impurities present. Other impurities, such as chlorine dioxide, ozone, and oxygen, also act as inhibitors.

The effect of oxygen is not only to contribute to the induction period but to influence markedly the rate of the reaction after it has started. To a good approximation the rate of the reaction is inversely proportional to the concentration of oxygen,[3] and as the gases are purified from oxygen, the rate becomes extremely high. Since minute traces of oxygen have such a marked effect on the rate, some erroneous conclusions were reached by the earlier workers, and various contradictory expressions for the rate of reaction were put forward.

On the basis of a survey of the experimental work that had been carried out before 1926, Thon[4] proposed that the rate of the reaction could best be represented by

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{kI[\mathrm{H_2}][\mathrm{Cl_2}]}{[\mathrm{O_2}]\,([\mathrm{H_2}] + [\mathrm{Cl_2}]/10)} \qquad (13)$$

where I is the intensity of the light absorbed. This expression implies an infinite rate in the complete absence of oxygen, and Cremer[5] has pointed out that the expression is obeyed only down to an oxygen pressure of about 0.04 mm. A more accurate expression for the rate, valid down to much lower pressures, was given by Bodenstein and Unger;[6] this is

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{kI[\mathrm{H_2}][\mathrm{Cl_2}]}{m[\mathrm{Cl_2}] + [\mathrm{O_2}]\,([\mathrm{H_2}] + [\mathrm{Cl_2}]/10)} \qquad (14)$$

[1] C. H. Burgess and D. L. Chapman, *J. Chem Soc.*, **89**, 1399 (1906).

[2] J. G. A. Griffiths and R. G. W. Norrish, *Proc. Roy. Soc.* (*London*), **A, 130,** 591 (1931); **A, 135,** 69 (1932); **A, 147,** 140 (1934).

[3] D. L. Chapman and P. S. MacMahon, *J. Chem. Soc.*, **95,** 959 (1909); M. Bodenstein and W. Dux, *Z. physik. Chem.*, **85,** 297 (1913).

[4] N. Thon, *ibid.*, **124,** 327 (1926).

[5] E. Cremer, *ibid.*, **128,** 285 (1927).

[6] M. Bodenstein and W. Unger, *ibid.*, **B, 11,** 253 (1930).

At oxygen pressures higher than 0.04 mm, the first term in the denominator can be neglected, so that Eq. (13) is obeyed. At extremely low oxygen concentrations, the rate approximates to

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{kI}{m}[\mathrm{H_2}] \tag{15}$$

so that the rate is then independent of the concentration of chlorine.

A number of alternative chain mechanisms have been proposed to account for this behavior; that of Nernst was considered on page 182, but it is inadequate to explain the results. The most satisfactory mechanism would appear to be the following, which was proposed in 1921 by Göhring:[1]

(1) $\mathrm{Cl_2} + h\nu \rightarrow 2\mathrm{Cl}$
(2) $\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H}$
(3) $\mathrm{H} + \mathrm{Cl_2} \rightarrow \mathrm{HCl} + \mathrm{Cl}$
(4) $\mathrm{H} + \mathrm{O_2} \rightarrow \mathrm{HO_2}$
(5) $\mathrm{Cl} + \mathrm{O_2} \rightarrow \mathrm{ClO_2}$
(6) $\mathrm{Cl} + X \rightarrow \mathrm{ClX}$

Here X may be any substance which removes chlorine atoms. This reaction scheme will later be compared with that for the hydrogen-bromine reaction.

Denoting as $2I$ the rate of formation of the chlorine atoms by reaction (1), and the specific rates of the remaining reactions by k_2, k_3, k_4, k_5, and k_6, the rate of the over-all reaction is derived as follows, on the basis of the steady-state treatment: The rate of formation of chlorine atoms is

$$\frac{d[\mathrm{Cl}]}{dt} = 2I - k_2[\mathrm{Cl}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Cl_2}] - k_5[\mathrm{Cl}][\mathrm{O_2}] - k_6[\mathrm{Cl}][X] = 0 \tag{16}$$

and the rate of formation of hydrogen atoms is

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Cl}][\mathrm{H_2}] - k_3[\mathrm{H}][\mathrm{Cl_2}] - k_4[\mathrm{H}][\mathrm{O_2}] = 0 \tag{17}$$

Equation (16) gives for the concentration of chlorine atoms

$$[\mathrm{Cl}] = \frac{2I + k_3[\mathrm{H}][\mathrm{Cl_2}]}{k_2[\mathrm{H_2}] + k_5[\mathrm{O_2}] + k_6[X]} \tag{18}$$

while Eq. (17) gives

$$[\mathrm{Cl}] = \frac{k_3[\mathrm{H}][\mathrm{Cl_2}] + k_4[\mathrm{H}][\mathrm{O_2}]}{k_2[\mathrm{H_2}]} \tag{19}$$

Equating these expressions gives

$$k_2[\mathrm{H_2}](2I + k_3[\mathrm{H}][\mathrm{Cl_2}]) = (k_2[\mathrm{H_2}] + k_5[\mathrm{O_2}] + k_6[X])(k_3[\mathrm{H}][\mathrm{Cl_2}] + k_4[\mathrm{H}][\mathrm{O_2}]) \tag{20}$$

[1] R. Göhring, *Z. Elektrochem.*, **27**, 511 (1921).

Omitting the very small term $k_4k_5[H][O_2]^2$, this gives, for the concentration of hydrogen atoms,

$$[H] = \frac{2Ik_2[H_2]}{k_3k_6[Cl_2][X] + [O_2](k_2k_4[H_2] + k_3k_5[Cl_2] + k_4k_6[X])} \tag{21}$$

It can be shown (see p. 214) that reaction (3) is much faster than reaction (2); consequently, the rate of formation of hydrogen chloride is given fairly exactly by

$$\frac{d[HCl]}{dt} = k_3[H][Cl_2] \tag{22}$$

Introducing expression (21) for [H] into this gives

$$\frac{d[HCl]}{dt} = \frac{2k_2k_3[H_2][Cl_2]I}{k_3k_6[Cl_2][X] + [O_2](k_2k_4[H_2] + k_3k_5[Cl_2] + k_4k_6[X])} \tag{23}$$

$$= \frac{\frac{2k_3}{k_4}I[H_2][Cl_2]}{\frac{k_3k_6}{k_2k_4}[Cl_2][X] + [O_2]\left([H_2] + \frac{k_3k_5}{k_2k_4}[Cl_2] + \frac{k_6}{k_2}[X]\right)} \tag{24}$$

Apart from the final term in the denominator, this expression is of the form of the empirical equation [Eq. (14)], the constants being related by

$$k = \frac{2k_3}{k_4}, \qquad m = \frac{[X]k_3k_6}{k_2k_4}, \qquad \frac{1}{10} = \frac{k_3k_5}{k_2k_4}$$

The scheme of reactions therefore gives a kinetic law which is essentially in agreement with the experimental.

The species HO_2 which appears in reaction (4) is, of course, unstable. It is eventually converted into water and oxygen by reactions such as

$$2HO_2 \rightarrow H_2O_2 + O_2$$

and

$$HO_2 + H_2 \rightarrow H_2O_2 + H$$

followed by the decomposition of the hydrogen peroxide.

The Thermal Reaction. Hydrogen and chlorine react thermally at temperatures above about 200°C, and the kinetics have been studied by many workers.[1] The results are not conclusive, although it appears in general that the reaction proceeds in a manner similar to the photochemical process. In place of the intensity of light absorbed, which appears in

[1] H. Sirk, *Z. physik. Chem.*, **61**, 545 (1908); K. H. A. Melander, *Arkiv Kemi, Mineral. Geol.*, **5**, No. 12 (1913–1915); J. A. Christiansen, *Z. physik. Chem.*, **B, 2**, 405 (1929); R. N. Pease, *J. Am. Chem. Soc.*, **56**, 2388 (1934); G. Kornfeld and S. Khodschaian, *Z. physik. Chem.*, **B, 35**, 403 (1937).

Eq. (14), the chlorine concentration appears as the square in the numerator,

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k'[\mathrm{H_2}][\mathrm{Cl_2}]^2}{m'[\mathrm{Cl_2}] + [\mathrm{O_2}](l[\mathrm{H_2}] + k'''[\mathrm{Cl_2}])} \tag{25}$$

The thermal reaction is complicated by the fact that the initial thermal decomposition of a molecule of chlorine may take place on the surface, so that different results are obtained with different sizes and shapes of vessels and with different types of surfaces. In the photochemical case the species X could be part of the surface, so that the theory allows for the surface removal of chlorine atoms; however the photochemical formation of the atoms must take place entirely in the gas phase. It may also be noted that this surface complication does not arise in the thermal formation of hydrogen bromide, since the rate of this reaction depends on the equilibrium concentration of bromine atoms, which are removed by the reverse of the reaction by which they are formed.

Pease[1] has carried out experiments with the object of elucidating the wall effect in the thermal hydrogen-chlorine reaction. These have for the most part consisted of comparing the rates of reaction in packed and unpacked vessels. If the chains are started on the surface but end largely in the gas phase, increasing the surface will increase the rate, while if they start in the gas phase and end on the surface, the rate will be decreased by increasing the surface. On the other hand, if both formation and recombination of atoms take place in the gas phase, or if both take place on the surface, changing the amount or nature of the surface may have little or no effect on the kinetics. This was in fact found to be the situation: changing the surface-volume ratio had little effect on the rate. These results alone cannot allow a decision as to whether the chains both start and stop in the gas phase, or start and stop at the surface. However in the presence of oxygen in excess it is to be expected that more chain ending will take place in the gas phase, by the collision of hydrogen atoms with oxygen molecules, and Pease therefore investigated the effect of packing the vessels in the presence of 10 per cent of oxygen. Under these conditions it was found that packing gave a large increase in the rate, from which it may be concluded that chains start on the surface. With little oxygen present they therefore end primarily at the surface. This conclusion that chains are initiated on the surface is further confirmed by quantitative arguments: The energy of activation for a homogeneous dissociation of a chlorine molecule must be at least 57 kcal, the energy of dissociation, and the rate of this process can be shown to be too slow to account for the overall rate of the reaction. If the dissociation takes place on the surface, the activation energy may be as low as one-half of the energy of dissociation,

[1] Pease, *loc. cit.*

and the rate may then be sufficient to account for the rate of the formation of hydrogen chloride.

Influence of Water Vapor on the Reaction. A considerable amount of difficulty was created by the observation of Coehn and Jung[1] that hydrogen and chlorine do not combine at all in the complete absence of water vapor. The photochemical reaction was studied, and it was reported that the rate increases with increasing partial pressure of water vapor and reaches a limiting value at a pressure of 10^{-5} mm. This result led to the temporary abandonment of the scheme of reactions suggested by Göhring, since it was found to be impossible to explain the effect in terms of a modification of his mechanism. Several alternative proposals were put forward,[2] some involving the participation of termolecular reactions.

It now appears, however, that the results of Coehn and Jung were erroneous, and the Göhring scheme, or a simple modification of it, may be accepted. Rodebush and Klingelhoefer[3] showed directly that the process $Cl + H_2 \rightarrow HCl + H$ proceeds in the complete absence of moisture, and later Bodenstein and Bernreuther[4] found no effect of intensive drying on the photochemical reaction as a whole. They attribute the result of Coehn and Jung to contamination of the reaction mixture with gold chloride, used in the preparation of the chlorine; this gave a long induction period after the manner of the other inhibitors mentioned previously.

Individual Specific Rates. On the basis of the over-all rates of the thermal and photochemical reactions, and from the results of other experiments, conclusions have been reached as to the individual specific rates and activation energies for some of the elementary processes. The arguments and conclusions have been reviewed by Morris and Pease,[5] whose discussion will be largely followed here. The values obtained for the activation energies are summarized in Table 38, which includes also the results for bromine and iodine.

The activation energy for the reaction $Cl + H_2 \rightarrow HCl + H$ has been determined directly by Rodebush and Klingelhoefer[6] by passing atomic chlorine into hydrogen. The activation energy was calculated from the temperature coefficient of the rate of formation of hydrogen chloride and also from the rate at one temperature, assuming simple collision theory;

[1] A. Coehn and G. Jung, *Z. physik. Chem.*, **110**, 705 (1924).

[2] J. Franck and E. Rabinowitsch, *Z. Elecktrochem.*, **36**, 794 (1930); M. Bodenstein, *Trans. Faraday Soc.*, **27**, 413 (1931); G. K. Rollefson and H. Eyring, *J. Am. Chem Soc.*, **54**, 170 (1932).

[3] W. H. Rodebush and W. C. Klingelhoefer, *ibid.*, **55**, 130 (1933).

[4] F. Bernreuther and M. Bodenstein, *Sitzber. preuss. Akad. Wiss. Physik.-math. Klasse*, **6**, 333 (1933).

[5] J. C. Morris and R. N. Pease, *J. Chem. Phys.*, **3**, 796 (1935).

[6] Rodebush and Klingelhoefer, *loc. cit.*

the agreement was very good, the activation energy obtained by the two methods being 6.0 kcal. The activation energy can also be determined from the results of the over-all photochemical reaction on the basis of the Göhring mechanism. In the complete absence of oxygen, the rate equation (24) reduces to

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{(2k_2/k_6)I[\mathrm{H_2}]}{[X]} \tag{26}$$

in agreement with the experimental result of Bodenstein and Unger [Eq. (15)]. The temperature coefficient of the over-all rate in the absence of oxygen is therefore that of k_2/k_6, and thus of k_2, since it may be supposed

TABLE 38. ACTIVATION ENERGIES FOR ELEMENTARY PROCESSES OCCURRING IN THE HYDROGEN-HALOGEN REACTIONS

Reaction	Activation energy, kcal, with Y equal to		
	Cl	Br	I
$Y + H_2 \rightarrow HY + H$	6.0	17.6	34.2
$H + Y_2 \rightarrow HY + Y$	2–3.6	1.2	0
$H + HY \rightarrow H_2 + Y$	5 0	1 2	1.5

that reaction (6) has no activation energy. The activation energy of the over-all process in the absence of oxygen was found to be 5.8 to 5.9 kcal,[1] in excellent agreement with the result of the direct method.

The activation energy of the reverse reaction, $H + HCl \rightarrow Cl + H_2$, is found from the above value and the heat of the reaction, which is 1.0 kcal; the activation energy of the reaction is therefore 5 kcal.

The energy of activation for the reaction $H + Cl_2 \rightarrow HCl + Cl$ cannot be arrived at with the same degree of precision. The reaction is so rapid that direct measurement cannot be carried out, and the value must be obtained from an analysis of the over-all rate. The rate of formation of hydrogen chloride in the presence of excess of oxygen is given approximately by [*cf.* Eq. (13)]

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{(2k_3/k_4)[\mathrm{Cl_2}]I}{[\mathrm{O_2}]} \tag{27}$$

so that the activation energy under these circumstances is a measure of $E_3 - E_4$. This gives a value of about 2 kcal,[2] so that (since E_4 cannot be

[1] E. Hertel, *Z. physik. Chem.*, **B, 15,** 325 (1931); J. C. Potts and G. K. Rollefson, *J. Am. Chem. Soc.*, **57,** 1027 (1935).

[2] Hertel, *loc. cit.*; M. Padoa and C. Butironi, *Atti Line.*, **25,** 215 (1916); *Gazz chim. ital*, **47,** 6 (1917); F. Porter, D. C. Bardwell, and S. C. Lind, *J. Am. Chem. Soc.*, **48,** 2603 (1926).

negative) a lower limit of 2 kcal can be assumed for E_3. A similar lower limit was given by Krauskopf and Rollefson[1] on the basis of a determination of the relative amount of water formed in experiments with oxygen present.

An upper limit for the activation energy may be determined from the experimental fact that there is no measurable inhibition of the reaction by hydrogen chloride, in contrast with the situation with the hydrogen-bromine reaction. This implies that the reaction $H + HCl \rightarrow H_2 + Cl$ proceeds at least 100 times as slowly as $H + Cl_2 \rightarrow HCl + H$, from which, assuming equal frequency factors, it can be concluded that the activation energies differ by at least 1.4 kcal. Since the activation energy for the former reaction is 5.0 kcal, it follows that that for $H + Cl_2 \rightarrow HCl + Cl$ is less than 3.6 kcal. The value must therefore be between 2 and 3.6 kcal.

The rate of the chain-ending process $H + O_2$ has also been investigated. The activation energy of the process is certainly very small; it has been seen to be 2 kcal less than that of the reaction $H + Cl_2 \rightarrow HCl + Cl$, the energy for which must be less than 3.6 kcal; consequently the energy of activation for $H + O_2$ is not greater than 1.6 kcal. Since the activation energy of this reaction is 2 kcal less than that of $H + Cl_2$, it might be expected to proceed about fifty times as fast, but Bodenstein and Schenck[2] found experimentally that it actually occurs with about one-twentieth of the speed. This implies that only 1 collision in 1,000 of the collisions with sufficient energy of activation is effective, and this suggests that a third body is necessary; as has been seen, the ratio of trimolecular to bimolecular collisions is, on the basis of collision theory, which is probably applicable to these simple reactions, of the order of 1:1,000. That the process involves a third body has been shown directly by Bates and his coworkers,[3] who studied the inhibition of the photodecomposition of HI in the presence of oxygen.

Comparison of the Hydrogen-Halogen Reactions. The reaction scheme proposed for the hydrogen-chlorine reaction differs in several important respects from that for the hydrogen-bromine reaction. Now that the activation energies are known, the reason for the differences can easily be seen; reference may be made to Table 38, in which the activation energies are compared, and to pages 204 and 210, where the reaction schemes are given. The main differences are seen to be (1) the inclusion of the reaction $H + HBr \rightarrow H_2 + Br$ and the exclusion of $H + HCl \rightarrow H_2 + Cl$, and (2) the different chain-terminating steps, $Br + Br \rightarrow Br_2$ being assumed for bromine and the three processes $H + O_2$, $Cl + O_2$, and $Cl + X$ in the chlorine reaction.

[1] K. B. Krauskopf and G. K. Rollefson, *ibid.*, **56**, 327 (1934).

[2] M. Bodenstein and P. W. Schenck, *Z. physik. Chem.*, **B, 20**, 420 (1933).

[3] J. R. Bates and G. I. Lavin, *J. Am. Chem. Soc.*, **55**, 81 (1933); G. A. Cook and J. R. Bates, *ibid.*, **57**, 1775 (1935).

The reason for neglecting the reaction $H + HCl \rightarrow H_2 + Cl$ is seen from the activation energies given in Table 38. The reaction will proceed at a negligible speed in comparison with $H + Cl_2 \rightarrow HCl + Cl$, the activation energy being 2 to 3 kcal greater; the fact that there is no inhibition by HCl was in fact used to obtain a value for this activation-energy difference. In the bromine reaction, on the other hand, $H + Br_2$ and $H + HBr$ proceed at comparable speeds, so that the latter reaction is significant and hydrogen bromide inhibits the reaction.

The reaction $H + O_2$ is significant in the chlorine reaction because its speed is one-twentieth of that of $H + Cl_2$. Since the reaction $H + Br_2$ is appreciably faster than $H + Cl_2$, the activation energy being 1 to 2 kcal less, the $H + O_2$ reaction is negligible as compared with $H + Br_2$. The same applies to the other chain-ending processes $Cl + O_2$ and $Cl + X$, which are also probably three-body reactions. On the other hand $Br + Br$ is the only significant chain-ending process in the case of the bromine reaction. It is as a result of this fact that the photochemical rate is proportional to the square root of the light intensity, the concentration of bromine atoms being proportional to this.

There is, however, evidence that under certain circumstances the reaction $Cl + Cl \rightarrow Cl_2$ may be the most important chain-breaking process. Thus Ritchie and Norrish,[1] working with oxygen-free mixtures, found a dependence of the rate on the 0.6 power of the light intensity, and an exponent of 0.5 was found by Potts and Rollefson[2] and more recently by Kramer and Moignard.[3] Another variation found by Ritchie and Norrish was inhibition by hydrogen chloride in oxygen-free mixtures, and this may be due to the occurrence of the reaction $H + HCl$ on the surface of the vessel.

It is clear that the rather marked differences between the reactions of chlorine, bromine, and iodine with hydrogen are due to differences between activation energies of elementary processes, and a theoretical treatment of the problem[4] has contributed toward an understanding of it; in particular it explains why the hydrogen-iodine reaction is elementary while the others are not. In Table 39 the calculated values of the activation energies of the relevant elementary processes are collected.

Consider first the reaction between hydrogen and iodine; the calculated value for the molecular reaction is 48 kcal, which is somewhat higher than the experimental value of 40 kcal. In order for reaction to proceed by a radical mechanism, the initial step would be $\frac{1}{2}I_2 \rightarrow I$, which requires 17

[1] M. Ritchie and R. G. W. Norrish, *Proc. Roy. Soc.* (*London*), **A, 140,** 112, 713 (1933).

[2] Potts and Rollefson, *loc. cit.*

[3] W. J. Kramer and L. A. Moignard, *Trans. Faraday Soc.*, **45,** 903 (1949).

[4] A. Wheeler, B. Topley, and H. Eyring, *J. Chem. Phys.*, **4,** 178 (1936).

kcal, for the production of 1 mole of iodine atoms, and this would have to be followed by the third and fourth reactions for the production of 2 moles of hydrogen iodide. The activation energy for the over-all process is therefore 40 + 17 + 0 = 57 kcal, and since this is higher than that for the molecular mechanism, the latter will predominate, as is found to be the case.

The situation is otherwise with chlorine and bromine. With chlorine the calculated activation energy for the elementary molecular process is 50 kcal, while that for the production of two molecules of hydrogen chloride by the atomic mechanism is 28 + 8 + 0 = 36 kcal. The atomic mechanism will therefore predominate; the reaction therefore involves free atoms, and the kinetics are relatively complicated, owing to the number of stages involved. The atomic mechanism also predominates in the case of the

TABLE 39. CALCULATED ACTIVATION ENERGIES OF THE HYDROGEN-HALOGEN REACTIONS

Reaction	Activation energy, kcal, with Y equal to		
	Cl	Br	I
$H_2 + Y_2 \rightarrow 2HY$	50	45	48
$\frac{1}{2}Y_2 \rightarrow Y$ ..	28	23	17
$Y + H_2 \rightarrow YH + H$.	8	18	40
$H + Y_2 \rightarrow HY + Y$	0	0	0
Sum of three last values	36	41	57

hydrogen-bromine reaction, the activation energy being 23 + 18 + 0 = 41 kcal, as compared with 45 kcal for the molecular process.

Formation and decomposition of phosgene

Another reaction whose mechanism is fairly well understood is that represented by the over-all equation

$$CO + Cl_2 = COCl_2$$

The rates of formation and decomposition of phosgene have been investigated by Christiansen[1] and more accurately by Bodenstein and Plaut,[2] who obtained results in essential agreement.

The rate of formation of phosgene was found to obey the equation

$$\frac{d[COCl_2]}{dt} = k[Cl_2]^{3/2}[CO] \qquad (28)$$

[1] J. A. Christiansen, *Z. physik. Chem.*, **103**, 99 (1922).
[2] M. Bodenstein and H. Plaut, *ibid.*, **110**, 399 (1924).

and the rate of its decomposition obeyed the equation

$$-\frac{d[COCl_2]}{dt} = k'[Cl_2]^{1/2}[COCl_2] \tag{29}$$

Equating these rates gives the expression for the equilibrium constant

$$K = \frac{k}{k'} = \frac{[COCl_2]}{[CO][Cl_2]} \tag{30}$$

the value of which was determined as a function of the temperature. The specific rates and activation energies of both reactions were also determined.

The expressions for the rates show that the mechanisms are complex, and in particular the presence of the concentration of chlorine molecules to the one-half and three-halves powers indicates that chlorine atoms play a part in the reactions. Bodenstein and Plaut point out that the observed results can be explained equally well in terms of two alternative mechanisms, one of which involves the intermediate formation of COCl and the other of Cl_3. The first scheme may be represented by

(1) $\quad Cl_2 \rightleftharpoons 2Cl$

(2) $\quad Cl + CO \rightleftharpoons COCl$

(3) $\quad COCl + Cl_2 \rightleftharpoons COCl_2 + Cl$

Processes (1) and (2) are supposed to be rapid in both directions, and in addition process (2) involves a third body. The equilibria expressed in reactions (1) and (2) may be written as

$$\frac{[Cl]^2}{[Cl_2]} = K_1 \tag{31}$$

and

$$\frac{[COCl]}{[CO][Cl]} = K_2 \tag{32}$$

Solving for [COCl] and [Cl] gives

$$[COCl] = K_1^{1/2}K_2[CO][Cl_2]^{1/2} \tag{33}$$

and

$$[Cl] = K_1^{1/2}[Cl_2]^{1/2} \tag{34}$$

Since the rate of formation of phosgene is controlled by reaction (3), the specific rate for which may be written as k_3, the over-all rate is given by

$$\frac{d[COCl_2]}{dt} = k_3[COCl][Cl_2] \tag{35}$$

$$= k_3K_1^{1/2}K_2[CO][Cl_2]^{3/2} \tag{36}$$

which is of the same form as Eq. (28). The rate of decomposition of phosgene is similarly given by

$$-\frac{d[COCl_2]}{dt} = k_{-3}[COCl_2][Cl] \tag{37}$$

$$= k_{-3}K_1^{1/2}[COCl_2][Cl_2]^{1/2} \tag{38}$$

which agrees with Eq. (29).

The alternative scheme for the reaction may be represented by

(1) $Cl_2 \rightleftharpoons 2Cl$

(2) $Cl + Cl_2 \rightleftharpoons Cl_3$

(3) $Cl_3 + CO \rightleftharpoons COCl_2 + Cl$

Again the rate of reaction is supposed to be controlled by reaction (3), reactions (1) and (2) being postulated to be rapid in both directions. The treatment is very similar to the one just given and gives rise to kinetic equations of the right form.

On the basis of the thermal reactions alone, a decision cannot be made between the two possible mechanisms. However investigations of the photochemical formation of phosgene[1] suggest that COCl is a more probable intermediate than Cl_3.

Thermal decomposition of nitrogen pentoxide

The experimental methods employed by Daniels and Johnston[2] to study the decomposition of nitrogen pentoxide,

$$2N_2O_5 = 2N_2O_4 + O_2$$

were discussed in Chap. 2 (p. 38). The reaction was the first homogeneous first-order reaction to be investigated, and it was not for four years (in 1925) that another example of this class was found. The reaction consequently played a very important role in the development of the theory of the rates of reactions, and only recently has an important feature of it been elucidated.

Since the original investigation of Daniels and Johnston a great many studies have been made on the reaction, and the main conclusions of these may be outlined briefly. The question of whether the rate of the reaction is influenced by the walls of the vessel or by the presence of impurities has been investigated very thoroughly, with the result that it appears that the decomposition is uncatalyzed. Part of the evidence for this is given by the fact that excellent agreement between the results of different investiga-

[1] M. Bodenstein, S Lenher, and C. Wagner, *ibid.*, **B, 3,** 459 (1929); M. Bodenstein, W. Brenschade, and H. J. Schumacher, *ibid* , **B, 28,** 81 (1935); **B, 40,** 120 (1938).

[2] F. Daniels and E. H. Johnston, *J. Am. Chem. Soc.*, **43,** 53 (1921).

tions has been obtained, in spite of the use of different types of vessels and of different methods of purifying the pentoxide.[1] Rice and Getz[2] made a special study of the possible influence of catalysts. Their rates agreed with those of Daniels and Johnston within the limits of experimental error, and they also found no change in the rate if the gases were carefully freed from dust or were thoroughly dried with phosphorus pentoxide. Various methods of preparing the pentoxide were employed in this work, with no effect on the rate. Hirst[3] found that argon had no influence, while Hunt and Daniels[4] found the same negative result with a large excess of nitrogen. Busse and Daniels[5] found that hydrogen, bromine, chlorine, and other substances were without influence. In this connection the results of the influence of various solvents, discussed on page 113, are very relevant. Lueck[6] and Eyring and Daniels[7] found very little variation in the rate in a variety of solvents; this is a much more stringent test of the effect of foreign materials, owing to the high concentration involved. On the whole it may therefore be said that foreign substances have little or no influence on the kinetics of the reaction.

Ozone is one substance which does influence the kinetics, and its effect was at one time not clear. Ozone ensures the complete absence of lower oxides of nitrogen by oxidizing them rapidly to nitrogen pentoxide; consequently it was expected that in the presence of ozone there should be no net decomposition until the ozone had been used up, after which the reaction should proceed normally. However, Daniels, Wulf, and Karrer[8] reported that no decomposition proceeds even after the ozone is used up, a result which suggests that pure nitrogen pentoxide cannot decompose but that a lower oxide must be present initially. On the other hand, Hirst[9] and White and Tolman[10] found the opposite result that after the ozone was used up, the decomposition took place at the same rate as in the original experiments of Daniels and Johnston; the results of Daniels, Wulf, and Karrer therefore seem to be in error. Schumacher and Sprenger[11] further clarified the influence of ozone, showing that it oxidizes nitrogen dioxide to nitrogen trioxide, which reacts with another nitrogen dioxide molecule to give nitro-

[1] H. S. Hirst, *J. Chem. Soc.*, **127**, 657 (1925); E. C. White and R. C. Tolman, *J. Am. Chem. Soc.*, **47**, 1240 (1925).

[2] F. O. Rice and D. Getz, *J. Phys Chem.*, **31**, 1572 (1927).

[3] Hirst, *loc. cit.*

[4] J. K. Hunt and F. Daniels, *J. Am. Chem. Soc.*, **47**, 1602 (1925).

[5] W F Busse and F. Daniels, *ibid*, **49**, 1257 (1927).

[6] R. H. Lueck, *ibid*, **44**, 757 (1922).

[7] H Eyring and F Daniels, *ibid.*, **52**, 1472, 1486 (1930).

[8] F. Daniels, O. R. Wulf, and S. Karrer, *ibid.*, **44**, 2402 (1922).

[9] Hirst, *loc. cit.*

[10] White and Tolman, *loc. cit.*

[11] H. J. Schumacher and G. Sprenger, *Z. physik. Chem.*, **A, 140**, 281 (1929).

gen pentoxide. When the ozone is exhausted, they, too, found that the reaction proceeded normally.

The kinetics of the decomposition at very low pressures have been investigated carefully by a number of investigators. The importance of this study is in connection with the Lindemann theory of unimolecular reactions. According to this theory, the order of the reaction should become the second at very low pressures, and at such pressures there should be a falling off of the first-order rate "constant." Hirst and Rideal,[1] who were the first to investigate this experimentally, reported that the rate constant rises at low pressures, but Hibben[2] found no change in the constant down to 0.0018 mm pressure. Sprenger,[3] on the other hand, reported that the reaction stopped completely at 0.01 mm pressure. This confused situation has now become clarified on the experimental side by exhaustive studies carried out in a number of laboratories. Ramsperger, Nordberg, and Tolman[4] found that the high-pressure rate constant is maintained down to 0.05 mm but falls at lower pressures and has reached about half its value at 0.005 mm. This result was approximately confirmed in a later investigation by Schumacher and Sprenger,[5] who failed to find the stopping of the reaction previously reported by Sprenger. Hodges and Linhorst[6] also found a falling off of the rate at 0.06 mm and report that below 0.004 mm the reaction approximately obeys a second-order law. The investigations at very low pressures are complicated by adsorption of the nitrogen pentoxide on the walls of the vessel, but on the whole it seems to have been established that a falling off really occurs. Another complication reported by Ramsperger and Tolman is that the ratio of final to initial pressures is, in the low-pressure experiments, less that 2.5, which corresponds to the change $2N_2O_5 = 4NO_2 + O_2$; this is probably due to the greater importance of the dissociation $N_2O_5 = NO_2 + NO_3$ at these pressures.

The fact that there is a falling off of the rate constant at low pressures does not, however, constitute evidence for the Lindemann theory, since the falling off takes place at much too low a pressure. According to the theory, the pressure at which the falling off occurs depends on the molecular diameter and the number of degrees of freedom contributing to the vibration of the molecule. Even the most favorable assumption as to the values of

[1] H. S. Hirst and E. K. Rideal, *Proc. Roy Soc* (*London*), **A, 109,** 526 (1925).

[2] J. H. Hibben, *Proc. Natl. Acad. Sci. U.S.*, **13,** 626 (1927); *J Am. Chem. Soc*, **50,** 940 (1928).

[3] G. Sprenger, *Z. physik. Chem.*, **136,** 49 (1928).

[4] H. C. Ramsperger, M. E. Nordberg, and R. C. Tolman, *Proc. Natl. Acad. Sci. U.S.*, **15,** 453 (1929); H. C. Ramsperger and R. C. Tolman, *ibid.*, **16,** 6 (1930).

[5] H J. Schumacher and G. Sprenger, *ibid.*, 129.

[6] J. H. Hodges and E. F. Linhorst, *ibid.*, **17,** 28 (1931); *J. Am. Chem. Soc.*, **56,** 836 (1934).

these quantities leads to the conclusion that an appreciable change in the constant should have occurred at a pressure of 0.1 mm, and this is certainly not the case. All attempts to explain this result by modifying the Lindemann theory or stretching the experimental data ended in failure. A more plausible explanation will be mentioned later.

The stoichiometric equation for the decomposition, $2N_2O_5 = 2N_2O_4 + O_2$, involves two molecules of N_2O_5 on the left-hand side and therefore cannot represent the mechanism of the process, which is unimolecular. Various initial steps involving only one molecule of N_2O_5 have been considered, and the process

$$N_2O_5 \rightarrow N_2O_3 + O_2$$

first proposed by Busse and Daniels,[1] was accepted for some time. However, it can be shown on theoretical grounds (*cf.* p. 387) that this reaction, which involves a change in spin angular momentum, would occur very slowly, and an alternative initial step is necessary. Two other possibilities are

$$N_2O_5 \rightarrow N_2O_4 + O$$

and

$$N_2O_5 \rightarrow NO_2 + NO_3$$

of which the first can be excluded on energetic grounds. The second has been accepted by Ogg[2] as the basis of a mechanism which has the additional advantage of explaining the failure of the rate to fall off at low pressures in the manner predicted by a simple application of the Lindemann theory. The existence of NO_3 as an intermediate is also suggested from an analysis of other reactions.

The mechanism suggested by Ogg is as follows:

(1) $N_2O_5 \rightarrow NO_2 + NO_3$

(2) $NO_2 + NO_3 \rightarrow N_2O_5$

(3) $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$

(4) $NO + N_2O_5 \rightarrow 3NO_2$

According to this scheme, NO_2 and NO_3 react to give the alternative products N_2O_5 and $NO_2 + O_2 + NO$. The activation energy for reaction (2) is probably zero or very small, as it resembles a radical-recombination reaction, but reaction (3) is endothermic and consequently has an activation energy. It follows that k_3 is very much less than k_2, and consequently reaction (3) controls the rate of the decomposition. Calculation of the

[1] Busse and Daniels, *loc. cit.*

[2] R. A. Ogg, *J. Chem. Phys.*, **15**, 337 (1947).

steady concentration of NO_3, and substitution of the value in the expression for the rate of (3), consequently gives the rate of the over-all reaction.

The steady-state treatment for NO_3 gives

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_3][NO_2] - k_3[NO_3][NO_2] = 0 \qquad (39)$$

whence

$$[NO_3] = \frac{k_1[N_2O_5]}{(k_2 + k_3)[NO_2]} \qquad (40)$$

Every time a molecule of NO_3 reacts with one of NO_2 to give $NO_2 + O_2 + NO$, two molecules of N_2O_5 are decomposed, since the NO molecule produced decomposes an extra N_2O_5 molecule by reaction (4); consequently

$$-\frac{d[N_2O_5]}{dt} = 2k_3[NO_3][NO_2] \qquad (41)$$

$$= \frac{2k_1k_3[N_2O_5]}{k_2 + k_3} \qquad (42)$$

or approximately

$$-\frac{d[N_2O_5]}{dt} = \frac{2k_1k_3[N_2O_5]}{k_2} \qquad (43)$$

since $k_2 \gg k_3$. The theory thus accounts for the fact that the reaction is of the first order, in spite of the fact that the rate-controlling step is the second-order reaction (3). Moreover, the apparent first-order rate constant, $2k_1k_3/k_2$, is the product of an equilibrium constant, k_1/k_2, and a second-order rate constant, k_3. The Lindemann theory would therefore not apply to it, so that the fact that the constant does not fall off at the pressure predicted by this theory is explained; the actual falling off obtained at lower pressures must be due to a change of mechanism under these conditions.

The mechanism proposed is consistent with the known thermochemical values. The energy of activation of the reaction is clearly $E_1 + E_3 - E_2$, so that as the observed value is 24.6 kcal.

$$E_1 + E_3 - E_2 = 24.6 \text{ kcal} \qquad (44)$$

Addition of the reactions (1) and (3) gives

$$N_2O_5 = NO_2 + O_2 + NO$$

so that $E_1 + E_3$ must be not less than the total energy change in this reaction, known to be 24.3 kcal, *i.e.*,

$$E_1 + E_3 \geqslant 24.3 \text{ kcal} \qquad (45)$$

Assuming, as is probable, that $E_2 \approx 0$, it follows from (44) that

$$E_1 + E_3 \approx 24.6 \text{ kcal} \tag{46}$$

which is consistent with (45). The value of E_1 is probably about 20 kcal, so that E_3 is about 5 kcal; since E_2 is close to zero, these values are consistent with the fact that reaction (3) is very slow compared with (2).

Thermal decomposition of ozone

The decomposition of ozone has been very extensively investigated, but the details of the reaction are by no means understood. The principal difficulty is that under most conditions a wall reaction occurs together with the homogeneous change, and the two processes are difficult to separate.

In early investigations Chapman and coworkers[1] studied the reaction under conditions in which it was shown to be largely homogeneous and concluded that the reaction is of the second order. It was later found[2] that the rate of decomposition was inversely proportional to the pressure of oxygen present, and to account for this and for the order of the reaction, Jahn[3] proposed the mechanism

(1) $$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

(2) $$O + O_3 \xrightarrow{k_2} 2O_2$$

Application of the steady-state treatment to this gives

$$k_1[O_3] - k_{-1}[O][O_2] - k_2[O][O_3] = 0 \tag{47}$$

whence

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2] + k_2[O_3]} \tag{48}$$

The rate of decomposition of ozone is thus given by

$$-\frac{d[O_3]}{dt} = k_1[O_3] - k_{-1}[O_2][O] + k_2[O][O_3] \tag{49}$$

$$= \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]} \tag{50}$$

Except at the very beginning of the reaction, when $[O_2]$ is small, the condi-

[1] D. L. Chapman and H. E. Clarke, *J. Chem Soc.*, **93**, 1638 (1908); D L Chapman and H E. Jones, *ibid.*, **97**, 2463 (1910); *cf* E G Warberg, *Sitzber. kgl. preuss. Akad Wiss.*, **48**, 1126 (1901).

[2] S. Jahn, *Z. anorg. Chem.*, **48**, 260 (1906); E. P. Perman and R. H. Greaves, *Proc. Roy. Soc. (London)*, **80**, 353 (1908).

[3] Jahn, *loc. cit.*

tion $k_{-1}[O_2] \gg k_2[O_3]$ holds, since the activation energy of $O + O_2$ is zero,[1] while that of $O + O_3 \rightarrow 2O_2$ is probably about 5 kcal. The rate is then given approximately by

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2]} \tag{51}$$

in agreement with the experimental results. It would appear in the light of later work that this simple scheme is probably quite satisfactory for the purely homogeneous part of the reaction.

The energy of activation of the homogeneous reaction was given as 26 kcal by Clement,[2] as 27.8 kcal by Belton, Griffith, and McKeown,[3] and as 29.6 kcal by Wulf and Tolman;[4] according to the latter workers the rate can be represented by the equation

$$-\frac{d[O_3]}{dt} = \frac{[O_3]^2}{[O_2]} 5.89 \times 10^{13} T^{1/2} e^{-29,600/RT} \tag{52}$$

Reaction (1) is endothermic by 24.6 kcal, so that the difference between this value and the over-all activation energy, *i.e.*, 5 kcal, is the activation energy for reaction (2). The frequency factor $5.89 \times 10^{13}T^{1/2}$ is considerably higher than for most second-order reactions, and on the basis of this type of argument Wulf and Tolman rejected the Jahn mechanism. However later calculations by Wulf[5] indicated that the mechanism was possible and indeed likely; reaction (1) has a large entropy of reaction, so that the entropy of activation for the over-all process may be larger than usual.

Investigations by Riesenfeld and Bohnholtzer[6] and by Riesenfeld and Schumacher[7] indicated that first-order and second-order reactions are taking place simultaneously, the former predominating at low pressures. The first-order reaction was found to be considerably influenced by the surface and is probably largely a heterogeneous reaction; the second-order reaction, on the other hand, probably occurs entirely in the gas phase. This simultaneous occurrence of reactions of different orders accounts for the conflicting results that have been obtained on the reaction.

[1] U. Beretta and H. J. Schumacher, *Z. physik. Chem.*, **B, 17,** 417 (1932); W. F. Jackson, *J. Am. Chem. Soc.*, **56,** 2631 (1934); W. Groth, *Z. physik. Chem.*, **B, 37,** 315 (1937).

[2] J. K. Clement, *Ann. Physik.* **IV, 14,** 341 (1904).

[3] J. W. Belton, R. O. Griffith, and A. McKeown, *J. Chem. Soc.*, **128,** 3153 (1926).

[4] O R. Wulf and R. C. Tolman, *J. Am. Chem. Soc.*, **49,** 1183, 1202, 1650 (1927).

[5] O. R. Wulf, *ibid.*, **54,** 156 (1932).

[6] E. H. Riesenfeld and W. Bohnholtzer, *Z. physik. Chem.*, **130,** 241 (1927).

[7] E. H. Riesenfeld and H. J. Schumacher, *ibid.*, **138,** 268 (1928).

The decomposition has also been investigated[1] in carbon tetrachloride solution, where it follows simple first-order kinetics, complicated somewhat by reaction with the solvent. The activation energy is 26.2 kcal, slightly lower than in the gas phase. This behavior suggests that the rate is now controlled by reaction (1), the subsequent reaction (2) being suppressed by reaction of oxygen atoms with the solvent. The chlorine-catalyzed decomposition is discussed on page 312.

Thermal para-ortho hydrogen conversion

The conversion of *p*-hydrogen into *o*-hydrogen is found to take place homogeneously, the rate being convenient to measure between 700 and 800°C.[2] The order of the reaction is three-halves, suggesting the mechanism

(1) $$H_2 \rightarrow 2H$$

(2) $$H + p\text{-}H_2 \rightarrow o\text{-}H_2 + H$$

The concentration of hydrogen atoms is in accordance with the equilibrium equation

$$[H]^2 = K[H_2] \tag{53}$$

since there is no net change in the number of hydrogen atoms when reaction (2) occurs. The rate of the conversion is therefore

$$\frac{d[o\text{-}H_2]}{dt} = k_2[H][p\text{-}H_2] \tag{54}$$

$$= k_2 K^{1/2}[H_2]^{3/2} \tag{55}$$

The activation energy of the process is seen to be given by

$$E = E_2 + \tfrac{1}{2}D \tag{56}$$

where D is the dissociation energy of hydrogen and has the value of approximately 52 kcal. Since E_2 can be shown by direct measurement to be about 7 kcal (*cf.* p. 46), it follows that the over-all activation energy should be 59 kcal. The fact that the experimental value is close to this is strong support for the mechanism.

Reactions of the alkali-metal atoms

One group of reactions whose mechanisms are fairly well understood are the reactions between an alkali metal and either a halogen or a halide.

[1] E. J. Bowen, E. A. Moelwyn-Hughes, and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A, 134,** 211 (1931).

[2] K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B, 4,** 119 (1929); A. Farkas, *Z. Elektrochem.*, **36,** 782 (1930); *Z. physik. Chem.*, **B, 10,** 419 (1930); A. Farkas and L. Farkas, *Proc. Roy. Soc. (London)*, **A, 162,** 124 (1935).

Most of the work has been done with sodium, and the reactions studied fall into one of three classes according to the nature of the other reacting substance; this may be (1) a halogen, (2) an inorganic halide, and (3) an organic halide. The reactions in the first two classes, which will be treated in the present section, are always accompanied by the emission of radiation, which in the case of sodium corresponds to the sodium D line. The reactions of the third class emit appreciable radiation only when the organic halide contains more than one halogen atom.

Highly Dilute Flames. The reactions of the first two classes have for the most part been investigated by a modification, due to Polanyi and his collaborators,[1] of the ordinary flow method; the procedure is commonly known as the method of highly dilute flames. The two reactants are passed into a tube from opposite ends, the pressure within the tube being kept so low that the mean free paths are greater than the tube diameter. Under these conditions the gases mix by diffusion. The products of the reaction are solids, which are deposited on the vessel walls, and as each gas reacts, its partial pressure falls to zero, as represented diagramatically in Fig. 25, in which the reacting substances are represented by A and B. If the reaction is of the first order with respect to both A and B, the rate of the reaction is proportional to the product of their pressures $p_A p_B$, which is also represented in the figure. The form of the curve $p_A p_B$ can be determined, if the product is a solid, from the thickness of the deposit at various points on the wall of the tube, and the specific rate of the reaction is related to the half breadth of the curve. The more rapid the reaction is, the smaller will be the half breadth: the exact relationship is

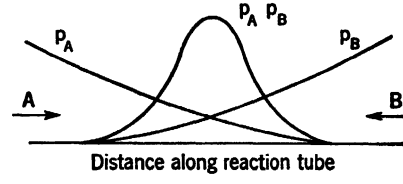


FIG. 25 The method of highly dilute flames: variation of the partial pressures of the entering gases, and of their product, with distance along the tube.

$$k = \frac{27}{2b^3 q U k_A k_B} \tag{57}$$

where k is the specific rate, b the half breadth, U the amount of decomposition in moles per liter, and k_A and k_B are the diffusion resistances of the two gases. By using this method, combined with studies of the luminescence accompanying the reactions, Polanyi and his coworkers obtained much information about the rates and mechanisms of these reactions. The

[1] H. Beutler, S. von Bogdandy, and M. Polanyi, *Naturwissenschaften*, **14**, 164 (1926); H. Beutler and M. Polanyi, *ibid*, **13**, 711 (1925); *Z. physik*, **47**, 379 (1928); S. von Bogdandy and M. Polanyi, *Z. physik. Chem.*, **B, 1**, 21 (1928); M. Polanyi, "Atomic Reactions," Williams and Norgate, London, 1932.

method is directly applicable to those reactions which have zero activation energy; for those having an appreciable activation energy a further modification, known as the method of diffusion flames, is necessary.

Alkali-metal–Halogen Reactions. The reaction between sodium and chlorine will be taken as typical of the reactions of the first class. The first step is believed to be

$$\text{(1)} \qquad \text{Na} + \text{Cl}_2 \rightarrow \text{NaCl} + \text{Cl}$$

since the over-all rate of the reaction is almost exactly equal to the calculated rate for such a reaction on the basis of standard kinetic-theory diameters and a zero energy of activation. Other possible initial reactions such as $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$ and $\text{Na}_2 + \text{Cl}_2 \rightarrow 2\text{NaCl}$ can be excluded as they would occur much too slowly. Moreover the presence of chlorine atoms in the reaction has been confirmed by direct chemical evidence. Since the radiation emitted in the reaction corresponds to the D line, the sodium atoms must be excited to their ^2P states, a process which requires 48.3 kcal; the heat liberated in reaction (1) is only 40.7 kcal, so that further reactions must be involved.

The chlorine atom produced in reaction (1) may react with a sodium atom, but at an appreciable rate only in the presence of a third body, which may be the vessel wall. A more rapid process is reaction with diatomic sodium molecules, which at the temperatures involved are present in appreciable concentrations. The reaction is

$$\text{(2)} \qquad \text{Na}_2 + \text{Cl} \rightarrow \text{NaCl} + \text{Na}$$

which liberates 80 kcal of heat, sufficient to bring about excitation of a sodium atom. Further and more direct evidence for the reaction is that the intensity of the luminescence diminishes with increase of temperature, owing to the dissociation of the sodium molecules. The decrease is exponential; a plot of the logarithm of the intensity against the reciprocal of the absolute temperature gives a straight line, the slope of which gives an energy of 18.0 kcal, in excellent agreement with the directly determined value[1] of the dissociation energy of diatomic sodium. An additional piece of evidence is that the intensity varies with the square of the total sodium pressure, the concentration of Na_2 being proportional to this.

Since the energy liberated in reaction (2) is sufficient to excite a sodium atom, it might be expected that the sodium atom produced in the reaction would be excited. Quenching experiments with inert gases, particularly nitrogen, suggest, however, that this is not the case. The reduction in intensity brought about by the addition of quenching substances is much greater than that which would correspond to collisions between the added

[1] R. Ladenburg and E. Thiele, *Z. physik. Chem.*, **B, 7**, 174 (1930).

materials and the sodium atoms. It is therefore believed that the energy produced in reaction (2) does not pass into the sodium atom but goes into the sodium chloride molecule, which becomes vibrationally excited, the process being represented as

$$(2a) \qquad Na_2 + Cl \rightarrow NaCl' + Na$$

The excited NaCl molecule then transfers its additional energy to a sodium atom by collision,

$$(3) \qquad NaCl' + Na(^2S) \rightarrow NaCl + Na(^2P)$$

the sodium atom being excited electronically. The radiation emitted

TABLE 40 OBSERVED AND CALCULATED SPECIFIC RATES FOR THE REACTIONS $Na + X_2$ AND $X + Na_2$

Reaction	Specific rate, cc $mole^{-1}$ sec^{-1}		
	Observed	Calculated, collision theory	Calculated, activated-complex theory
$Na + Cl_2$	4.1	0.6	4.5
$Na + I_2$	6.1	0.5	6.0
$Cl + Na_2$	1.5	0.56	5.1
$Br + Na_2$	1.5	0.46	3.0
$I + Na_2$	0.26	0.41	2.1

corresponds to the liberation of a photon $h\nu$ by the excited (^2P) sodium atom, which passes into its normal (^2S) state,

$$(4) \qquad Na(^2P) \rightarrow Na(^2S) + h\nu$$

The reason that the effect of quenching is greater than that expected if the quenching substances removed energy only from the $Na(^2P)$ is that the excited sodium chloride molecules exist for a considerable period of time before passing their excess energy on to a sodium atom, and are correspondingly more vulnerable.

The reactions of sodium with bromine and iodine have also been investigated, with very similar results. The rate constants for the reactions corresponding to (1) and (2) have been estimated in each case from the experimental results and are given in Table 40, the units being cubic centimeters per mole per second. Calculated constants, based on the usual kinetic-theory diameters and assuming zero activation energy, are also

given. The reactions have also been treated theoretically by Magee[1] on the basis of the theory of absolute reaction rates. According to the treatment, the interatomic distances in the activated complex are somewhat larger than those given by the kinetic theory, and the calculated rates are therefore higher; the values are included in Table 40 and are shown to be in better agreement with experiment.

Work has also been done using potassium in place of sodium.[2] The results are essentially the same, and the main reactions occurring are believed to be analogous to those with sodium; however, complications arise owing to the greater preponderance of wall reactions, which are responsible for a continuum as well as the two potassium lines which are observed. The rates of the main reactions are approximately those given by collision theory using zero activation energy.

Alkali-metal–Halide Reactions. The reactions of this class which have been investigated involve as the halides mercuric chloride and bromide, cadmium chloride, and hydrogen chloride, bromide, and iodide. The reaction with mercuric chloride may be regarded as typical of the reactions involving the metal halides,[3] and the primary process is believed to be

$$\text{(1)} \qquad \text{Na} + \text{HgCl}_2 \rightarrow \text{NaCl} + \text{HgCl}$$

The energy liberated in this process, 25 kcal, is as before insufficient to excite a sodium atom. The over-all rate of the reaction is of the same order (actually, as before, a little greater) as that predicted by collision theory with zero activation energy. If these reactions were analogous to those involving the halogens themselves, the radical HgCl produced in the above reaction would react with an Na_2 molecule; however this does not occur, since the temperature and pressure effects found with the halogen reactions are here not observed. It is therefore believed that the second stage in the process is reaction with a sodium atom,

$$\text{(2)} \qquad \text{Na} + \text{HgCl} \rightarrow \text{NaCl}' + \text{Hg}$$

which is exothermic by 63 kcal. Some of the energy liberated is carried by the NaCl molecule as vibrational energy and may be transferred on collision to a sodium atom, which becomes excited to the ^2P electronic state,

$$\text{(3)} \qquad \text{NaCl}' + \text{Na}(^2S) \rightarrow \text{NaCl} + \text{Na}(^2P)$$

[1] J. L. Magee, *J. Chem. Phys.*, **8**, 687 (1940).

[2] H. Otouka, *Z. physik. Chem.*, **B, 7**, 422 (1930); M. Krocsak and G. Schay, *ibid.*, **B, 19**, 344 (1932); E. Roth and G. Schay, *ibid.*, **B, 28**, 323 (1935).

[3] St. von Bogdandy and M. Polanyi, *ibid* , **B, 1**, 21 (1928); H. Ootuka and G. Schay, *ibid.*, 68; Ootuka, *op. cit.*, 407; E. Horn, M. Polanyi, and H. Sattler, *Z. physik. Chem.*, **B, 17**, 220 (1932); J. Berger and G. Schay, *ibid.*, **B, 28**, 332 (1935).

These reactions occur with less luminescence than the reactions with the halogens.

The reactions between sodium and the hydrogen halides[1] are not so well understood. The first step in the case of hydrogen chloride appears to be

$$(1) \qquad Na + HCl \rightarrow NaCl + H - 5.2 \text{ kcal}$$

which, being endothermic, necessarily involves an activation energy. From the observed over-all rate of the reaction, and using collision theory, Hartel has found an activation energy of 4.5 kcal and Bawn and Evans one of 6.1 kcal. The values are in satisfactory agreement; the activation energy must be as great as the endothermicity and appears to be approximately equal to it. Bawn and Evans also investigated the reaction between sodium and deuterium chloride and found an activation energy of 6.4 kcal.

The luminescence is assumed to be brought about by subsequent reactions of the hydrogen atoms produced, but the nature of these has not been fully elucidated. The radical NaH may be formed at the walls from H and Na and may react with a second sodium atom with liberation of energy

$$(2) \qquad H + NaH \rightarrow Na + H_2 + 60 \text{ kcal}$$

The energy may pass into the sodium directly, or into the hydrogen and hence by collision into a sodium atom.

PROBLEMS

1. Using Eq. (2) and the following values for the activation energies:

$$E_1 = 45.2 \text{ kcal}, \qquad E_2 = 17.6 \text{ kcal}, \qquad E_3 = 1.2 \text{ kcal},$$

$$E_4 = 1.2 \text{ kcal}, \qquad E_5 = 0 \text{ kcal}$$

obtain the activation energy of the hydrogen-bromine reaction, (*a*) at the beginning of the reaction, (*b*) in the presence of a large excess of hydrogen bromide.

2. The first-order rate constant for the gaseous decomposition of nitrogen pentoxide at 25°C is 3.38×10^{-5} sec^{-1}, and the activation energy is 24.7 kcal. Calculate the frequency factor and the entropy of activation.

[1] G. Schay, *ibid.*, **B, 11,** 291 (1931); H. von Hartel, *ibid.*, **B, 11,** 316 (1931); C. E. H. Bawn and A. G. Evans, *Trans. Faraday Soc.*, **31,** 1391 (1935).

CHAPTER 9

SOME COMPLEX ORGANIC REACTIONS

The reactions of organic substances have been the subject of a very considerable amount of experimental study. Homogeneous gas reactions of this type are almost invariably found to be complex, in that the presence of organic free radicals has been detected, and in many cases specific chain mechanisms have been proposed. In hardly any case is there complete agreement among investigators as to the details of the mechanism, and in arriving at an opinion as to the most probable mechanism in any given case, a great many pieces of evidence have to be taken into consideration. In the present chapter some of the more significant results of the investigations, particularly of thermal and photochemical decompositions of organic molecules, will be presented. In each case the evidence from the over-all reactions will be discussed, followed by a consideration of the work that has been done on the individual reactions that are believed to play a part in the process.[1]

The first suggestion that organic reactions may involve reaction chains seems to have been made in 1925 by Taylor[2] who discussed in particular the mercury-photosensitized reaction between hydrogen and ethylene, the quantum yield for which was greater than unity. The mechanism proposed was

$$\begin{aligned} \mathrm{Hg}(^3P) + \mathrm{H_2} &\rightarrow 2\mathrm{H} + \mathrm{Hg}(^1S) \\ \mathrm{H} + \mathrm{C_2H_4} &\rightarrow \mathrm{C_2H_5} \\ \mathrm{C_2H_5} + \mathrm{H_2} &\rightarrow \mathrm{C_2H_6} + \mathrm{H}, \text{ etc.} \end{aligned}$$

Taylor also found,[3] in support of this mechanism, that the reaction could be sensitized by causing metal alkyls to decompose in the presence of hydrogen and ethylene, the free radicals liberated in the decomposition bringing about reaction.

Many organic reactions, including most decompositions, obey simple kinetic laws, and it was consequently assumed for some time that they

[1] For a more detailed treatment see E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, 1946; "Free Radical Mechanisms," *ibid.*

[2] H. S. Taylor, *Trans. Faraday Soc.*, **21**, 560 (1925).

[3] H. S. Taylor, *Proc. Am. Phil. Soc.*, **65**, 90 (1926).

are elementary processes. However Rice and his coworkers showed that free radicals undoubtedly play an important part in them. An important advance was made in 1934 when Rice and Herzfeld[1] pointed out that complex radical mechanisms may sometimes lead to simple over-all kinetics and proposed specific mechanisms for a number of reactions. The general consensus of opinion is that these mechanisms, or very similar ones, certainly play a significant part in organic reactions but that in most cases a molecular change occurs in addition.

The Rice-Herzfeld mechanisms

The main object of the work of Rice and Herzfeld was to show that the kinetic laws obeyed by many complex reactions, and the products of the reactions, can be explained on the basis of specific free-radical mechanisms; this fact had not previously been realized, since earlier free-radical mechanisms had given rise to kinetic laws that were more complicated than those usually found with organic reactions. At the time the Rice-Herzfeld mechanisms were proposed, detailed investigations of many of the reactions had not been carried out, so that it was necessary to assign hypothetical rates and activation energies to most of the elementary reactions postulated as occurring in the mechanisms. It has therefore been necessary to revise the details of many of the reaction schemes, although the general conclusions are on the whole still valid.

One important point that the mechanism had to cover was that the kinetics were in many cases simple, the reactions frequently having orders of one-half, unity, and three-halves. Another feature of the reactions is that the production of radicals usually involves the rupture of a carbon-carbon bond, which requires rather more than 80 kcal of energy per mole; the over-all activation energy of most of the reactions is, however, considerably less than this. As will be seen, the Rice-Herzfeld mechanisms are consistent with both these points. In particular, the experimental activation energies can be explained in terms of plausible activation energies for the individual elementary processes postulated as playing a part.

The mechanisms proposed will be discussed in a general way, and three cases will be considered, according as the order of the over-all reaction is unity, one-half, or three-halves. It will be seen later that the order is influenced largely by the nature of the initiating and of the chain-ending steps. The case of a mechanism leading to first-order kinetics will be considered first.

First-order Kinetics. The following reaction scheme, which is probably often valid for an organic decomposition, is typical of schemes which give

[1] F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

rise to first-order kinetics. The first step is the dissociation of the reacting molecule M into two radicals and involves the splitting of a carbon-carbon bond:

(1) $$M \rightarrow R_1 + R_1'$$

The radical R_1' is assumed to play no part in the reaction,[1] but R_1 initiates the following chain of reactions:

(2) $$R_1 + M \rightarrow R_1H + R_2$$

(3) $$R_2 \rightarrow R_1 + M'$$

(4) $$R_1 + R_2 \rightarrow M''$$

In reaction (2) the radical R_1 reacts with the original molecule M and removes a hydrogen atom, leaving the new radical R_2. The equivalent C-C bond in R_2 then splits to give the original radical R_1 and the molecule M', which differs from R_1' by lacking a hydrogen atom. Reactions (2) and (3) may be repeated many times, so that a large number of molecules may be decomposed by each radical R_1 formed in the original reaction (1). The number of such molecules is restricted by the chain-breaking reaction (4), which in this case is assumed to be a reaction between R_1 and R_2.

The steady-state expressions for the concentrations of R_1 and R_2 are

$$\frac{d[R_1]}{dt} = k_1[M] - k_2[R_1][M] + k_3[R_2] - k_4[R_1][R_2] = 0 \qquad (1)$$

and

$$\frac{d[R_2]}{dt} = k_2[R_1][M] - k_3[R_2] - k_4[R_1][R_2] = 0 \qquad (2)$$

These give rise to

$$[R_1] = \frac{k_1}{4k_2} + \left[\left(\frac{k_1}{4k_2}\right)^2 + \frac{k_1k_3}{2k_2k_4}\right]^{\frac{1}{2}} \qquad (3)$$

The constant k_1 is very small, since reaction (1) has a very high activation energy, which is at least as great as the strength of the C-C bond. Equation (3) therefore approximates to

$$[R_1] = \left(\frac{k_1k_3}{2k_2k_4}\right)^{\frac{1}{2}} \qquad (4)$$

The over-all rate of decomposition of M is given by

$$-\frac{d[M]}{dt} = k_1[M] + k_2[R_1][M] \qquad (5)$$

[1] Exceptions to this are found in individual cases, which have to be considered separately; thus in the ethane decomposition the original process produces two methyl radicals.

so that, substituting for $[R_1]$,

$$-\frac{d[M]}{dt} = \left[1 + \left(\frac{k_2k_3}{2k_1k_4}\right)^{1/2}\right] k_1[M] \tag{6}$$

Since k_1 and k_4 are small compared with k_2 and k_3, the term in parentheses is large compared with unity, so that the rate is given approximately by

$$-\frac{d[M]}{dt} = \left(\frac{k_1k_2k_3}{2k_4}\right)^{1/2} [M] \tag{7}$$

The reaction is therefore of the first order. If the activation energies for the four steps are E_1, E_2, E_3, and E_4, the activation energy for the over-all process is

$$E = \tfrac{1}{2}(E_1 + E_2 + E_3 - E_4) \tag{8}$$

Since E_1 is usually much larger than E_2 and E_3, the over-all activation energy E is usually appreciably smaller than E_1, in agreement with experiment.

It is seen from the mechanism that the molecule M disappears in two ways: by decomposing into radicals and by attack by a radical. The ratio of the rate of its disappearance to the rate of radical formation by the initial process (1) is the average chain length of the process,

$$\text{Average chain length} = \frac{k_1[M] + k_2[R_1][M]}{k_1[M]} \tag{9}$$

or, approximately,

$$\text{Average chain length} = \frac{k_2[R_1][M]}{k_1[M]} \tag{10}$$

since $k_1[M]$ is much smaller than $k_2[R_1][M]$. Substitution for $[R_1]$ using Eq. (4) gives

$$\text{Average chain length} = \left(\frac{k_2k_3}{2k_1k_4}\right)^{1/2} \tag{11}$$

Three-halves-order Kinetics. The fact that the above scheme of reactions gave rise to first-order kinetics depends upon the particular chain-ending step that was assumed. If, instead of reaction (4), the chains are ended by combination of two radicals of type R_1,

$$(4') \qquad 2R_1 \rightarrow M'''$$

it is found in a similar way that the over-all order of the reaction is three-halves. The concentration of radicals R_1 is found to be

$$[R_1] = \left(\frac{k_1}{k_4'}\right)^{1/2} [M]^{1/2} \tag{12}$$

and the rate of reaction is given by

$$-\frac{d[M]}{dt} = k_1[M] + k_2[R_1][M] \tag{13}$$

$$= \left[1 + k_2\left(\frac{[M]}{k_1 k_4'}\right)^{1/2}\right] k_1[M] \tag{14}$$

This is approximately equal to

$$-\frac{d[M]}{dt} = k_2\left(\frac{k_1}{k_4'}\right)^{1/2}[M]^{3/2} \tag{15}$$

i.e., the order of the reaction is three-halves instead of unity as in the previous case.

One-half-order Kinetics. In the same way it can be shown that if the chains are terminated by bimolecular collisions of R_2 molecules,

$$(4'') \qquad 2R_2 \rightarrow M'''' \tag{4''}$$

the order is one-half.

Chain-breaking Reaction. The examples considered above show that the order of the over-all reaction depends critically on the manner in which the chains are broken. This matter has been treated systematically by Goldfinger, Letort, and Niclause,[1] who have shown that it is important to distinguish between two types of radicals:

1. Radicals which propagate the chains by participating in bimolecular reactions; these are called β-radicals. In the above scheme the radical R_1, which reacts with M, is clearly of this type.

2. Radicals which propagate the chain by undergoing a unimolecular decomposition; these they call μ-radicals. The radical R_2, which in the above scheme decomposes by reaction (3), is of this type.

Goldfinger, Letort, and Niclause conclude that if the radicals are initiated by a unimolecular reaction [such as (1) above], the over-all order depends upon the type of chain-ending step as follows:

1. If chain ending is brought about by reaction between two β-radicals, the order is three-halves.

2. If the chains are terminated by reaction between a β-radical and a μ-radical, the order is unity.

3. If two μ-radicals participate in the chain-ending step, the order is one-half.

These conclusions were arrived at in the cases considered above. The

[1] P. Goldfinger, M. Letort, and M. Niclause, "Contribution à l'Etude de la Structure Moléculaire," Victor Henri Commemorative Volume, p. 283, Desoer, Liége, 1948.

analysis also shows that if the chain-initiating reaction is bimolecular instead of unimolecular, the orders are correspondingly higher by one-half; *e.g.*, with bimolecular initiation and $\beta\beta$ ending, the order is two.

Which process is more important in terminating the chains depends partly upon the relative concentrations of the radicals R_1 and R_2. Thus if the concentration of R_1 is much higher than that of R_2, the most important chain-ending process may be $2R_1 \rightarrow M'''$, while if R_2 is in excess, $2R_2 \rightarrow M''''$ may predominate. In intermediate cases the reaction $R_1 + R_2 \rightarrow M''$ will be most important, although the conditions leading to this case are not as clear-cut.

The relative magnitudes of $[R_1]$ and $[R_2]$ depend upon the relative rates of reactions (2) and (3). This is so because reaction (2) produces R_2 and destroys R_1, while reaction (3) produces R_1 and destroys R_2; the other reactions, (1) and (4), are less rapid and do not influence the relative concentrations to the same extent. To a good approximation, therefore,

$$\frac{[R_1]}{[R_2]} = \frac{k_3}{k_2} \tag{16}$$

If the magnitudes of k_2 and k_3 were entirely determined by the energies of activation E_2 and E_3, and if, for example, E_3 were greater than E_2, it would follow that k_2 would be greater than k_3 so that $[R_2] > [R_1]$. The chain-breaking reaction might therefore be largely $2R_2 \rightarrow M''''$, and the reaction should be of the one-half order. In fact, in almost all cases, E_2 is less than E_3 by a considerable amount, so that the argument would lead to one-half-order kinetics as the general rule in these mechanisms. Actually, this is by no means found to be the case. It would therefore appear that factors other than the energy of activation control the relative magnitudes of the rates of reactions (2) and (3) and of the chain-breaking steps. It is evident that the entropies of activation for the various radical-recombination reactions may vary considerably according to the size of the radicals involved; the same may be true of the transmission coefficient. As yet, there is very little information as to the absolute values of these quantities in individual cases.[1]

Molecular mechanisms

In a number of reactions the presence of free radicals has been established by direct evidence, and a mechanism has been proposed which is consistent with the over-all order of the process and explains the reaction products which are obtained. In such cases it may be assumed that the free-radical process plays a part; it cannot be concluded, however, without

[1] For recent discussions see T. L. Hill, *J Chem. Phys.*, **17**, 503 (1949); M. G. Evans and M. Szwarc, *Trans. Faraday Soc.*, **45**, 940 (1949).

additional evidence, that a molecular mechanism is not also taking place. In some cases, in fact, the indications are that together with the free-radical process there is occurring a simple rearrangement of atoms which gives rise to the reaction products in a single stage.

In particular, the nitric oxide inhibition work has been interpreted, particularly by Hinshelwood and his coworkers, as giving evidence for the simultaneous occurrence of molecular mechanisms. It was seen on page 190 that some of the results of the work appear to suggest that excess of nitric oxide removes all the radicals; if this is so the residual rate, which is usually an appreciable fraction of the uninhibited rate, corresponds to the molecular mechanism. The same argument can be presented in a somewhat different form in terms of chain lengths. If the nitric oxide really destroyed all the radicals, the ratio of the uninhibited rate to the inhibited rate would be the chain length; this usually is found to have a value of the order of 10. On the other hand, chain lengths calculated on the basis of Rice-Herzfeld mechanisms, as explained on page 235, are usually very much larger than this. These results can only be reconciled if a molecular mechanism is important.

It has been seen that some of the evidence indicates, on the contrary, that free radical reactions are still proceeding in the presence of excess of nitric oxide. Whenever this is the case for a reaction the above interpretation is not, of course, correct; the molecular mechanism is then less important than the simple interpretation would indicate.

On theoretical grounds, the result that the two mechanisms occur side by side is not surprising. The initial step in the free-radical mechanism is the production of at least one reactive radical, and this step is necessarily slow, owing to the fact that the activation energy is at least as great as the strength of the bond. Each radical may, however, induce the reaction of a great many molecules, so that the activation energy of the over-all reaction is less, and the rate is greater, than that of the initial step. The activation energy of a molecular reaction is always somewhat less than the energy corresponding to the breaking of a bond, since the energy set free in the stabilization of the products contributes toward reducing the latter. It is therefore not remarkable that the activation energy of the over-all free-radical mechanism is not very different from that of the molecular reaction, so that both take place to an appreciable extent and can be detected experimentally.

Decomposition of methane

Thermal Decomposition. The first work of any importance on the thermal decomposition of methane was published independently in 1932

by Kassel[1] and Storch.[2] Kassel studied the reaction by taking pressure measurements in a carbon-coated quartz vessel and worked at four temperatures from 976 to 1113°C. There was frequently an induction period, but apart from this the pressure p was found to vary with the time according to the law

$$\frac{dp}{dt} = kp_0 \tag{17}$$

where p_0 is the initial pressure. The variation of k with the temperature corresponds to an energy of activation of 79 kcal. The homogeneity of the reaction was tested by packing, and the extra surface was found to have little effect. In Storch's investigation the methane was decomposed by a hot wire, the temperature of which was varied. The rate of pressure change was found to correspond to an activation energy of 77 kcal, but this value was found by averaging about 20 values ranging from 40 to 120 kcal. The reaction has recently been reinvestigated by Gordon,[3] who analyzed for methane and the products of reaction by use of the mass spectrograph; the main products were found to be ethylene, ethane, acetylene, and hydrogen.

Role of Free Radicals. The nature of the free radicals which play a part in the decomposition of methane and other hydrocarbons has been the subject of some controversy. Rice and his coworkers[4] used tellurium mirrors as a means of detecting and distinguishing between methyl and methylene radicals, the former giving rise to dimethyl telluride ($CH_3TeTeCH_3$) and the latter to telluroformaldehyde [$(TeCH_2)_x$]. Using this technique, they found that in the decomposition of methane, butane, and acetone only methyl radicals were present, with no trace of methylene. On the other hand Belchetz and Rideal[5] have obtained results which appear to show that methylene radicals are the primary products in the decomposition of these substances. Their procedure was to stream the reactant over a heated carbon or platinum filament and to detect the radicals by causing them to react with mirrors of tellurium and iodine. In the case of methane they found methylene but no trace of methyl radicals, which they conclude to be secondary products arising from reactions such as

$$CH_2 + CH_4 \rightarrow 2CH_3$$

[1] L. S. Kassel, *J. Am. Chem. Soc.*, **54**, 3949 (1932).

[2] H. H. Storch, *ibid.*, 4185.

[3] A. S. Gordon, *ibid.*, **70**, 395 (1948).

[4] F. O. Rice and A. L. Glasebrook, *ibid.*, **56**, 2472 (1934); F. O. Rice and M. D. Dooley, *ibid.*, 2747.

[5] L. Belchetz and E. K. Rideal, *Trans. Faraday Soc.*, **30**, 170 (1934); *J. Am. Chem. Soc.*, **57**, 1168 (1935).

If this were the case, the failure of Rice and others to obtain methylene would be due to the fact that under the experimental conditions employed by them all the methylene radicals had reacted. In agreement with this idea Rice[1] has confirmed the result of Belchetz and Rideal using the same experimental technique. It would seem, however, that these results using filaments are not relevant to the homogeneous decomposition but only to that catalyzed by the surface. The experiments of Storch are also concerned with the surface reaction.

Hobbs and Hinshelwood,[2] using the nitric oxide inhibition method, found a chain length of 4.7 at 850°C, the pressure of methane being 100 mm.

Reaction Mechanism. A mechanism for the decomposition was proposed by Rice and Dooley;[3] according to them the primary step is

(1) $$CH_4 \rightarrow CH_3 + H$$

which is followed by the chain-propagating processes

(2) $$CH_3 + CH_4 \rightarrow C_2H_6 + H$$

and

(3) $$H + CH_4 \rightarrow CH_3 + H_2$$

and the chain-ending processes

(4) $$2H \rightarrow H_2$$

(5) $$2CH_3 \rightarrow C_2H_6$$

(6) $$H + CH_3 \rightarrow CH_4$$

This scheme accounts for the reaction as far as the formation of ethane, which Storch's work indicated to be an intermediate product. The mechanism has been criticized by Kassel,[4] who preferred a mechanism in which the initial step is

$$CH_4 \rightarrow CH_2 + H_2$$

However, as has been seen, the evidence is against the participation of methylene radicals in the homogeneous reaction.

A further difficulty that has been felt about the Rice-Dooley mechanism is that if the chain-ending step is taken to be predominantly reaction (4), which is necessary in order to obtain first-order kinetics, the calculated over-all activation energy is found to be that of reaction (1), which is approximately 103 kcal; this is much too high. The conclusion that the

[1] F. O. Rice, *ibid.*, **61**, 213 (1939).
[2] J. E. Hobbs and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 167**, 447 (1938).
[3] Rice and Dooley, *loc. cit.*
[4] L. S. Kassel, *J. Am. Chem. Soc.*, **57**, 833 (1935).

disappearance of methane is first order has been drawn from Kassel's results, but it may readily be shown that the experiments do not prove this. To a first approximation it will be assumed that the only reaction products are ethane, ethylene, and hydrogen. If the initial concentration of methane is denoted by a, and if after some reaction has occurred the concentrations of ethane and ethylene are x and y, respectively, the corresponding concentrations of methane and hydrogen can be shown to be $a - 2x - 2y$ and $x + 2y$, respectively. The total concentration is therefore

$$\begin{aligned} c &= [CH_4] + [C_2H_6] + [C_2H_4] + [H_2] \\ &= (a - 2x - 2y) + x + y + (x + 2y) \\ &= a + y \end{aligned} \tag{18}$$

The rate of change of pressure is proportional to dc/dt, and therefore to dy/dt, which is the rate of formation of ethylene; this does not correspond to the rate of disappearance of methane unless the rate of change of x is negligible, which is probably not the case. It would therefore appear that Kassel's rates and activation energies do not correspond to the decomposition of methane but to the formation of ethylene. If other products, such as acetylene and carbon, are taken into consideration, the situation is considerably more complicated, but the general conclusion is much the same.

One possible explanation of the results is that a small stationary concentration of ethane is maintained by the equilibrium

$$2CH_4 \rightleftharpoons C_2H_6 + H_2$$

This is endothermic by about 15 kcal and would maintain an ethane concentration which is proportional to the first power of the methane pressure. The ethane may then decompose by the first-order mechanism to be discussed on page 249, which has an activation energy of about 70 kcal; this would give rise to first-order kinetics for the formation of ethylene and to an activation energy of about 15 + 70 = 85 kcal, which is sufficiently close to the experimental value. This scheme does not necessarily imply that the initial ethane formation proceeds by a molecular mechanism; any mechanism, such as that proposed by Rice and Dooley, would yield the same result.

Some of the individual reactions which may play a part in the formation of ethane from methane will now be discussed in some detail.

Reaction between H and CH_4. In the Rice-Dooley mechanism the reaction between a hydrogen atom and a methane molecule is assumed to give rise to a methyl radical and a hydrogen molecule:

(3) $$H + CH_4 \rightarrow CH_3 + H_2$$

These are probably the main products when reaction occurs, although an alternative reaction

$$(3') \qquad H + CH_4 \rightarrow CH_4 + H$$

also has to be considered, and a good deal of work, both experimental and theoretical, has been devoted to determining which process is more important.

In several investigations[1] hydrogen atoms were produced by the Wood-Bonhoeffer discharge-tube method and brought into the presence of methane; it was found that no disappearance of hydrogen atoms (in excess of the normal due to recombination) took place, indicating that reaction (3) requires a fairly high activation energy. Geib and Harteck investigated the reaction up to 183°C, and from the fact that there was no reaction, deduced that the activation energy of (3) must be at least 17 kcal.

The work with hydrogen atoms can give no information as to the rate of reaction (3'), but if deuterium atoms are used, it is possible to draw conclusions as to its rate from the rate of formation of deuteromethanes. Unfortunately, it is rather difficult to interpret the experimental results, since reaction (3) also gives exchange, being followed by reactions such as $CH_3 + D \rightarrow CH_3D$. It can, however, be said with certainty that reactions (3) and (3') both require a fairly high activation energy; thus Geib and Steacie,[2] producing deuterium atoms by the discharge-tube method, found no production of deuteromethanes up to 100°C, indicating an activation energy of at least 11 kcal for both the reactions.

A series of investigations of this type was also carried out in which the deuterium atoms were produced by photosensitization using mercury. In the earlier work it was erroneously assumed that the excited mercury has no interaction with the methane molecules, and for this reason the conclusions may be somewhat in error. Steacie and Phillips,[3] following preliminary work by Taylor, Morikawa, and Benedict,[4] produced deuterium atoms in this way and measured the rate of formation of deuteromethanes; assuming a steric factor of 0.1, they calculated an activation energy of 11.7 kcal, which probably refers to reaction (3). Farkas and Melville[5] carried out a somewhat similar investigation over a wider range of tem-

[1] E. Boehm and K. F. Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926); K. F. Bonhoeffer and P. Harteck, *ibid.*, **139**, 64 (1928); H. v. Wartenburg and G. Schultze, *ibid.*, **B, 2**, 1 (1929); K H. Geib and P. Harteck, *ibid.*, **A, 170**, 1 (1934).

[2] K. H. Geib and E. W. R Steacie, *ibid.*, **B, 29**, 215 (1935).

[3] E. W. R. Steacie and N. W. F. Phillips, *J. Chem. Phys.*, **4**, 461 (1936).

[4] H. S. Taylor, K. Morikawa, and W. S. Benedict, *J. Am. Chem. Soc.*, **57**, 383 (1935).

[5] A. Farkas and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A, 157**, 625 (1936).

peratures and measured not only the rate of the exchange but the concentration of deuterium atoms by following the rate of the ortho-para deuterium conversion. They obtained an activation energy of 13 kcal, which they assign to reaction (3′); however, from the fact that the concentration of deuterium atoms is found to be reduced greatly at higher temperatures, it must be concluded that there is a shifting of the equilibrium $D + CH_4 \rightleftharpoons CH_3 + HD$, and it therefore seems preferable to conclude that the more important reaction is (3).

In a reinvestigation of the mercury-photosensitized reaction, Morikawa, Benedict, and Taylor[1] found that the situation was complicated by the fact that methane itself is dissociated by excited mercury atoms,

$$Hg(^3P) + CH_4 \rightarrow Hg(^1S) + CH_3 + H$$

so that some of the exchange which occurs in methane-deuterium mixtures must be attributed to the above reaction followed by either

$$CH_3 + D \rightarrow CH_3D$$

or

$$CH_3 + DH \rightarrow CH_3D + H$$

In view of this, it is difficult to be certain about the rates of the individual reactions, but it is concluded that

$$D + CH_4 \rightarrow CH_3 + HD$$

has an activation energy of 15 kcal and that the reverse reaction has an activation energy of 11 kcal. Since these reactions constitute a chain process for the deuterization of methane, these figures explain the fact that the quantum yield of the process rises rapidly in the region of 300°C, where these reactions become important.

The investigations on the reactions of hydrogen and deuterium atoms with methane thus seem to indicate with some certainty that the activation energy is 11 to 13 kcal (assuming a steric factor of 0.1) but do not allow a clear-cut decision to be made as to whether the products are $CH_3 + H_2$ or $CH_4 + H$. The evidence seems, however, to favor the former alternative, and this conclusion has received strong theoretical support. Gorin, Kauzmann, Walter, and Eyring[2] calculated that the activation energy of reaction (3′) is 37 kcal, and a similar high value was also obtained by Rice and Teller.[3] These calculations are always subject to large errors, but the result is sufficiently high to exclude the possibility

[1] K. Morikawa, W. S. Benedict, and H. S. Taylor, *J. Chem. Phys.*, **5**, 212 (1937).
[2] E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, *ibid.*, **7**, 633 (1939).
[3] F. O. Rice and E. Teller, *ibid.*, **6**, 489 (1938).

of the reaction occurring at ordinary temperatures. For reaction (3) a value of 9.5 kcal was calculated, and for the corresponding reaction involving a deuterium atom and methane, a value of 10.5 kcal was obtained, in satisfactory agreement with experiment.

One important result of the theoretical work of Gorin, Kauzmann, Walter, and Eyring was the conclusion that an alternative process to be considered is

$$H + CH_4 \rightarrow CH_5$$

since they calculate that the complex CH_5 is stable by 8 kcal with respect to $H + CH_4$. The activation energy required for the formation of this complex is the same as that for the formation of $CH_3 + H_2$, so that the complex is to be regarded as a stable intermediate which may decompose into either $CH_4 + H$ or $CH_3 + H_2$. However, in view of its relatively long life it may undergo reaction with a hydrogen atom with the formation of methane and a hydrogen molecule

$$CH_5 + H \rightarrow CH_4 + H_2$$

a process which therefore contributes to the reduction in atom concentration in the presence of methane. It is to be noted that for CH_5 to persist it must have its energy removed by collision with a third body, since otherwise it must dissociate.

Reaction between CH_3 and H_2. The reverse reaction to the above, *viz.*,

$$CH_3 + H_2 \rightarrow CH_4 + H$$

occurs fairly rapidly; this is known from the fact that in systems of decomposing organic compounds the hydrogen-atom concentration, as determined by the rate of the para-ortho hydrogen conversion, is always higher than that corresponding to thermal equilibrium.[1]

Evidence as to the rate and activation energy of the reaction was obtained by H. S. Taylor and C. Rosenblum[2] in an investigation of the photolysis of acetone in the presence of hydrogen. From the way in which the amount of methane produced increases with the pressure of hydrogen, they deduce an activation energy of 11 ± 2 kcal. A similar type of investigation by Cunningham and Taylor,[3] in which the methyl radicals were produced by both thermal and photochemical decomposition of mercury dimethyl, gave a value of 8 kcal. The reaction between methyl radicals and deuterium was studied by Smith and Taylor,[4] the methyl radicals being produced by the photolysis of mercury dimethyl. On the

[1] F. Patat and H. Sachsse, *Z. physik Chem.*, **B, 31,** 105 (1935).
[2] H. S. Taylor and C. Rosenblum, *J. Chem. Phys.*, **6,** 119 (1938).
[3] J. P. Cunningham and H. S. Taylor, *J. Chem. Phys.*, **6,** 359 (1938).
[4] J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7,** 390 (1939).

basis of an assumed mechanism which fits the results well, a value of 8 kcal for the reaction

$$CH_3 + D_2 \rightarrow CH_3D + D$$

was obtained. One complication in work of this kind is that methane production appears to take place by a process other than the one under consideration.

The evidence seems, therefore, to favor a value of about 8 kcal for the reaction

$$H_2 + CH_3 \rightarrow CH_4 + H$$

and a value of 11 to 13 kcal for the reverse reaction. This would indicate that the reaction as written above is exothermic by 3 to 4 kcal, a conclusion that is at variance with other results. A value of 102.5 has been obtained by Butler and Polanyi[1] for the dissociation energy of the C-H bond in methane, while Anderson, Kistiakowsky, and Van Artsdalen[2] have obtained 102 kcal by a completely independent method (see p. 272); this value together with the value of 104.2 for the dissociation energy of hydrogen at 25°C suggest that the reaction as written above should be endothermic by about 2 kcal. There is evidently a discrepancy between the data for the bond dissociation energies and the energies of activation for the forward and reverse reactions $H_2 + CH_3 \rightleftharpoons CH_4 + H$, and further work is necessary. A possible explanation[3] is that the value of about 8 kcal assigned to $H_2 + CH_3 \rightarrow CH_4 + H$ really applied to the three-body process

$$CH_3 + H_2 + CH_3 \rightarrow 2CH_4$$

and that the activation energy of $H_2 + CH_3$ is much higher. In view of the possible stability of CH_5, this reaction might be regarded as occurring by the steps

$$CH_3 + H_2 \rightarrow CH_5$$
$$CH_3 + CH_5 \rightarrow 2CH_4$$

Reaction $CH_3 + CH_4 \rightarrow C_2H_6 + H$. The reaction

(2) $$CH_3 + CH_4 \rightarrow C_2H_6 + H$$

has frequently been postulated as playing a part in free-radical processes, but is now known to occur very slowly under the usual experimental con-

[1] E. T. Butler and M. Polanyi, *Nature*, **146**, 129 (1940); *Trans. Faraday Soc.*, **39**, 19 (1943).

[2] H. G. Anderson, G. B. Kistiakowsky, and E. R. van Artsdalen, *J. Chem. Phys.*, **10**, 305 (1942); Van Artsdalen, *ibid.*, **10**, 653 (1942); Anderson and Van Artsdalen, *ibid.*, **11**, 6 (1943).

[3] *Cf.* H. A. Taylor and M. Burton, *ibid.*, **7**, 676 (1939).

ditions. Since a C-H bond of strength 102 kcal is broken and a C-C bond of strength about 84 kcal is formed, the reaction must be endothermic by at least about 18 kcal. The reverse reaction has moreover been found (see p. 251) to have an activation energy of at least 30 kcal, so that the activation energy of (2) is at least 48 kcal. The only other reaction which may occur on a collision between a methyl radical and a methane molecule is

$$(2') \qquad CH_3 + CH_4 \rightarrow CH_4 + CH_3$$

the rate of which could be measured by the use of deuterium. No information seems to be available as to the rate or activation energy of this process; however by analogy with

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$

which has an activation energy of 8 kcal (see p. 255), a fairly low energy is to be anticipated.

Reaction between H and CH_3. Collision between a hydrogen atom and a methyl radical, particularly in the presence of a third body, may give rise to three sets of products:

$$(6) \qquad H + CH_3 \rightarrow CH_4$$
$$(6') \qquad H + CH_3 \rightarrow CH_3 + H$$
$$(6'') \qquad H + CH_3 \rightarrow CH_2 + H_2$$

but very little information is available as to the rates of the three reactions. Reaction (6) probably occurs only in the presence of a third body, since the complex CH_4^* would dissociate in a period of about 10^{-12} sec.[1] Reaction (6′) is considered to be unlikely on theoretical grounds,[2] but indirect evidence for (6″) is obtained from experiments on the interaction of ethane with atomic deuterium.[3] The methane produced was found to be very highly exchanged, and it is necessary to postulate reaction (6″) in order to account for this. This result is consistent with the fact that the reaction is probably quite exothermic.[4]

Recombination of Methyl Radicals. In their first experiments on the formation of methyl radicals by the pyrolysis of lead tetramethyl, Paneth and Hofeditz[5] found that the radicals disappear rapidly, and they determined a half life of the order of 0.006 sec. The removal of the radicals undoubtedly occurs by reactions such as

[1] G. E. Kimball, *ibid.*, **5**, 310 (1937).

[2] Gorin, Kauzmann, Walter, and Eyring, *loc. cit.*

[3] N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.* **6**, 203 (1937).

[4] *Cf.* K. J. Laidler and E. J. Casey, *J. Chem. Phys.*, **17**, 1087 (1949).

[5] F. Paneth and W. Hofeditz, *Ber.*, **63**, 1335 (1929); F. Paneth, W. Hofeditz, and A. Wunsch, *J. Chem. Soc.*, 372 (1935).

(5) $$CH_3 + CH_3 \rightarrow C_2H_6$$

and

(5′) $$CH_3 + CH_3 \rightarrow C_2H_4 + H_2$$

since the temperature is not high enough for reactions like

$$CH_3 + H_2 \rightarrow CH_4 + H$$

to occur. Paneth and Lautsch[1] showed that the recombination is largely a surface reaction, since the half life could be increased by increasing the diameter of the tube. The type of surface available is relatively unimportant, so that the main function of the surface is presumably to remove the excess energy and so stabilize the product. Paneth and Hofeditz found that if a part of the surface is at a temperature of −180°C, every collision of a radical with it results in adsorption and consequent recombination. The main product of such recombinations is undoubtedly ethane so that reaction (5) is most important, although it has been asserted that the disproportionation reaction also occurs to a significant extent; no other products appear to be formed, however.

The reaction between two methyl radicals has been treated theoretically by Gorin, Kauzmann, Walter, and Eyring.[2] The conclusion drawn was that there is no true activation energy for the reaction; the radicals attract one another by polarization forces, which are opposed by the centrifugal force of rotation, and the net force corresponds to a potential-energy barrier over which the system must pass. These workers obtain for the rate of recombination at 600°C a value of about 2×10^{-11} cc molecule^{-1} sec^{-1}, on the assumption that a third body is present to remove the excess energy.

The experimental evidence regarding the rate of the reaction is indefinite but for the most part supports the conclusion that only a very small activation energy is necessary and that a third body such as a surface is required. That the activation energy is small is supported by the work of Taylor and Rosenblum[3] on the photolysis of acetone, both alone and in the presence of hydrogen. Both methane and ethane are produced, the former by the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

and the latter by the recombination of methyl radicals. The temperature dependence of the reaction between CH_3 and H_2 being known (p.

[1] F. Paneth and W. Lautsch, *Ber.*, **64**, 2708 (1931).

[2] Gorin, Kauzmann, Walter, and Eyring, *loc. cit.*; see also C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 1536 (1935); Kimball, *loc. cit.*; E. Gorin, *Acta Physicochim. U.R.S.S.*, **9**, 681 (1938); T. L. Hill, *J. Chem. Phys.*, **17**, 503 (1949).

[3] Taylor and Rosenblum, *loc. cit.*

244), that of the radical recombination could be deduced from the temperature dependence of the ratio of the rates of production of CH_4 and C_2H_6, and it was found to be very small. A similar result was found from investigations of the thermal and photochemical decomposition of mercury dimethyl, both alone and in the presence of hydrogen,[1] and from work on the reaction of methyl radicals in the presence of deuterium.[2]

Decomposition of ethane

Thermal Decomposition. The decomposition of ethane was investigated experimentally by Pease,[3] who used a flow system and worked at 650°C. He found that the main products were ethylene and hydrogen, the over-all reaction being represented approximately by

$$C_2H_6 = C_2H_4 + H_2$$

The reaction was found to be homogeneous and of the first order, a result that was confirmed by Frey and Smith,[4] using a static method, and by Marek and McCluer,[5] using the flow method described on page 49. Paul and Marek[6] calculated an activation energy of 77 kcal from the results of Marek and McCluer, but this value seems to be too high; thus Sachsse[7] found a value of 69.8 kcal and Steacie and Shane[8] one of 68.7 kcal, and these values fall in line with the values for the other hydrocarbons.

Role of Free Radicals. The presence of free radicals in the reaction system was detected by Rice and Dooley[9] using the mirror-removal method, and this result has been confirmed by Eltenton[10] using the mass spectrometer. Attempts have also been made to sensitize the decomposition by the introduction of free radicals, but only very slight increases in velocity have been achieved;[11] however these experiments were carried out at low temperatures, at which the equilibrium is so far on the ethane side that very little decomposition is to be expected. The reaction is found to be

[1] Cunningham and Taylor, *loc. cit.*
[2] Smith and Taylor, *loc. cit.*
[3] R. N. Pease, *J. Am. Chem. Soc.*, **50**, 1179 (1928).
[4] F. E. Frey and D. F. Smith, *Ind. Eng. Chem.*, **20**, 948 (1928).
[5] L. F. Marek and W. B. McCluer, *ibid*, **23**, 878 (1931).
[6] R. E. Paul and L. F. Marek, *ibid.*, **26**, 454 (1934).
[7] H. Sachsse, *Z. physik. Chem.*, B, **31**, 87 (1935).
[8] E. W. R. Steacie and G. Shane, *Can J. Research*, B, **18**, 203 (1940).
[9] F. O Rice and M. D. Dooley, *J Am. Chem. Soc* , **55**, 4245 (1933).
[10] G. C. Eltenton, *J. Chem. Phys.*, **10**, 403 (1942).
[11] D. V. Sickman and O. K. Rice, *ibid.*, **4**, 608 (1936); L. S. Echols and R. N. Pease, *J. Am. Chem. Soc.*, **58**, 1317 (1936).

inhibited by propylene[1] and by nitric oxide,[2] and, as will be seen later, the inhibition experiments provide valuable information as to the nature of the free-radical processes occurring.

Reaction Mechanism. A free-radical mechanism consistent not only with the fact that the reaction is of the first order but also with the experimental activation energy was proposed in 1934 by Rice and Herzfeld,[3] whose scheme is as follows:

(1)	$C_2H_6 \rightarrow 2CH_3$	$E_1 = 84$ kcal
(2)	$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	$E_2 = 8$ kcal
(3)	$C_2H_5 \rightarrow C_2H_4 + H$	$E_3 = 40$ kcal
(4)	$H + C_2H_6 \rightarrow H_2 + C_2H_5$	$E_4 = 7$ kcal
(5)	$H + C_2H_5 \rightarrow C_2H_6$	$E_5 = 0$ kcal

The assignment of activation energies given above corresponds to the values usually assumed today and not to those of Rice and Herzfeld. Application of the usual steady-state treatment leads to the first-order expression

$$-\frac{d[C_2H_6]}{dt} = \left(\frac{k_1k_3k_4}{2k_5}\right)^{1/2}[C_2H_6] \tag{19}$$

so that the energy of activation is

$$E = \tfrac{1}{2}(E_1 + E_3 + E_4 - E_5) = 66 \text{ kcal}$$

in good agreement with the observed value.

The scheme proposed, however, involves some difficulties. As was seen earlier in the chapter, a free-radical mechanism gives rise to first-order kinetics only if a chain-ending step such as (5) occurs to the exclusion of such reactions as

(6)	$2H \rightarrow H_2$
(7)	$2C_2H_5 \rightarrow C_4H_{10}$

and

(8)	$H + CH_3 \rightarrow CH_4$

Of these reactions, (6) and (8) involve few atoms and will depend upon the presence of a third body to a greater degree than (5) and (7); they may perhaps be excluded on this account. In the original scheme of Rice and Herzfeld, reaction (4) was assigned an activation energy of 17 kcal,

[1] A. I. Dinzes, A. D. Stepukhovitch, D. A. Kyvatkowskii, and A. V. Frost, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 1754 (1937).

[2] L. A. K. Staveley, *Proc. Roy. Soc.* (*London*), **A, 162,** 557 (1937); J. E. Hobbs and C. N. Hinshelwood, *ibid.*, **A, 167,** 447 (1938).

[3] F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56,** 284 (1934).

and reaction (2) one of 20 kcal; these values would mean that the concentration of ethyl radicals would be small. In addition, a small activation energy was assigned to (7), and it then appeared that it would occur to a much smaller extent than (5). However, reactions (2) and (4) are now known to occur with low activation energies, so that the concentration of ethyl radicals is much higher than that of hydrogen atoms and methyl radicals. Consequently, it might be expected that reaction (7), the recombination of ethyl radicals, would be the most important chain-breaking step. This, however, gives rise to half-order kinetics and to an incorrect value of the energy of activation. Thus taking reactions (1), (2), (3), (4), and (7), the rate of decomposition is given by

$$-\frac{d[C_2H_6]}{dt} = k_3\left(\frac{k_1}{k_7}\right)^{1/2}[C_2H_6]^{1/2} \tag{20}$$

and the activation energy is

$$E = E_3 + \tfrac{1}{2}(E_1 - E_7) = 82.5 \text{ kcal}$$

which is much too high.

It was pointed out by Küchler and Theile[1] that the scheme of reactions (1) to (4) and (7) will yield first-order kinetics if it is assumed that the first step, reaction (1), is of the second order instead of the first; this modification has been accepted by Rice and Herzfeld.[2] The rate of decomposition is now given by

$$-\frac{d[C_2H_6]}{dt} = k_3\left(\frac{k_1}{k_7}\right)^{1/2}[C_2H_6] \tag{21}$$

but the activation energy is as above and is still too high. On the whole, the original Rice-Herzfeld mechanism seems to be more plausible than that of Küchler and Theile. It is possible that the recombination of ethyl radicals has a small frequency factor, owing to steric effects, and that the chain-breaking step $H + C_2H_5$ really does occur to the exclusion of others.

Inhibition of the Reaction. That a free-radical mechanism is involved, but that a molecular mechanism probably also occurs, is suggested by the experiments with nitric oxide. Staveley[3] found marked inhibition of the reaction by traces of nitric oxide and determined mean chain lengths of 20.6 at 50 mm initial pressure and 6.4 at 500 mm. A much more detailed study of the decomposition was made by Hobbs and Hinshelwood,[4] who found chain lengths that agreed well with those of Staveley and found that

[1] L. Küchler and H. Theile, *Z. physik. Chem.*, **B, 42,** 359 (1939).
[2] F. O. Rice and K. F. Herzfeld, *J. Chem. Phys.*, **7,** 671 (1939).
[3] Staveley, *loc. cit.*
[4] Hobbs and Hinshelwood, *loc. cit.*

the chain length varies with the ethane concentration according to the function $[C_2H_6]^{-0.35}$. The chain lengths observed are considerably shorter than those calculated on the basis of the reaction mechanism, assuming that no molecular mechanism is occurring; this indicated that in fact the molecular mechanism is playing a significant part.

The result that the chain length varies with $[C_2H_6]^{-0.35}$ can be expressed qualitatively by saying that the amount of nitric oxide required for a given amount of inhibition is greater the greater the concentration of ethane. This suggests that nitric oxide and ethane enter into competition for the free radicals, and this is consistent with the fact that one of the reactions occurring is (2), *viz.*,

$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$

which competes with

$$CH_3 + NO \rightarrow ?$$

the products of which have not been established. If the concentration of ethane is increased, the first process is favored, and more nitric oxide is therefore required to produce a given amount of inhibition. Hobbs and Hinshelwood treat the inhibition quantitatively and conclude the chain-ending step to be partly a binary and partly a ternary process.

The kinetics of the reaction fully inhibited by nitric oxide were studied by Staveley,[1] who found the reaction to be of the first order and to have an activation energy of 74.5 kcal; a similar investigation by Steacie and Shane[2] gave a value of 77.3 kcal. The energy of activation of the inhibited, molecular, process is therefore appreciably greater than that of the overall reaction in the absence of inhibition, which means that most of the ethane molecules decompose by the chain process. The number of molecules of ethane which undergo a split into methyl radicals [reaction (1)] is of course very small compared with those that decompose molecularly, but each radical initiates such a long chain that most of the ethane decomposing does so by the chain process.

Reaction between H and C_2H_6. The reaction

$$(4) \qquad H + C_2H_6 \rightarrow H_2 + C_2H_5$$

postulated as occurring in the decomposition of ethane, is analogous to the reaction $H + CH_4 \rightarrow H_2 + CH_3$, which was seen on page 243 to occur with an activation energy of about 11 kcal. Since the strength of the C—H bond in ethane is less than that in methane, being about 98 kcal as compared with 102 kcal, an even smaller activation energy is to be expected with

[1] Staveley, *loc. cit.*

[2] Steacie and Shane, *op. cit.*, 351.

ethane. In agreement with this, Trost and Steacie,[1] using hydrogen atoms produced by the discharge-tube method, have obtained a value of 9 kcal, assuming a steric factor of 0.1. Another possible reaction in the case of ethane is

$$H + C_2H_6 \rightarrow CH_3 + CH_4 \qquad (4')$$

but in the original Rice-Herzfeld mechanism this reaction and similar "cracking reactions" (so-called because a carbon-carbon bond is broken) were assigned high activation energies, which would exclude their occurrence in free-radical mechanisms except at extremely high temperatures. This conclusion has been confirmed by more direct investigations, which suggest that the activation energy of (4′) is at least 30 kcal. This work will now be discussed, and it will be seen that the question of the activation energy of (4′) is closely connected with that of the rate of the reaction

$$H + C_2H_5 \rightarrow 2CH_3 \qquad (5')$$

The reaction between hydrogen atoms and ethane has been investigated by a number of workers,[2] all of whom found that considerable amounts of methane are produced. This was at first attributed to the fact that reaction (4′) occurs readily but is now believed to be due to reaction (4) followed by (5′). This conclusion is supported by experiments of Steacie and Phillips[3] on the reaction of deuterium atoms, produced by the discharge-tube method, with ethane. Exchange took place with an activation energy of 6.3 kcal, which is ascribed to the reaction

$$D + C_2H_6 \rightarrow C_2H_5 + HD$$

This is followed by

$$D + C_2H_5 \rightarrow C_2H_5D$$

which occurs slowly on the surface of the vessel. Some deuterized methane was also produced in these experiments, and this is attributed to

$$D + C_2H_5 \rightarrow CH_3 + CH_2D$$

The result that the activation energy of reaction (4) is 9 kcal (this being the latest value[4]), and that the activation energy of (4′) is high, is consistent

[1] W. R. Trost and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 361 (1948); *cf.* Steacie, *ibid.*, **6**, 37 (1938).

[2] Trenner, Morikawa, and Taylor, *loc. cit.*; E. W. R. Steacie, *J. Chem. Phys.*, **6**, 37 (1938); Trost and Steacie, *loc. cit*

[3] E. W. R. Steacie and N. W. R. Phillips, *J. Chem. Phys.*, **4**, 461 (1936).

[4] Trost and Steacie, *loc. cit.*

with, but could hardly have been predicted from, the results obtained from the photosensitized decomposition of ethane. The products of the reaction are mainly methane and propane, with smaller amounts of butane, and if the reaction is carried out in the presence of added hydrogen, more methane is produced. These results can be explained in terms of the mechanism

$$\begin{aligned} Hg(^3P) + C_2H_6 &\rightarrow C_2H_5 + H + Hg(^1S) \\ Hg(^3P) + H_2 &\rightarrow 2H + Hg(^1S) \\ H + C_2H_6 &\rightarrow H_2 + C_2H_5 \\ H + C_2H_5 &\rightarrow 2CH_3 \\ CH_3 + C_2H_6 &\rightarrow CH_4 + C_2H_5 \end{aligned}$$

followed by chain-ending processes such as

$$\begin{aligned} 2H &\rightarrow H_2 \\ CH_3 + C_2H_5 &\rightarrow C_3H_8 \end{aligned}$$

The conclusions as to the relative activation energies of reactions (4) and (4′) also receive support on theoretical grounds. Thus Rice and Teller[1] point out that for reaction (4′) to proceed, the hydrogen atoms have to be forced into the plane of the carbon atom, and from the known bending vibrations they estimate that an energy of 40 kcal is required for the reaction. On the basis of similar considerations, Gorin, Kauzmann, Walter, and Eyring[2] arrive at an energy of 37 kcal for the reaction, which they point out is analogous to the inversion type of reaction

$$H + CH_4 \rightarrow CH_4 + H$$

which also has a high energy of activation.

Reaction between H and C_2H_5. As has been seen, the fact that the reaction $H + C_2H_6 \rightarrow CH_3 + CH_4$ requires a very high activation energy is indirect evidence that reactions such as

$$(5') \qquad H + C_2H_5 \rightarrow 2CH_3$$

occur readily, since otherwise there would be no way of accounting for the production of methane in organic decompositions. Other investigations have also given results which it seems to be impossible to explain without assuming reaction (5′). Thus Moore and Taylor[3] found large amounts of methane in the photolysis of a mixture of mercury diethyl and hydrogen and conclude that reaction (5′) occurs with an activation energy of less than 5 kcal.

[1] F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).
[2] Gorin, Kauzmann, Walter, and Eyring, *loc. cit.*
[3] W. J. Moore and H. S. Taylor, *J. Chem. Phys.*, **8**, 396 (1940).

Cracking reactions such as (5′) are not the only ones that appear to occur when a hydrogen atom reacts with a free radical. It may be assumed that the first product is always a complex $C_2H_6^*$, of high energy, and that either this may be stabilized to a normal ethane molecule [reaction (5)], or it may dissociate, possible products being $2CH_3$ [reaction (5′)], $H + C_2H_5$, or $H_2 + C_2H_4$,

$$(5'') \qquad H + C_2H_5 \rightarrow C_2H_5 + H$$

$$(5''') \qquad H + C_2H_5 \rightarrow H_2 + C_2H_4$$

The formation of ethane requires a third body, which may be the surface, and does not appear to take place under most experimental conditions, although at very low temperatures, when wall effects become important, it appears to be significant.[1] The fact that normally the reaction does not take place to any great extent is indicated by the very slight exchange of ethane which occurs in reactions of deuterium atoms with ethane.

That reaction (5″) occurs readily is indicated by the work of Steacie, Alexander, and Phillips[2] on the mercury-photosensitized reaction of ethane in the presence of deuterium. The products of the reaction are mainly methane, propane, and butane, all of which are highly deuterized. The ethyl radicals are produced either by the interaction of $Hg(^3P)$ with ethane or by the reaction

$$D + C_2H_6 \rightarrow DH + C_2H_5$$

and cannot be deuterized directly by either of these processes. Since the butane, which must be produced by the interaction of ethyl radicals, is deuterized, it follows that the ethyl radicals must be produced by the reaction

$$D + C_2H_5 \rightarrow C_2H_4D + H$$

which is the only reaction that accounts for their deuterization.

There is little evidence as to the occurrence of reaction (5‴). Ethylene is not found in systems containing hydrogen atoms and ethyl radicals, but this may be due to the ready occurrence of reaction (5‴) followed by a re-formation of ethyl radicals by

$$H + C_2H_4 \rightarrow C_2H_5$$

Decomposition of C_2H_5 into C_2H_4 and H. The reaction

$$(3) \qquad C_2H_5 \rightarrow C_2H_4 + H$$

[1] K. H. Geib and P. Harteck, *Ber.*, **66**, 1815 (1933).

[2] E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, *Can. J. Research*, **B, 16**, 314 (1938).

is of great importance in connection with the mechanism for the decomposition of ethane, since it and the process

(4) $$H + C_2H_6 \rightarrow C_2H_5 + H_2$$

probably constitute the chain-propagating steps. The activation energy of (3) is probably not much higher than the strength of the carbon-hydrogen bond in the ethyl radical, which can be calculated from the strength of the C-H bond in ethane, 98 kcal, and the heat of hydrogenation of ethylene, 33 kcal; thus

$$H + C_2H_5 \rightarrow C_2H_6 + 98 \text{ kcal}$$
$$H_2 + C_2H_4 \rightarrow C_2H_6 + 33 \text{ kcal}$$
$$2H \rightarrow H_2 + 104 \text{ kcal}$$

whence, using Hess's law,

$$C_2H_5 \rightarrow C_2H_4 + H - 39 \text{ kcal}$$

The energy of activation of the reaction is at least this and can be taken as approximately 40 kcal. On account of the endothermicity of the reaction, the equilibrium constant is still well over to the left at 900°K,[1] so that although the reaction can be assumed as a chain-propagating reaction, it does not give rise to an appreciable amount of ethylene.

Reaction between CH_3 and C_2H_6. The reaction

(2) $$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$$

postulated by Rice and Herzfeld as playing an important part in the ethane decomposition, was investigated directly by Smith and Taylor.[2] Methyl radicals were produced by the photolysis of mercury dimethyl and were caused to react with ethane at temperatures of 100 to 300°C. From the rate of formation of methane over this temperature range, they estimated an activation energy of 8.3 kcal for the reaction. That the energy would be low had previously been concluded by Rice and Teller[3] on theoretical grounds.

Decomposition of the higher paraffins

Since the results for the thermal decomposition of propane and the butanes are very similar to those for ethane, only a very brief account will be given.

The decompositions are all homogeneous and of the first order and in the case of propane follow the equations

[1] A. V. Frost, *J. Phys. Chem.* (*U.S.S.R.*), **8**, 290 (1936).
[2] J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).
[3] Rice and Teller, *loc. cit.*

$$C_3H_8 = C_3H_6 + H_2$$
$$C_3H_8 = C_2H_4 + CH_4$$

although small amounts of ethane and butane are also formed. With the butanes the main course of the reaction can be represented by

$$C_4H_{10} = C_4H_8 + H_2$$
$$C_4H_{10} = C_3H_6 + CH_4$$
$$C_4H_{10} = C_2H_4 + C_2H_6$$

The activation energies of the over-all reactions are given in Table 41, which includes for comparison the values for methane and ethane. The figures are seen to fall smoothly.

The presence of free radicals has been detected in the decompositions of both propane and normal butane, using the mirror technique and in other ways. The reactions are found to be inhibited by nitric oxide, the results resembling the ethane decomposition from the point of view of the influence of the pressure of the hydrocarbon; this indicates that similar

TABLE 41. ACTIVATION ENERGIES FOR ORGANIC DECOMPOSITIONS

Paraffin	*E, kcal*
CH_4	79.5
C_2H_6	68.7
C_3H_8	63.3
n-C_4H_{10}	58.7

chain-propagating steps are involved. Chain lengths of less than 10 are obtained, suggesting (if the simple interpretation of the nitric oxide work is valid) that molecular processes as well as the free-radical reactions play a part; the latter, however, are responsible for the decomposition of the majority of the hydrocarbon molecules.

Activation Energies for the Elementary Processes. Activation energies for the most important elementary reactions involved in paraffin decompositions will now be given; the values which are obtained from investigations at one temperature only correspond to a steric factor of 0.1, as recommended by Evans and Szwarc.[1]

For the initial splitting to form free radicals, the activation energies are probably equal to the bond-dissociation energies, values for which are given below:

$CH_4 \rightarrow CH_3 + H$	102 kcal
$C_2H_6 \rightarrow 2CH_3$	84 kcal
$C_3H_8 \rightarrow CH_3 + C_2H_5$	84 kcal
n-$C_4H_{10} \rightarrow 2C_2H_5$	84 kcal

[1] M. G. Evans and M. Szwarc. *Trans. Faraday Soc.*, **45**, 940 (1949).

The second step is the reaction between a methyl radical and a paraffin molecule, the activation energies for which are

$$(CH_3 + CH_4 \rightarrow CH_4 + CH_3 \quad 10 \text{ kcal})$$
$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \quad 8 \text{ kcal}$$
$$CH_3 + C_3H_8 \rightarrow CH_4 + C_3H_7 \quad 5.5 \text{ kcal}$$
$$CH_3 + C_4H_{10} \rightarrow CH_4 + C_4H_9 \quad 5.5 \text{ kcal}$$

The larger radicals now decompose with activation energies that are probably equal to or only slightly greater than the dissociation energies of the bonds broken, values of which are

$$C_2H_5 \rightarrow C_2H_4 + H \quad 39 \text{ kcal}$$
$$C_3H_7 \rightarrow C_2H_4 + CH_3 \quad 26 \text{ kcal}$$
$$C_4H_9 \rightarrow C_2H_4 + C_2H_5 \quad 26 \text{ kcal}$$

The activation energies for the reactions of hydrogen atoms with paraffins are

$$H + CH_4 \rightarrow CH_3 + H_2 \quad 11\text{–}13 \text{ kcal}$$
$$H + C_2H_6 \rightarrow C_2H_5 + H_2 \quad 9 \text{ kcal}$$
$$H + C_3H_8 \rightarrow C_3H_7 + H_2 \quad 9 \text{ kcal}$$
$$H + C_4H_{10} \rightarrow C_4H_9 + H_2 \quad 9 \text{ kcal}$$

The activation energies for all the radical recombinations are undoubtedly small and are usually taken to be zero; a third body may be required especially in the case of simple radicals.

The activation energies for the various elementary reactions are seen to vary regularly, and the over-all reactions appear to proceed by analogous mechanisms.

Decomposition of acetaldehyde

Acetaldehyde decomposes both thermally and photochemically, the main products in each case being methane and carbon monoxide. Both a molecular and a free-radical decomposition seem to be involved in the two types of decomposition, which bear a very strong resemblance to one another. The thermal decomposition will be discussed first.

Thermal Decomposition. The thermal reaction, like the photochemical, has been investigated very extensively and is found to be almost entirely homogeneous under the conditions of the investigations. The order of the reaction has been a matter of considerable controversy. Investigation of the dependence of the initial rate on the pressure has led Hinshelwood and his coworkers[1] to conclude that different modes of activation within

[1] C. J. M. Fletcher and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 141,** 41 (1933); C. N. Hinshelwood, C. J. M. Fletcher, and C. A. Winkler, *ibid.*, **A, 146,** 327 (1934); C. A. Winkler and C. N. Hinshelwood, *ibid.*, **A, 149,** 355 (1935).

the molecule are involved, since the data can be fitted to a segmented rate-pressure curve. Other workers, particularly Letort,[1] consider that the true order of the reaction is three-halves, although it has been questioned whether the data conform to such an order within the experimental error. The fact that the reaction is of the second order with respect to time has been noted on page 17, where it was pointed out that the higher order with respect to time than with respect to concentration implies that the reaction is inhibited by its products. The activation energy of the reaction at higher pressures is 48 kcal.

The influence of foreign gases on the rate of the decomposition has been investigated very fully and is a matter of some importance. Certain substances, such as oxygen, iodine, bromine, nitric oxide, nitrous oxide, and hydrogen sulfide catalyze the reaction homogeneously, and mechanisms involving the introduction of new free radical processes have been proposed. Thus the action of iodine[2] is thought to be due to reaction with the acetaldehyde with the formation of an alkyl iodide, which gives rise to free radicals. The sensitizing action of oxygen was first described by Letort,[3] who has recently shown[4] that traces of oxygen will induce decomposition at temperatures below 400°C, when the acetaldehyde is thermally stable. Slight acceleration of the rate of reaction at high temperatures has also been found[5] with hydrogen and helium, which cannot react chemically, and this has been attributed to the fact that the reaction proceeds in part by a unimolecular process, the rate of which at low pressures is increased by foreign molecules.

Evidence for Free Radicals. It is generally believed that free radicals play a part in the decomposition of acetaldehyde, although some doubt has recently been cast upon this. The presence of methyl radicals was detected using the Paneth technique by Rice, Johnston, and Evering[6] and others. Most of these tests were carried out at much higher temperatures than those used in studying the kinetics of the reaction (about 500°C), so that it might be argued that no radicals are present at the lower temperatures; however Burton, Ricci, and Davis,[7] using radioactive lead mirrors,

[1] M. Letort, Thesis, University of Paris (1937); *J chim. phys.*, **34**, 206 (1937).

[2] G. K. Rollefson and R. F. Faull, *J. Am. Chem. Soc* , **59**, 625 (1937).

[3] M. Letort, *Compt. rend.*, **197**, 1042 (1933); **200**, 312 (1935); *J. chim. phys.*, **34**, 428 (1937); *cf.* F. H. Verhoek, *Trans. Faraday Soc* , **31**, 1527 (1935); J. C. Morris, *J. Am. Chem. Soc.*, **66**, 584 (1944).

[4] M. Letort, *Comp. rend.*, **226**, 77 (1948).

[5] C. N. Hinshelwood and P. J. Askey, *J. Chem. Soc.*, 812 (1936); C. J. M. Fletcher and C. N. Hinshelwood, *Trans. Faraday Soc.*, **30**, 614 (1934); C J. M. Fletcher, *J. Am. Chem. Soc.*, **58**, 2646 (1936).

[6] F. O. Rice, W. R. Johnston, and B. L. Evering, *ibid.*, **54**, 3529 (1932).

[7] M. Burton, J. E. Ricci, and T. W. Davis, *ibid.*, **62**, 265 (1940).

were able to prove the presence of radicals at 500°C. The work of Morris[1], however, has cast some doubt upon whether radicals play a role when absolutely pure acetaldehyde decomposes, the experiments involving acetaldehyde and deuteroaldehyde (CD_3CDO) which had been freed from oxygen by treatment with hydroquinone followed by distillation. If free radicals play a part in the decomposition, the products, when CH_3CHO and CD_3CDO are decomposed together, should include not only CH_4 and CD_4 but also the mixed products CD_3H and CH_3D. Analyzing the products of the reaction by infrared absorption, Morris found no mixing when the highly purified aldehydes were used. On the other hand a mixture of aldehydes purified in the usual way gave mixed methanes in amounts corresponding to the occurrence of about one-half of the reaction by a chain mechanism. Morris's interpretation of these results is that some oxidizing impurity, which is removed by hydroquinone, is responsible for the initiation of chain processes in ordinary acetaldehyde, but the nature of the impurity has not been established. An alternative explanation is that the distillation from hydroquinone contaminates the aldehydes with an inhibitory substance that prevents chain processes from taking place.

Numerous investigations have shown that the decomposition of acetaldehyde can be sensitized by free radicals. Thus Allen and Sickman[2] showed that azomethane, which produces methyl radicals, induces the decomposition of acetaldehyde at 300°C (at which temperature it does not normally occur) and that chain lengths up to 500 were obtained. Similar results were found using ethylene oxide, diethyl ether, ethyl bromide, ethyl iodide, diacetyl, and other substances as sensitizers.

The influence of nitric oxide on the reaction is rather complex and has only recently been elucidated. Smith and Hinshelwood[3] have shown that at higher pressures of acetaldehyde the addition of nitric oxide increases the rate, the effect being very gradual with the first addition of nitric oxide. However, at lower pressures of acetaldehyde the addition of small amounts of nitric oxide causes inhibition, followed by catalysis at higher concentrations of the oxide. It therefore appears that nitric oxide acts in two ways; it inhibits, as usual, by removing radicals but also catalyzes the reaction homogeneously. The characteristics of the inhibited reaction were also studied; its order is approximately the second, probably indicating a low-pressure unimolecular process, and the activation energy was found to be 47 kcal, *i.e.*, almost identical with that of the uninhibited process.

[1] J. C. Morris, *ibid*, **63**, 2535 (1941); **66**, 584 (1944).

[2] A. O. Allen and D. V. Sickman, *ibid.*, **56**, 2031 (1934); D. V. Sickman and A. O. Allen, *ibid.*, 1251.

[3] J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 180**, 237 (1942).

The inhibition obtained with propylene[1] is more easily interpreted, since the problem of homogeneous catalysis does not arise. The results resembled those obtained with the nitric oxide inhibition of the ethane decomposition, in that the inhibition curves vary with the initial acetaldehyde pressure. This, as was seen with ethane (p. 251), suggests that an important step in the free-radical mechanism is the reaction of a free radical with a molecule of acetaldehyde.

Reaction Mechanism. Such a step is in fact a part of the scheme proposed by Rice and Herzfeld[2] to account for the decomposition. The mechanism, together with the activation energies now assigned to the various reactions, is

(1)	$CH_3CHO \rightarrow CH_3 + CHO$	$E_1 = 76$ kcal
(2)	$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$	$E_2 = 10$ kcal
(3)	$CH_3CO \rightarrow CH_3 + CO$	$E_3 = 18$ kcal
(4)	$2CH_3 \rightarrow C_2H_6$	$E_4 = 0$ kcal

Reactions (2) and (3) constitute the chain-propagating steps, the carriers being the methyl and acetyl radicals.

With reaction (4) as the chain-ending step, the steady-state treatment leads to an order of three-halves (in approximate agreement with experiment) and to an activation energy of

$$E = E_2 + \tfrac{1}{2}(E_1 - E_4) = 48 \text{ kcal}$$

The scheme is therefore in good agreement with experiment, but it must be remembered that the assignment of activation energies is based partly on the over-all activation energy (see p. 263).

Photochemical Decomposition. There is still considerable controversy about the mechanism of the photochemical decomposition of acetaldehyde, but it is generally agreed that as in the case of the thermal decomposition, two processes take place simultaneously, one involving the participation of free radicals and the other not.

Most of the investigations have been carried out in the region between 2800 and 3400 A; acetaldehyde absorbs in this region, which shows a banded structure superimposed on a continuum. The first detailed study of the reaction was carried out by Leighton and Blacet,[3] who found that the main products are methane and carbon monoxide and that the quantum yield at ordinary temperatures varies from 0.2 to about unity. More recently Blacet and his coworkers[4] have investigated the products of the

[1] F. O. Rice and O. L. Polly, *J. Chem. Phys*, **6**, 273 (1938).

[2] F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

[3] P. A. Leighton and F. E. Blacet, *ibid.*, **55**, 1766 (1933).

[4] F. E. Blacet and J. G. Roof, *ibid.*, **58**, 278 (1936); F. E. Blacet and D. Volman, *ibid.*, **60**, 1243 (1938); F. E. Blacet and W. J. Blaedel, *ibid.*, **62**, 3374 (1940).

reaction more thoroughly, finding appreciable amounts of hydrogen, diacetyl, glyoxal, and formaldehyde. The existence of these secondary products is direct evidence that a free-radical mechanism is involved, and by analogy with the thermal reaction the most likely processes are

(1) $$CH_3CHO + h\nu \rightarrow CH_4 + CO$$

and

(2) $$CH_3CHO + h\nu \rightarrow CH_3 + CHO$$

the latter being followed by chain processes.

Quantum yields greater than unity constitute a proof that chain reactions are taking place, and these were found by Leermakers,[1] who investigated the reaction at temperatures up to 310°C. He found that the highest quantum yields are obtained at the high temperatures and low light intensities, the highest values observed being over 300. His results for the rate of the reaction could be fitted to the equation

$$\frac{d[CO]}{dt} = kI + k'I^{1/2}[CH_3CHO] \qquad (22)$$

where k and k' are constants and I is the intensity of light absorbed. The constant k has the value of 0.3 and is independent of temperature; the first term in the expression is therefore interpreted as representing the rate of the molecular part of the reaction, which, like all purely photochemical processes, has no energy of activation. The constant k' increases with temperature, and this, together with the appearance of the square root of I in the second term, indicates that this term represents the rate of the free-radical part of the reaction. From the temperature coefficient of k', an activation energy of about 10 kcal is deduced. At low temperatures the first term is much greater than the second, which means that the decomposition takes place largely by a molecular process with a quantum yield of 0.3. At sufficiently high temperatures, on the other hand, the second term, representing the free-radical process, predominates, and the quantum yield is then much higher and gives a measure of the chain length.

The presence of free radicals in the reaction has been demonstrated by various direct methods. The Paneth method, using heated tellurium mirrors, was employed by Pearson and Purcell,[2] who found removal of the mirrors and identified dimethyl ditelluride, thus proving methyl radicals to be present. The nitric oxide inhibition method was employed by Mitchell and Hinshelwood,[3] who found that small amounts of nitric oxide brought about a large reduction in the quantum yield.

[1] J. A. Leermakers, *ibid.*, **56**, 1537 (1934).

[2] T. G. Pearson and R. H Purcell, *J. Chem. Soc.*, 1151 (1935); *cf.* D. Volman and P. A. Leighton, *J. Chem. Phys.*, **7**, 781 (1939).

[3] J. W. Mitchell and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 159**, 32 (1937).

The question of the relative importance of the two primary processes (1) and (2) at different wave lengths has been the subject of some careful investigation, but the results are conflicting. Gorin[1] studied the photolysis in the presence of iodine and found that at a given wave length the ratio of methane to methyl iodide produced was constant, being independent of pressure, temperature, and light intensity. Working with the wave lengths 3130 and 2537 A, he found that when iodine was present, the total quantum yield was in both cases unity, so that the lower yields obtained in the absence of iodine must be attributed to radical-recombination reactions. At the higher wave length it was found that the free-radical process was more important than the molecular, by a factor of almost three, while at the lower wave length the molecular process was more important by about the same factor. Gorin's work was repeated and somewhat extended by Blacet and coworkers,[2] whose results conflict with Gorin's; thus they conclude that at 3130 A the only primary process is reaction (2), the split into free radicals, while at shorter wave lengths the two primary processes have about the same importance. There thus remains some doubt about the relative importance of the two primary reactions.

Mechanism of the Photochemical Process. Various reaction schemes have been proposed to account for the free-radical portion of the reaction, the most plausible being that of Leermakers,[3] which corresponds to the mechanism of Rice and Herzfeld for the thermal process. The main reactions are postulated to be

$$\text{(1)} \qquad CH_3CHO + h\nu \rightarrow CH_3 + CHO$$

$$\text{(2)} \qquad CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$$

$$\text{(3)} \qquad CH_3CO \rightarrow CH_3 + CO$$

$$\text{(4)} \qquad 2CH_3 \rightarrow C_2H_6$$

and application of the usual steady-state treatment gives, for the rate,

$$\frac{d[CO]}{dt} = k_2\left(\frac{I}{k_4}\right)^{1/2}[CH_3CHO] \tag{23}$$

If this scheme is the correct one, it follows that the coefficient k' appearing in the second term of Eq. (22) is equal to $(k_2/k_4)^{1/2}$. Several independent determinations[4] of the activation energy corresponding to k' have given

[1] E. Gorin, *Acta Physicochim. U.R.S.S.*, **9**, 681 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

[2] F. E. Blacet and D. E. Loeffler, *J. Am. Chem. Soc.*, **64**, 893 (1942); F. E. Blacet and J. D. Haldman, *ibid.*, 889.

[3] Leermakers, *loc. cit.*

[4] *Ibid.*; E. I. Akeroyd and R. G. Norrish, *J. Chem. Soc.*, 890 (1936); Mitchell and Hinshelwood, *loc. cit.*, Blacet and Loeffler, *loc cit.*; D. C. Grahame and G. K. Rollefson, *J. Chem. Phys.*, **8**, 98 (1940).

a value of about 10 kcal, so that if reaction (4) has zero activation energy, that of (2) must be 10 kcal.

Leermakers has suggested that other reactions, such as

$$\text{(5)} \qquad CHO + CH_3CHO \rightarrow CH_4 + CO + CHO$$

may play a part and finds that the correct rate equation can still be deduced if this is so. Evidence against this idea and in favor of the simple scheme of reactions (1) to (4) has been obtained by Akeroyd and Norrish,[1] who found that in mixtures of acetone and acetaldehyde the decomposition of the acetone was not sensitized by the free radicals produced from the aldehyde. If reaction (5) occurred, it would be expected that the analogous process

$$CHO + CH_3COCH_3 \rightarrow CH_4 + CO + CH_3CO$$

would take place so that the rate of the acetone decomposition would be increased.

Grahame and Rollefson[2] have pointed out that a comparison of the activation energies for the thermal and photochemical reactions provides a value for the activation energy of the intial carbon-carbon bond split in the thermal process, on the assumption that the mechanisms of the two reactions are the same. Thus the thermal activation energy is given by

$$E_t = E_2 + \tfrac{1}{2}(E_1 - E_4) \tag{24}$$

and the photochemical value by

$$E_p = E_2 - \tfrac{1}{2}E_4 \tag{25}$$

so that

$$E_1 = 2(E_t - E_p) \tag{26}$$

Taking the values of 48 and 10 kcal, respectively, for E_t and E_p gives

$$E_1 = 2(48 - 10) = 76 \text{ kcal}$$

which is somewhat higher than the value originally assumed by Rice and Herzfeld.

On the whole, the results of the investigations on the thermal and photochemical reactions are consistent with the hypothesis that a molecular and a free-radical reaction are taking place independently and that both the free-radical mechanisms correspond to that proposed by Rice and Herzfeld. The possibility that other chain processes are important must be borne in mind, however.

[1] Akeroyd and Norrish, *loc. cit.*

[2] Grahame and Rollefson, *loc. cit.*; *cf.* D. C. Grahame, *J. Chem. Phys.*, **7**, 680 (1939).

Decomposition of acetone

The Thermal Decomposition. The thermal decomposition of acetone is found[1] to be largely homogeneous and of the first order, the activation energy being 68 kcal. That free radicals play a part in the reaction, at any rate at high temperatures, is indicated by a number of investigations, including a measurement of the hydrogen-atom concentration, sensitization experiments, and inhibition experiments.

The presence of hydrogen atoms in the reaction system was demonstrated by Patat and Sachsse,[2] by the method using the para-ortho hydrogen conversion. An attempt to sensitize the decomposition by mercury dimethyl was made by Rice, Rodowskas, and Lewis,[3] who found that in the range 350 to 400°C no decomposition took place, but acetonylacetone was formed. From this result it can be concluded that the processes

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$$
$$2CH_2COCH_3 \rightarrow CH_3COCH_2CH_2COCH_3$$

occur at these temperatures, but that the chain processes necessary for the decomposition of acetone do not take place. Working at higher temperatures, over 500°C, Rice and Walters[4] showed that diacetyl can sensitize the decomposition of acetone, as could oxygen and ethylene oxide. It thus appears that methyl radicals can induce chains above 500°C but not at temperatures around 400°C.

Evidence that chain processes occur in the decomposition comes from inhibition experiments. Work with propylene was carried out by Rice and Polly[5] and by Smith and Hinshelwood,[6] and considerable inhibition was found. The latter found that nitric oxide, as with acetaldehyde, has both inhibiting and catalytic effects, which tend to mask one another. The inhibition experiments indicate that the mean chain length is very short.

The following chain mechanism for the decomposition was suggested by Rice and Herzfeld,[7] whose estimated activation energies are given:

[1] C. N. Hinshelwood and W. K. Hutchison, *Proc. Roy. Soc.* (*London*), **A, 111,** 245 (1926); F. O. Rice and R. E. Vollrath, *Proc. Natl. Acad. Sci. U.S.*, **15,** 702 (1929); C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 149,** 340 (1935); J. R. Huffman, *J. Am. Chem. Soc.*, **58,** 1815 (1936).

[2] F. Patat and H. Sachsse, *Naturwissenschaften*, **23,** 247 (1935); *Z. physik. Chem.*, **B, 31,** 105 (1935).

[3] F. O. Rice, E. L. Rodowskas, and W. R. Lewis, *J. Am. Chem. Soc.*, **56,** 2497 (1934).

[4] F. O. Rice and W. D. Walters, *ibid.*, **63,** 1701 (1941).

[5] Rice and Polly, *loc. cit.*

[6] J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 183,** 33 (1944).

[7] Rice and Herzfeld, *loc. cit.*

(1)	$CH_3COCH_3 \rightarrow CH_3 + CH_3CO$	$E_1 = 70$ kcal
(2)	$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$	$E_2 = 15$ kcal
(3)	$CH_2COCH_3 \rightarrow CH_3 + CH_2CO$	$E_3 = 48$ kcal
(4)	$CH_3 + CH_2COCH_3 \rightarrow CH_3COC_2H_5$	$E_4 = 8$ kcal

This chain-ending process gives a first-order rate equation and an activation energy of

$$E = \tfrac{1}{2}(E_1 + E_2 + E_3 - E_4) = 62.5 \text{ kcal}$$

and this would agree better with the observed value if, as is likely, the activation energy of (4) were taken as zero. The predicted chain length (*cf.* p. 235) is about 300, so that the much lower values obtained from the inhibition experiments suggest that part of the reaction proceeds by a molecular mechanism (see, however, p. 238).

Photochemical Reaction. The photodecomposition of acetone has also been investigated very thoroughly, and the results in general confirm the conclusions drawn from studies of the thermal decomposition. One of the most significant results that has been obtained is that the activation energy of the process

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$$

is significantly higher than that of the analogous processes occurring with the paraffins and with acetaldehyde; consequently at the low temperatures used for the photolytic work the reaction occurs very slowly and chains are not developed. This result is consistent with the fact that it is difficult to sensitize the thermal decomposition except at rather high temperatures.

The quantum yield of the photodecomposition is usually less than unity[1]; the main products are ethane and carbon monoxide, but methane is also an important product, and smaller amounts of hydrogen are found. Norrish[2] found that in the photolysis of methyl ethyl ketone the main products were ethane, propane, and butane, which is evidence that the primary photochemical step is a split into radicals, the process in the case of acetone being

$$CH_3COCH_3 + h\nu \rightarrow CH_3CO + CH_3$$

That acetyl radicals are produced is shown by the fact[3] that one of the minor products of the reaction is diacetyl, $CH_3COCOCH_3$, formed by the combination of two acetyl radicals.

The existence of methyl and acetyl radicals has been established by the

[1] G. H. Damon and F. Daniels, *J. Am. Chem. Soc.*, **55**, 2363 (1933).
[2] R. G. Norrish, *J. Chem. Soc.*, 874, 1456 (1934); *Trans. Faraday Soc.*, **30**, 103 (1934).
[3] M. Barak and D. W. G. Style, *Nature*, **135**, 307 (1935).

Paneth method and in other ways. Pearson and Purcell[1] found that various types of mirrors were removed and identified the products as methyl compounds. Later Glazebrook and Pearson[2] carried out a more comprehensive investigation using tellurium mirrors and found that methyl and acetyl radicals are formed in approximately equal amounts; they further found that the life of the acetyl radical is much shorter than that of the alkyl radicals. The amount of diacetyl produced in the photolysis decreases if inert gases are added to the reaction mixture, and the amount of carbon monoxide formed increases.[3] This indicates that the inert-gas molecules prevent the diffusion of acetyl radicals to the walls, so that the gas-phase reaction

$$CH_3CO \rightarrow CH_3 + CO$$

is favored over the formation of diacetyl, which takes place on the walls.

Although free radicals are undoubtedly present when acetone is photolyzed, the evidence is all against the existence of long chains; presumably the subsequent reactions require too high an activation energy. This is indicated by the low quantum yields and also by the fact that small amounts of nitric oxide have no inhibitory effects on the decomposition;[4] larger amounts, however, decrease the production of carbon monoxide and completely eliminate the formation of ethane.[5] This latter result indicates that no molecular mechanism takes place. Additional evidence that the primary process is exclusively the formation of radicals comes from the work of Gorin,[6] who photolyzed acetone in the presence of iodine, which reacts rapidly with the free radicals with the formation of methyl and acetyl iodides. The quantum yield of methyl iodide was found to be approximately unity, which would be the case if the formation of radicals were the only initial step.

The photolysis of acetone has been investigated at higher temperatures, up to 400°C, by a number of workers.[7] The amount of methane produced is found[8] to be much greater than at the low temperatures and is comparable to the amount of carbon monoxide produced. This can be explained

[1] T. G. Pearson and R. H. Purcell, *J. Chem. Soc* , 1718 (1934); 1151 (1935); *cf.* N. Prileshajeva and A. Terenin, *Trans. Faraday Soc* , **31**, 1483 (1935).

[2] H. H. Glazebrook and T. G. Pearson, *J Chem Soc.*, 567 (1937); *cf.* M. H. Feldman, J. E. Ricci, and M. Burton, *J. Chem. Phys.*, **10**, 618 (1942).

[3] T. Iredale and L. E. Lyons, *J. Chem Soc.*, 588 (1944).

[4] Mitchell and Hinshelwood, *loc. cit.*

[5] H. W. Anderson and G. K. Rollefson, *J. Am. Chem. Soc.*, **63**, 816 (1941).

[6] E. Gorin, *Acta Physicochim. U.R.S.S.*, **8**, 513 (1938); *J. Chem. Phys.*, **7**, 256 (1939).

[7] J. A. Leermakers, *J. Am. Chem. Soc.*, **56**, 1899 (1934); C. A. Winkler, *Trans. Faraday Soc.*, **31**, 76 (1935); Akeroyd and Norrish, *loc. cit.*; A. O. Allen, *J. Am. Chem. Soc.*, **63**, 708 (1941).

[8] Allen, *ibid.*

in terms of the free-radical mechanism of Leermakers,[1] which is equivalent to the Rice-Herzfeld scheme for the thermal process:

(1) $CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO$

(2) $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$

(3) $CH_2COCH_3 \rightarrow CH_3 + CH_2CO$

(4) $CH_3 + CH_2COCH_3 \rightarrow CH_3COC_2H_5$

In addition the reaction

(1′) $CH_3CO \rightarrow CH_3 + CO$

is responsible for the decomposition of the acetyl radical produced in (1). The reason that chains are not set up is again that reactions (2) and (3) have activation energies which are too high for the reactions to occur readily at the temperatures used. Moreover, since the activation energy of (2) is much less than that for (3) (see below), methane will be produced in greater quantities at the higher temperatures, and under these circumstances the acetonyl radicals will disappear by reactions such as

$$CH_3 + CH_2COCH_3 \rightarrow C_2H_5COCH_3$$

Various estimates have been made of the activation energies of some of the individual steps in the photochemical decomposition, and these will now be discussed.

Decomposition of the Acetyl Radical. In his investigations of the photolysis of acetone-iodine mixtures, Gorin[2] found that very little iodine was produced; this indicates that almost all the acetyl radicals formed in the primary process react with iodine, so that the acetyl radical must be fairly stable. From the increase in carbon monoxide production with temperature, a value of 17 kcal was estimated for the activation energy. By similar methods Benson and Forbes[3] obtained a value of 16 kcal, and Herr and Noyes[4] one of 18 kcal. All these values are in good agreement with a value of 16 kcal calculated by Bawn.[5] There is some evidence that the decomposition may require a third body.

Reaction $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$. The energy of activation of this reaction has been determined by Allen[6] and by Dorfman and Noyes[7] to be about 7 kcal.

Decomposition of CH_2COCH_3. That the activation energy of this reaction is high is indicated by the fact, already discussed, that in the

[1] Leermakers, *loc. cit.*; a more detailed scheme has been proposed by W. A. Noyes and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

[2] Gorin, *loc. cit.*

[3] S. W Benson and G. S. Forbes, *J. Am. Chem. Soc.*, **65**, 1399 (1943).

[4] D. S. Herr and W. A. Noyes, *ibid.* **62**, 2052 (1940).

[5] C. E. H. Bawn, *Trans. Faraday Soc.*, **34**, 598 (1938).

[6] A. O. Allen, *loc. cit.*

[7] L. M. Dorfman and W. A. Noyes, *J. Chem. Phys.*, **16**, 557 (1948).

photodecomposition of acetone, methane becomes an important product at higher temperatures; this is because reaction (2) occurs, but not (3) to any extent. Further evidence for the stability of the radical is the fact that acetonylacetone is a product of the reaction of methyl radicals with acetone at temperatures up to 400°C.

Photochemical Decomposition in Solution. The photochemical decomposition of acetone in solution in paraffin hydrocarbons was investigated by Bamford and Norrish,[1] who found that the products were different from those obtained in the gas phase. In particular, it was found that methane was produced instead of ethane, and this was attributed to reaction of methyl radicals with the solvent:

$$CH_3 + C_nH_{2n+2} \rightarrow CH_4 + C_nH_{2n+1}$$

The higher hydrocarbon radicals produced in this way become stabilized by disproportionation:

$$C_nH_{2n+1} + C_mH_{2m+1} \rightarrow C_nH_{2n} + C_mH_{2m+2}$$

This type of reaction with the solvent is found to be very common.

Decomposition of dimethyl ether

Thermal Decomposition. The products of the thermal decomposition of dimethyl ether correspond to the equation

$$CH_3OCH_3 \rightarrow CH_4 + CO + H_2$$

The reaction is homogeneous and of the first order and has an activation energy of 58.5 kcal.[2] The following free-radical mechanism has been proposed by Rice and Herzfeld,[3] whose activation energies are given:

(1)	$CH_3OCH_3 \rightarrow CH_3 + OCH_3$	$E_1 = 80$ kcal
(2)	$CH_3 + CH_3OCH_3 \rightarrow CH_4 + CH_2OCH_3$	$E_2 = 15$ kcal
(3)	$CH_2OCH_3 \rightarrow CH_3 + HCHO$	$E_3 = 38$ kcal
(4)	$CH_3 + CH_2OCH_3 \rightarrow C_2H_5OCH_3$	$E_4 = 8$ kcal

These are the main reactions constituting the chain; in addition, the radical CH_3O decomposes to give formaldehyde and a hydrogen atom,

$$(5) \qquad CH_3O \rightarrow HCHO + H$$

and the atom also acts as a chain carrier. Since chain ending is assumed to involve unlike radicals, the mechanism leads to first-order kinetics, and the activation energy is found to be

$$E = \tfrac{1}{2}(E_1 + E_2 + E_3 - E_4) = 62.5 \text{ kcal}$$

[1] C. H. Bamford and R. G. Norrish, *J. Chem. Soc.*, 1531 (1938).
[2] C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc. (London)*, **A, 115**, 215 (1927).
[3] F. O. Rice and K. F. Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

which is in reasonably good agreement with experiment. The calculated chain length is about 10^5. The above scheme accounts for the decomposition as far as formaldehyde, which is believed to decompose into CO + H_2 by a process in which free radicals play only a very unimportant role.[1]

The presence of free radicals in the reaction system has been demonstrated in a number of ways. The reaction is inhibited by nitric oxide,[2] and the mean chain length was found to be about 17 at 540°C. The smallness of this chain length as compared with that corresponding to the postulated free-radical mechanism suggests that a molecular process also occurs. The decomposition is also inhibited by propylene,[3] which, however, is less effective than nitric oxide in that larger amounts are required. In a study of the reaction by the method based on the para-ortho hydrogen conversion, Patat[4] found that the concentration of hydrogen atoms is smaller than that consistent with the assumption that the reaction takes place entirely by the free-radical mechanism; as has been seen, however, the method is not sufficiently reliable to allow quantitative conclusions to be drawn.

The decomposition has also been sensitized by various substances which give rise to methyl radicals. Leermakers[5] photolyzed acetone to produce methyl radicals and studied the rate of the sensitized decomposition of the ether by measuring the rate of production of methane. Methane is produced by reaction of methyl radicals with either methyl ether or acetone, and on the basis of the activation energy for methane production, Leermakers deduced that the activation energy of reaction (2) is 15 kcal, which was the value assumed by Rice and Herzfeld. For reaction (3) he deduced 35 kcal, also in good agreement with the postulated value. Sensitization of the reaction has also been achieved by the addition of diacetyl.[6]

Decomposition of diethyl ether

Thermal Decomposition. The kinetics of the thermal decomposition of diethyl ether were first investigated by Hinshelwood,[7] who found that the over-all reaction could be represented by the equation

[1] E. W. R. Steacie and W. A. Alexander, *J. Chem. Phys.*, **5**, 372 (1937); *Can. J. Research*, B, **15**, 295 (1937); *cf.* C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2129 (1936).

[2] L. A. K. Staveley and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 154**, 335 (1936); **A, 159**, 192 (1937).

[3] F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

[4] F. Patat, *Z. physik. Chem.*, B, **32**, 291 (1936).

[5] Leermakers, *loc. cit.*

[6] C. H. Klute and W. D. Walters, *J. Am. Chem. Soc.*, **67**, 550 (1945).

[7] C. N. Hinshelwood, *Proc. Roy. Soc* (*London*), **A, 114**, 84 (1927); *cf.* J. G. Davoud and C. N. Hinshelwood, *ibid*, **A, 171**, 39 (1939), **A, 174**, 50 (1940)

$$C_2H_5OC_2H_5 = CO + 2CH_4 + \tfrac{1}{2}C_2H_4$$

Acetaldehyde was found to be an intermediate product, so that at least part of the reaction appears to proceed as

$$C_2H_5OC_2H_5 = CH_3CHO + C_2H_6$$

followed by the decomposition of acetaldehyde and ethane. The reaction was found to be approximately of the first order, but the first order constants increased with pressure and in particular fell sharply at low pressures; in addition, it was found that the reaction was somewhat inhibited by the products. The activation energy was found to be about 53 kcal.

A study of the formation and decomposition of acetaldehyde as an intermediate product was made by Fletcher and Rollefson.[1] They found that the aldehyde decomposed more rapidly than it normally does, a result they attribute to the fact that radicals produced by the ether bring about decomposition of the aldehyde. They also found that free radicals produced in the decomposition of ethylene oxide could sensitize the ether decomposition. It was shown by Leermakers[2] that radicals produced in the photodecomposition of acetone also sensitize the decomposition. Free radicals in the reaction system have been detected using the Paneth method.[3]

In view of the result that the specific rate constant of the reaction varies with the pressure, the reaction has been studied over a very wide range of pressures. Even at the highest pressures investigated, about 300 atm, the specific rate was found to be still increasing.[4] This result indicates that the order of the reaction is in fact between unity and two.

A free-radical mechanism for the decompositions was proposed by Rice and Herzfeld[5] and is analogous to that proposed for the dimethyl ether decomposition, the main steps being

$$(1) \qquad C_2H_5OC_2H_5 \rightarrow CH_3 + CH_2OC_2H_5$$
$$(2) \qquad CH_3 + C_2H_5OC_2H_5 \rightarrow C_2H_6 + CH_2OC_2H_5$$
$$(3) \qquad CH_2OC_2H_5 \rightarrow CH_3 + CH_3CHO$$
$$(4) \qquad CH_3 + CH_2OC_2H_5 \rightarrow C_2H_5OC_2H_5$$

[1] Fletcher and Rollefson, *op. cit.*, 2129, 2135.

[2] Leermakers, *loc. cit.*

[3] F. O. Rice and W. R Johnston, *J. Am. Chem. Soc.*, **56**, 211 (1934).

[4] D. M. Newitt and M. A. Vernon, *Proc. Roy. Soc (London)*, **A, 135**, 307 (1932); E. W. R. Steacie and E. Solomon, *J. Chem. Phys.*, **2**, 503 (1934); E. W. R. Steacie, W. H. Hatcher, and S. Rosenberg, *ibid.*, **4**, 220 (1936).

[5] Rice and Herzfeld, *loc. cit.*

This gives rise to a first-order law. On the basis of this scheme Hobbs[1] has investigated the reaction by the nitric oxide method, following earlier work by Staveley and Hinshelwood,[2] who found a mean chain length of 4.4 at 540°C. The inhibition results differed markedly from those obtained with ethane in that the amount of inhibition was found to be independent of the ether pressure. It was seen on page 251 that the dependence of the degree of inhibition on the ethane pressure indicates that the reaction of nitric oxide with a radical is in competition with the reaction between the radical and ethane. Since no such competition exists in the case of the reaction under discussion, it follows that the nitric oxide reaction competes with a reaction which is independent of the ether concentration and is probably the unimolecular decomposition of the radical itself. This indicates that the radical concerned is the large radical $CH_2OC_2H_5$, so that the competing processes are

(3) $$CH_2OC_2H_5 \rightarrow CH_3 + CH_3CHO$$

and

$$NO + CH_2OC_2H_5 \rightarrow \text{removal of radical}$$

The essential difference between the ethane and the diethyl ether reactions is therefore that in the former case the most important reaction of the nitric oxide is with hydrogen atoms and methyl radicals, whereas with the ether the most important reaction is with the radicals $CH_2OC_2H_5$. This can come about only if in the ethane decomposition the H atoms and CH_3 radicals are present in much higher concentrations than the larger C_2H_5 radicals, while in the ether decomposition the larger radicals predominate. This situation will arise in the ether reaction provided that the activation energy of reaction (2) is appreciably less than that of (3). On this basis Hobbs has formulated expressions for the amount of inhibition which are consistent with his experimental results. A comparison between nitric oxide and propylene as inhibitors for this reaction has been made by Smith and Hinshelwood,[3] who find that both substances give the same limiting rates, although much more propylene is required than nitric oxide. An important difference, however, is that with propylene the amount of inhibition does depend upon the ether pressure, indicating that propylene reacts with the smaller radical CH_3 as well as with $CH_2OC_2H_5$. The interpretation given to these results is that propylene reacts comparatively slowly with the radical $CH_2OC_2H_5$ so that, in spite of the lower con-

[1] J. E. Hobbs, *Proc. Roy. Soc.* (*London*), **A, 167,** 465 (1938).

[2] Staveley and Hinshelwood, *loc. cit.*; *J. Chem. Soc.*, 1568 (1937).

[3] J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 180,** 237 (1942).

centration of methyl radicals, reaction between them and the inhibitor plays a significant role.

Photobromination of methane

Both the thermal and photochemical reactions between bromine and methane have been studied by Kistiakowsky, Van Artsdalen, and Anderson.[1] The kinetics of the photochemical reaction, which will now be considered, are important in providing a value for the energy of dissociation of the carbon-hydrogen bond in methane.

The reaction was studied from 150 to 230°C, and the main products were hydrogen bromide and methyl bromide; in addition, some methylene bromide was formed by the bromination of methyl bromide. The rate of reaction was found to obey the law

$$\frac{d[CH_3Br]}{dt} = \frac{kI^{1/2}[CH_4][Br_2]^{1/2}(1/P)^{1/2}}{1 + \dfrac{m[HBr]}{[Br_2]}} \tag{27}$$

where k and m are constants, I is the intensity of light absorbed, and P is the total pressure in the system. This law is seen to be closely analogous to that established by Bodenstein and his coworkers for the hydrogen-bromine reaction (*cf.* p. 204).

The dependence of the rate of reaction on the concentrations, light intensity, and total pressure establishes the mechanism

(1) $Br_2 + h\nu \rightarrow 2Br$

(2) $Br + CH_4 \rightarrow CH_3 + HBr$

(3) $CH_3 + Br_2 \rightarrow CH_3Br + Br$

(4) $CH_3 + HBr \rightarrow CH_4 + Br$

(5) $Br + Br + M \rightarrow Br_2 + M$

where M is a third body. This scheme gives rise to the law

$$\frac{d[CH_3Br]}{dt} = \frac{ak_2I^{1/2}[CH_4][Br_2]^{1/2}(1/P)^{1/2}}{1 + \dfrac{k_4[HBr]}{k_3[Br_2]}} \tag{28}$$

where a is a temperature-independent apparatus constant; the $1/P$ term arises from the fact that the rate of reaction (5) is proportional to the total pressure in the system.

[1] G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944); *cf.* H. G. Anderson, G. B. Kistiakowsky, and E. R. Van Artsdalen, *ibid.*, **10**, 305 (1942).

The temperature dependence of the constant k in Eq. (27) corresponds to an activation energy of 17.8 kcal, which applies to reaction (2). Since reaction (4) is the reverse of (2), the energy change in the reaction (2) is the difference between the activation energies of the two reactions, *i.e.*,

$$Br + CH_4 \rightarrow CH_3 + HBr - (17.8 - E_4) \text{ kcal}$$

Together with the thermochemical relationship

$$HBr \rightarrow H + Br - 85.8 \text{ kcal}$$

this result gives rise to

$$CH_4 \rightarrow CH_3 + H - (103.6 - E_4) \text{ kcal}$$

The activation energy of reaction (4) may be presumed to be very small, by analogy with the reaction between hydrogen atoms and hydrogen bromide, the activation energy for which is about 1 kcal. This was supported by the fact that the temperature coefficient of the constant m in Eq. (27) was 2 kcal, indicating that $E_4 - E_3$ has this value; since E_3 is almost certainly zero, this gives a value of 2 kcal for E_4. This value was confirmed by the photolysis of mixtures of methyl iodide and hydrogen bromide, the yield of methane, attributable to reaction (4), showing that E_4 is about 0.8 kcal greater than the activation energy of $CH_3 + I_2 \rightarrow CH_3I + I$, which almost certainly has zero activation energy.

If the value of 1.5 kcal for E_4 is accepted, the energy of dissociation of methane into a methyl radical and a hydrogen atom is 103.6 − 1.5, *i.e.*, approximately 102 kcal. At 0°K this value becomes 101 kcal.

A similar study of the photobromination of ethane led to a value of 98 kcal for the dissociation energy of the carbon-hydrogen bond.

PROBLEMS

1. Derive Eq. (19) on the basis of the reaction scheme given on page 249.

2. On the basis of reactions (1) to (4) on page 260, derive the rate equation in terms of the rate constants for the individual steps.

3. Derive Eq. (23) on the basis of reactions (1) to (4) on page 262.

4. Derive the rate equation for the acetone decomposition on the basis of reactions (1) to (4) on page 265.

5. Derive the rate equation for the decomposition of dimethyl ether on the basis of reactions (1) to (4) on page 268. Write down the expression for the energy of activation in terms of the values for the individual steps.

6. If the activation energy of the reaction $H + C_2H_6 \rightarrow H_2 + C_2H_5$ is 9.0 kcal, calculate that of the reverse reaction assuming the following heats of dissociation:

$$D\,(H—H) = 104.2 \text{ kcal}$$

$$D\,(C_2H_5—H) = 98.0 \text{ kcal}$$

CHAPTER 10

CATALYSIS

By the early part of the last century there had been discovered a number of reactions whose rates were influenced by the presence of a substance which itself remained unchanged at the end of the process. These reactions include the conversion of starch into sugars, the rate of which was influenced by acids, the decomposition of alcohols and of hydrogen peroxide, influenced by metallic surfaces, and the formation of ammonia in the presence of spongy platinum. Such reactions were classified by Berzelius[1] in 1836 under the collective title of *catalyzed processes* and were regarded by him as taking place under the influence of a *catalytic force*. The idea of a catalytic force has not proved fruitful, but the term *catalysis* is still employed to describe the influence on reactions of substances which emerge from the process unchanged. Substances which decrease the rate of reaction are usually referred to as *negative catalysts*, or as *inhibitors;* examples have already been noted, and further cases will be considered in the chapter on oxidation (Chap. 11).

Although by definition the amount of catalyst should be unchanged at the end of the reaction, it does not follow that the catalyst does not enter into chemical reaction as the reaction proceeds. Indeed, as knowledge of catalytic processes has developed, it has become increasingly clear that during the process the catalyst invariably enters into chemical union; in the case of one reacting substance, a complex may be formed between this (known as the *substrate*) and the catalyst, while in the case of more than one substrate the complex may involve one or more of the substrates combined with the catalyst. These complexes are formed as intermediates only and decompose to give the products of the reaction with the regeneration of the catalyst molecule, this process often taking place in one stage. When, for example, a reaction is catalyzed by hydrogen ions, an intermediate complex, involving the substrate and the hydrogen ion, is formed, and this later reacts further (*e.g.*, with the solvent) with the liberation of the ion and the formation of the products of the reaction.

Since the catalyst is unchanged at the end of the reaction, it gives no energy to the system; according to thermodynamics it can therefore have

[1] J. J. Berzelius, *Jahresber. Chem.*, **15**, 237 (1836).

no influence on the position of equilibrium. It follows from this that since the equilibrium constant K is the ratio of the rate constants in the forward and reverse directions, *i.e.*, $K = k_1/k_{-1}$, a catalyst must influence the forward and reverse rates in the same proportion. This conclusion has been verified experimentally in a number of instances; thus an acid will influence, to the same degree, the hydrolysis of an ester and the reverse esterification.

It is frequently found that an extremely small amount of a catalyst will cause a considerable increase in the rate of a reaction, so that a large amount of the reactant is transformed in a second; thus colloidal palladium at a concentration of 1 gram atom in 10^8 liters will cause hydrogen peroxide to decompose at a measurable rate. An idea of the effectiveness of a catalyst is sometimes given by expressing its *turnover number*, which is the number of molecules of substrate which are decomposed per minute by one molecule of the catalyst; as an example, the enzyme catalase has a turnover number of 5,000,000 for the decomposition of hydrogen peroxide. The turnover number, of course, varies with the temperature and in general with the initial concentration of substrate, so that it is not a particularly useful quantity in kinetic work, in which the appropriate specific rate coefficient is used.

Very often, especially when the reaction does not involve chains, the rate of a catalytic reaction is directly proportional to the concentration of the catalyst; *i.e.*,

$$v = F[C] \tag{1}$$

where $[C]$ represents the concentration of the catalyst and F is a function of the concentration of the substrate. It has been seen in Chap. 6 that this law is obeyed with reactions on surfaces, the rate being directly proportional to the surface area, *i.e.*, to the concentration of surface sites in the system.

If Eq. (1) were obeyed exactly, it follows that the rate of reaction in the absence of the catalyst would be zero. There has been considerable argument as to whether this law could ever be obeyed rigorously, since this would imply that a catalyst could initiate a reaction that otherwise could not occur at all. Many examples are known for which the law is not obeyed but for which it is necessary to introduce an additional term which is independent of the catalyst concentration, *viz.*,

$$v = F[C] + F' \tag{2}$$

so that at zero concentration of the catalyst the reaction occurs with the velocity F'. As an example of this type of behavior may be mentioned

the mutarotation of glucose (*cf.* p. 000), which is catalyzed by both hydrogen and hydroxyl ions and whose rate is given by the expression[1]

$$v = 0.0096 + 0.258[H_3O^+] + 9{,}750[OH^-] \quad (3)$$

Reactions are also known for which there is no measurable rate at zero concentration of the catalyst, *i.e.*, to which Eq. (1) applies, but there is always some doubt as to whether the reaction is not occurring at all or is occurring so slowly that its progress cannot be detected. Ostwald[2] believed that in such cases the reaction is occurring immeasurably slowly, but Armstrong[3] and Lowry[4] have maintained that there are certain reactions for which the rate is truly zero at zero catalyst concentration. As an example, Lowry quoted the mutarotation of glucose as a reaction which can occur only when an acid and a base are present simultaneously, since in the absence of one or both there seemed to be no mechanism by which the reaction could occur. The argument is a somewhat academic one, but it would appear that Ostwald's point of view is more tenable, since for any reaction that can be written down there is some mechanism by which it can occur, even if this has to involve the complete dissociation of the reactant and a reorganization of the atoms. Such a process would involve a very high free energy of activation, and the reaction would therefore take place negligibly slowly. From this point of view a catalyst is a substance which lowers the free energy of activation by allowing the reaction to occur by an alternative mechanism.

Mechanism of catalysis

This idea that a catalyst diminishes the free energy of activation of a process by introducing an alternative mechanism has been developed, and reaction schemes have been worked out in individual cases. The main feature of such schemes is that an intermediate complex is formed between the catalyst and at least one of the substrate molecules and that this complex undergoes subsequent reactions. In the simplest type of catalyzed reaction, involving only one substrate, the substrate and the catalyst form a complex, which subsequently decomposes with the formation of the products and the regeneration of the catalyst, this decomposition taking place in a single stage; many surface reactions are of this type, the complex being the adsorbed reactant molecule. In other cases, also exemplified by certain surface reactions, the complex involves the catalyst and two

[1] C. S. Hudson, *J. Am. Chem. Soc.*, **29**, 1571 (1907).

[2] W. Ostwald, *Physik. Z.*, **3**, 313 (1902).

[3] H. E. Armstrong, *Brit. Assoc. Advancement Sci., Rept.*, 962 (1885); *Proc. Roy. Soc. (London)*, **40**, 287 (1886).

[4] T. M. Lowry, *J. Chem. Soc.*, **129**, 2554 (1927).

substrate molecules. In more complicated types of catalysis, the catalyst may act in a different way, by giving rise to free radicals which initiate chain processes.

The case of a nonchain mechanism involving a single substrate will be considered first. A kinetic scheme to account for the phenomena associated with this type of catalysis was put forward by Herzfeld;[1] a slightly more general mechanism that appears to apply to most types of catalysis involving only one substrate and not involving chain reactions, is as follows:[2]

$$C + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + Y \tag{1}$$

$$X + W \xrightarrow{k_2} P + Z \tag{2}$$

Here C represents the catalyst and S the substrate; X is the intermediate complex and Y some substance which is formed in addition to it. W is a molecule which reacts with the complex to give the product or products P with elimination of a molecule Z. It is assumed that the reaction products are at such a low free-energy level that the reverse reaction $P + Z \rightarrow X + W$ may be neglected. The treatment to be given will apply only to initial rates of reaction; otherwise very clumsy kinetic expressions are obtained, and it is difficult to analyze the experimental data with respect to them.

In surface catalysis, X is an adsorption complex and Y and W are nonexistent; k_{-1} and k_2 are in this case first-order rate constants, while k_1 is a second-order constant. The species Y and Z are also probably nonexistent in most cases of enzyme catalysis involving only one substrate. The substances Y and W do, however, play roles in acidic and basic catalysis in solution; thus, if C is an acid, reaction (1) involves the transfer of a proton to S, so that Y is the base conjugate to C. Similarly, in basic catalysis, Y is the acid conjugate to the base C. In acid catalysis W is a basic or amphoteric substance which accepts a proton from X and is frequently a solvent molecule; it may also, however, be identical with Y. In basic catalysis W transfers a proton to X and may be the solvent or another acidic substance present in the system.

Two possibilities exist with regard to the stability of the intermediate complex X, and the kinetic laws obtained depend in an important manner upon what is assumed in this connection. In the first place, the complex may be one which is reconverted into the catalyst and the substrate at a rate which is significantly greater than the rate with which it undergoes

[1] K. F. Herzfeld, *Z. physik. Chem.*, **98**, 151 (1921).

[2] K. J. Laidler and I. M. Socquet, *J. Phys. and Colloid Chem.*, **54**, 519 (1950).

reaction (2) and gives the final products. The over-all rate of reaction can then be calculated by obtaining the concentration of X from the equilibrium (1) alone and multiplying this by $k_2[W]$, this procedure being equivalent to what was done in the case of surface reactions. Since this case corresponds to Arrhenius's concept of a chemical reaction as involving equilibrium between the reactants and the activated complex, the complexes relevant to this type of catalysis are frequently known as Arrhenius complexes.

The second possibility is that the intermediate complex is a much less stable species, so that the rate of its reaction (2) to give the final products is not small compared with the reverse rate of reaction (1). It is then not permissible to calculate the concentration of X by making use of the equilibrium (1), since the rate of (2) cannot be neglected. However, since the concentration of X in this case is low, it is permissible to make use of the steady-state treatment. A complex of this type is frequently known as a van't Hoff complex. Rate expressions for these two cases will now be obtained.

Equilibrium Treatment. In the case that the rate of reaction (2) can be neglected in calculating the concentration of the complex X, the concentrations of X, Y, C, and S are related by

$$\frac{[X][Y]}{[C][S]} = \frac{k_1}{k_{-1}} = K \tag{4}$$

where K is the equilibrium constant. This expression allows the concentration of X to be calculated in terms of the concentrations $[Y]$, $[C]$, and $[S]$, but the latter two concentrations do not correspond to the initial concentrations, since by hypothesis appreciable amounts of C and S have become combined in the intermediate complex X. If $[C]_0$ and $[S]_0$ are the initial concentrations of C and S, respectively, it follows that

$$[C] = [C]_0 - [X] \tag{5}$$

$$[S] = [S]_0 - [X] \tag{6}$$

Equation (4) therefore becomes

$$\frac{[X][Y]}{([C]_0 - [X])([S]_0 - [X])} = K \tag{7}$$

This is a quadratic in $[X]$ and can be solved for $[X]$; an expression for the rate can then be written down, since the rate is equal to $k_2[X][W]$. However, it is more convenient to consider two special cases.

Case 1. If the initial concentration of the substrate is much greater than that of the catalyst, *i.e.*, if $[S]_0 \gg [C]_0$, it follows that $[S]_0 - [X]$ is

very close to $[S]_0$, since $[X]$ cannot exceed $[C]_0$; Eq. (7) therefore approximates to

$$\frac{[X][Y]}{([C]_0 - [X])[S]_0} = K \tag{8}$$

whence

$$[X] = \frac{K[C]_0[S]_0}{K[S]_0 + [Y]} \tag{9}$$

The rate of reaction is therefore

$$-\frac{d[S]}{dt} = k_2[X][W] \tag{10}$$

$$= \frac{k_2K[C]_0[S]_0[W]}{K[S]_0 + [Y]} \tag{11}$$

This rate equation corresponds to a variation in rate of the type represented in Fig. 26; when $K[S]_0 < [Y]$, the rate varies linearly with $[S]_0$, while at higher substrate concentrations, when $K(S)_0 > [Y]$, the rate is independent of $[S]_0$. As long as the condition $[S]_0 \gg [C]_0$ holds, however, the rate varies linearly with $[C]_0$. It will be seen later, on the other hand, that if $[C]_0$ is increased so that the condition $[S]_0 \gg [C]_0$ no longer holds, the rate becomes independent of $[C]_0$.

This type of behavior is characteristic of reactions on surfaces and of enzyme reactions; for both of these, the species Y and W are nonexistent and the rate law becomes

$$-\frac{d[S]}{dt} = \frac{k_2K[C]_0[S]_0}{K[S]_0 + 1} \tag{12}$$

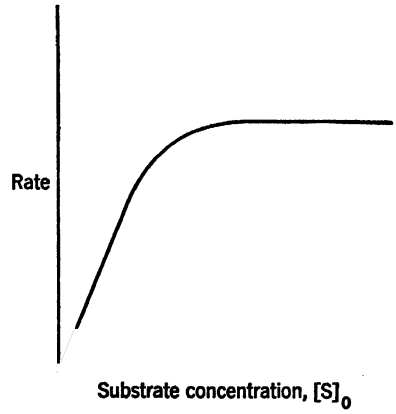


FIG. 26. The rate of reaction as a function of the substrate concentration for a catalyzed reaction.

For surface reactions this is equivalent to Eq. (26) on page 156 and corresponds to first-order kinetics at low concentrations and zero-order kinetics at higher ones. Equation (12) is also equivalent to the Michaelis-Menten law for enzyme systems (*cf.* p. 305); this law is usually expressed as

$$-\frac{d[S]}{dt} = \frac{k_2[C]_0[S]_0}{[S]_0 + K_m} \tag{13}$$

where K_m, the Michaelis constant, is equal to $1/K$ in the above treatment. This law has been shown to be obeyed by a variety of enzyme-catalyzed reactions.

In the case of acid- and base-catalyzed reactions, it is found that owing to the peculiar nature of the equilibria established in the solutions, the condition $K[S]_0 < [Y]$ always holds; the rate is therefore always exactly proportional to the first power of the substrate concentration.

Case 2. If on the other hand the initial concentration of the catalyst is much greater than that of the substrate, *i.e.*, if $[C]_0 \gg [S]_0$, $[C]_0$ can be set equal to $[C]_0 - [X]$ in Eq. (7), which then becomes

$$\frac{[X]\,[Y]}{[C]_0([S]_0 - [X])} = K \tag{14}$$

The rate of reaction is in this case

$$-\frac{d[S]}{dt} = \frac{k_2K[C]_0[S]_0[W]}{K[C]_0 + [Y]} \tag{15}$$

It is seen that the rate now varies linearly with the concentration of substrate (as long as the condition $[C]_0 \gg [S]_0$ holds), but that the variation with the catalyst concentration is nonlinear, the relationship between rate and $[C]_0$ being indicated in Fig. 27. At low catalyst concentrations the rate is proportional to the catalyst concentration, while at higher ones the rate is independent of $[C]_0$.

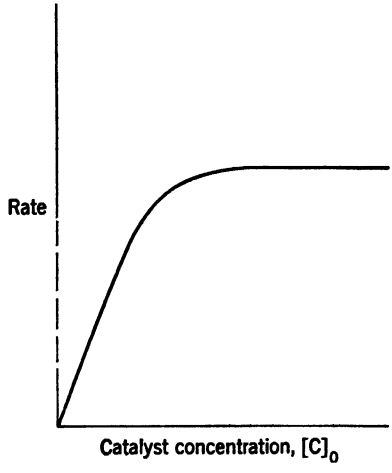


FIG. 27. The rate of a reaction as a function of the catalyst concentration.

This type of variation of the reaction rate with the catalyst concentration has been observed experimentally, but not many investigations have been carried out in which the condition $[C]_0 \gg [S]_0$ holds. In surface reactions the rate is usually found to vary linearly with the amount of surface, but at very high catalyst concentrations the attainment of a limiting rate has occasionally been reported.[1] In acid catalysis an example of the attainment of a limiting rate with increasing acid concentration has been found by Euler and Olander[2] in the hydrolysis of acetamide; this will be considered later after the rate equations have been developed for the case of acid and base catalysis.

Steady-state Treatment. If reaction (2) occurs sufficiently rapidly, the concentration of $[X]$ is small, and the steady-state treatment can

[1] *Cf.* W. F. Seyer and C. W. Yip, *Ind. Eng. Chem.*, **41**, 378 (1949).

[2] H. von Euler and A. Olander, *Z. physik. Chem.*, **131**, 107 (1927).

therefore be applied. The steady-state expression for $[X]$ is

$$\frac{d[X]}{dt} = k_1[C][S] - k_{-1}[X][Y] - k_2[X][W] = 0 \tag{16}$$

Substitution of $[C]_0 - [X]$ for $[C]$ and of $[S]_0 - [X]$ for $[S]$ gives

$$k_1([C]_0 - [X])([S]_0 - [X]) - k_{-1}[X][Y] - k_2[X][W] = 0 \tag{17}$$

Since $[X]$ is small, the term in $[X]^2$ can be neglected; with this approximation Eq. (17) gives rise to

$$[X] = \frac{k_1[C]_0[S]_0}{k_1[C]_0 + k_1[S]_0 + k_{-1}[Y] + k_2[W]} \tag{18}$$

The rate of reaction is therefore

$$-\frac{d[S]}{dt} = k_2[X][W] \tag{19}$$

$$= \frac{k_1k_2[C]_0[S]_0[W]}{k_1([C]_0 + [S]_0) + k_{-1}[Y] + k_2[W]} \tag{20}$$

This equation again indicates that at low concentrations of catalyst and of substrate the rate varies linearly with the concentration of each of these, and that at higher concentrations of either, the rate will become independent of that concentration.

In catalysis by surfaces and by enzymes, W and Y are usually nonexistent, and the rate law then becomes

$$-\frac{d[S]}{dt} = \frac{k_1k_2[C]_0[S]_0}{k_1([C]_0 + [S]_0) + k_{-1} + k_2} \tag{21}$$

An equation somewhat similar to this, but lacking the $k_1[C]_0$ term in the denominator, was first derived by Briggs and Haldane[1] with reference to enzyme-catalyzed reactions. Equation (21) is seen to predict the same type of variation of the rate with the substrate concentration as does Eq. (12), which is based on the equilibrium treatment, and in fact becomes equivalent to Eq. (12) if $k_2 \ll k_{-1}$. The Michaelis constant K_m[*cf.* Eq. (13)] is seen to be given by

$$K_m = \frac{k_1[C]_0 + k_{-1} + k_2}{k_1} \tag{22}$$

The kinetic laws derived above will now be applied in some detail to acid-base-catalyzed and enzyme-catalyzed reactions.

[1] G E. Briggs and J. B. S. Haldane, *Biochem. J.*, **19**, 338 (1925).

Acid-base catalysis

The study of catalysis by acids and bases has played a very important part in the development of chemical kinetics, since many of the reactions studied in the early days of the subject were of this type. Reference has already been made to the work of Kirchhoff on the hydrolysis of starch by dilute acids, and to Thénard's study of the decomposition of hydrogen peroxide catalyzed by alkalis. The first quantitative study of a chemical reaction has been seen to have been Wilhelmy's investigation of the inversion of cane sugar catalyzed by acids.

The early investigations of the kinetics of reactions catalyzed by acids and bases were carried out at the same time that the electrolytic dissociation theory was being developed, and the kinetic studies contributed considerably to the development of that theory. The reactions considered from this point of view were chiefly the inversion of cane sugar and the hydrolysis of esters. It was first realized by Ostwald[1] and Arrhenius[2] that the ability of an acid to catalyze these reactions is independent of the nature of the anion but is approximately proportional to its electrical conductivity. According to them, the conductivity of an acid is a measure of its strength, *i.e.*, of the concentration of hydrogen ions, and the hydrogen ions were assumed to be the sole effective acid catalysts. It was similarly shown[3] that for catalysis by alkalis the rate is proportional to the concentration of the alkali but independent of the nature of the cation, indicating that the active species is the hydroxyl ion.

The idea that the only catalyzing species in reactions of this type are the hydrogen and hydroxyl ions was a very useful one but has been found to require modification in a number of instances, as will be discussed later. Many reactions do exist, however, for which only these two ions are effective catalysts, so that it is of interest first to discuss the kinetic laws that are obeyed in such cases. These considerations will be applicable, for example, to the hydrolysis of esters, which have not been shown to be catalyzed by anything except these two ions.

If such a reaction is carried out in a sufficiently strongly acid solution, the concentration of hydroxyl ions may be reduced to such an extent that these ions do not have any appreciable catalytic action; the hydrogen ions are then the only effective catalysts, and the rate of reaction (at least at concentrations of catalyst and substrate that are not too high) would be given by an expression of the type

$$v = k_{H^+}[H_3O^+][S] \tag{23}$$

[1] W. Ostwald, *J. prakt. Chem.*, **30**, 39 (1884).
[2] S. Arrhenius, *Z. physik. Chem.*, **2**, 495 (1888); **4**, 244 (1889); **28**, 317 (1899).
[3] L. T. Reicher, *Ann.*, **228**, 257 (1885).

where k_{H^+} is the specific rate for the hydrogen-ion-catalyzed reaction. Such a reaction would be of the second over-all order with respect to concentration but of the first order with respect to time (*cf.* p. 18), since in a given run the hydrogen-ion concentration remains constant. The first-order law that is obtained in a measurement of the amount of reaction as a function of time may be expressed by the equation

$$v = k'_{H^+}[S] \tag{24}$$

and combining Eqs. (23) and (24), it is seen that the first-order constant is related to the second-order constant by

$$k'_{H^+} = k_{H^+}[H_3O^+] \tag{25}$$

Similarly, for catalysis by hydroxyl ions the first-order constant is given by

$$k'_{OH^-} = k_{OH^-}[OH^-] \tag{26}$$

For the general case in which catalysis may be effected simultaneously by hydrogen and hydroxyl ions and in which reaction may also occur spontaneously, *i.e.*, without a catalyst, the rate of reaction may be written as

$$v = k_0[S] + k_{H^+}[H_3O^+][S] + k_{OH^-}[OH^-][S] \tag{27}$$

The specific first-order rate is therefore given by

$$k = k_0 + k_{H^+}[H_3O^+] + k_{OH^-}[OH^-] \tag{28}$$

In these equations k_0 is the specific rate of the spontaneous reaction, and k_{H^+} and k_{OH^-} are known as the catalytic constants for H_3O^+ and OH^-, respectively.

The specific rate equation [Eq. (28)] may be expressed in more convenient form by making use of the fact that $[H_3O^+][OH^-] = K_w$, where K_w is the ionic product of water. Elimination of $[OH^-]$ gives

$$k = k_0 + k_{H^+}[H_3O^+] + \frac{k_{OH^-}K_w}{[H_3O^+]} \tag{29}$$

while elimination of $[H_3O^+]$ gives

$$k = k_0 + \frac{k_{H^+}K_w}{[OH^-]} + k_{OH^-}[OH^-] \tag{30}$$

In many cases one of these terms containing concentration is negligibly small compared with the other. If work is carried out with 0.1 N hydrochloric acid, for example, the second term in Eq. (29) is $k_{H^+} \times 10^{-1}$ while the third term is $k_{OH^-} \times 10^{-13}$ (since $K_w = 10^{-14}$); consequently, unless k_{OH^-} is at least 10^9 greater than k_{H^+}, the third term will be negligible compared with the second, so that at this acid concentration, catalv-

sis by hydroxyl ions will be negligible compared with that by hydrogen ions. Similarly, in 0.1 N sodium hydroxide solution, catalysis by hydrogen ions will usually be unimportant compared with that by hydroxyl ions. In general, it can be seen that there will be an upper range of hydrogen-ion concentrations at which catalysis by hydroxyl ions will be unimportant, and a lower range at which catalysis by hydroxyl ions will predominate and catalysis by hydrogen ions will be unimportant. Within these ranges the rate will be a linear function of $[H_3O^+]$ and of $[OH^-]$, respectively. In the former range the value of the catalytic constant k_{H^+} can readily be determined from the experimental data; in the lower range k_{OH^-} can be so determined. The constants for the hydrolysis of ethyl acetate were determined in this manner by Wijs,[1] who also obtained a value for K_w. This was done by making use of the fact that the minimum velocity is obtained when the second and third terms in Eqs. (29) and (30) are equal; this gives rise to

$$[H_3O^+]_{min} = \left(\frac{k_{OH^-} \cdot K_w}{k_{H^+}}\right)^{1/2} \qquad (31)$$

so that from the values of $[H_3O^+]_{min}$, k_{H^+}, and k_{OH^-}, the ionic product K_w can be obtained.

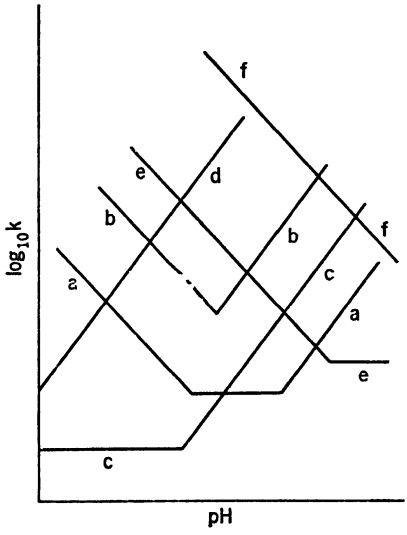


FIG. 28. The variation of the rates of acid-base-catalyzed reactions with the pH of the solution; the various cases are considered in the text. (*After Skrabal.*)

The various possibilities that may arise in reactions of this type have been classified by Skrabal,[2] who plotted the logarithm of the rate constant against the pH of the solution (*cf.* Fig. 28). The most general type of behavior is represented in curve *a*, which shows regions of catalysis by hydrogen and hydroxyl ions, respectively, separated by a region in which the amount of catalysis is unimportant in comparison with the spontaneous reaction. When the catalysis is largely by hydrogen ions, $k = k_{H^+}[H_3O^+]$ so that

$$\log k = \log k_{H^+} + \log[H_3O^+] \qquad (32)$$

or

$$\log k = \log k_{H^+} - \text{pH} \qquad (33)$$

[1] J. J. A. Wijs, *Z. physik. Chem.*, **11**, 492 (1893); **12**, 415 (1893).
[2] A. Skrabal, *Z. Elektrochem.*, **33**, 322 (1927).

The slope is therefore -1, which is the slope of the left-hand limb. The slope of the right-hand limb is similarly $+1$, and the velocity in the intermediate region is equal to $k_0[S]$, so that k_0 can be determined directly from the rate in this region. A curve of type *a* is given by the mutarotation of glucose.

If the specific rate of the spontaneous reaction is sufficiently small [the exact condition is $k_0 \ll (K_w k_{H^+} k_{OH^-})^{1/2}$], the horizontal part of the curve is not found, the two limbs intersecting quite sharply (curve *b*). This type of behavior is found with the halogenation of acetone and with the hydrolysis of amides, γ-lactones, and carboxylic esters. If either k_{H^+} or k_{OH^-} is negligibly small, the corresponding sloping limb of the curve is not found. If in the former case the spontaneous reaction is important, curve *c* is obtained, while if it is absent, curve *d* is obtained, the plot being a single straight line. Similarly, if k_{OH^-} is negligibly small, curves *e* and *f* may be obtained. Examples of each of these cases are known.

General Acid-Base Catalysis. According to modern views, which were developed largely by Brønsted,[1] Lowry,[2] and Lewis,[3] the properties of the hydrogen and hydroxyl ions which cause them to catalyze certain types of reactions are also shown by other substances, which it is therefore convenient to classify as acids and bases. The definition of an acid[4] that was proposed independently by Brønsted and Lowry is that it is a species having a tendency to lose a proton, while a base is a species that tends to accept a proton. This definition of an acid can readily be seen to include such substances as hydrogen chloride, which had previously been regarded as acidic; thus hydrogen chloride will readily lose a proton to other substances, as shown by the following examples:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$HCl + OH^- \rightarrow H_2O + Cl^-$$

In addition, the definition includes such species as the ammonium ion, which had not hitherto been regarded as acidic, but which will lose a proton in processes such as the following:

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$
$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

[1] J. N. Brønsted, *Rec. trav. chim.*, **42**, 718 (1923).

[2] T. M. Lowry, *Chemistry & Industry*, **42**, 43 (1923).

[3] G. N. Lewis, "Valency and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923; *J. Franklin Inst*, **226**, 293 (1938). *Cf.* W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley & Sons, Inc., New York, 1946.

[4] For a review see R. P. Bell, *Quart. Revs.*, **1**, 113 (1937).

The fact that the oxonium ion H_3O^+ is an acid according to this definition is shown by the following examples:

$$H_3O^+ + OH^- \rightarrow 2H_2O$$
$$H_3O^+ + NH_3 \rightarrow H_2O + NH_4^+$$
$$H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$$

the last reaction occurring in the electrolysis of acids.

Since, according to the Brønsted-Lowry view, a base is a species which tends to add on a proton, the second substance reacting, in the examples quoted above, has the properties of a base; this definition therefore covers H_2O, OH^-, and NH_3. In addition, negative ions, such as the anions of acids, must be regarded as bases, as is seen from the following reactions of the acetate ion:

$$H_3O^+ + CH_3COO^- \rightarrow H_2O + CH_3COOH$$
$$NH_4^+ + CH_3COO^- \rightarrow NH_3 + CH_3COOH$$

In all the examples given above, it is seen that an acid reacts with a base to give a new acid and a new base, *e.g.*,

$$\underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{NH_3} \rightarrow \underset{\text{base}}{H_2O} + \underset{\text{acid}}{NH_4^+}$$

A particular case is the equilibrium between an acid and a water molecule to give an oxonium ion and a base,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The base A^- is then said to be the corresponding, or conjugate, base to the acid HA. The value of the equilibrium constant for this reaction,

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \tag{34}$$

is a measure of the tendency of HA to give up its proton to water and is therefore a measure of the strength of the acid. In practice, since $[H_2O]$ is practically constant in all aqueous solutions (having the value of 55.5 moles per liter at ordinary temperatures), the equilibrium constant is usually written as

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{35}$$

and is known as the acid constant of HA. Similarly, the basic constant of the base A^- is defined with respect to the equilibrium

$$H_2O + A^- \rightleftharpoons OH^- + HA$$

and is given by

$$K_b = \frac{[OH^-][HA]}{[A^-]} \tag{36}$$

Combining Eqs. (35) and (36), it is seen that

$$K_a K_b = [H_3O^+][OH^-] = K_w \tag{37}$$

For this reason it is unnecessary to use both acidic and basic constants, and it is customary to employ only the former.

In the case of strong acids and bases, this method of defining the acid strength is not convenient in view of the almost complete reaction with water; instead, the most useful procedure is to consider that solutions of such acids and bases contain, respectively, an equivalent concentration of H_3O^+ or OH^- ions.

G. N. Lewis's definition of acids and bases is a little more general than that given above; according to him, acids are substances which accept, and bases those which donate, electron pairs with the formation of covalent bonds. This has the advantage of including as acids substances such as aluminum chloride which do not contain protons but which exhibit typical acidic properties. For most cases in aqueous solution, however, the two definitions are equivalent, and the Brønsted-Lowry one will be employed here in view of its wider use.

Since, as will be discussed in more detail later, acid and base catalysis involves the transfer of a proton to or from the substrate molecule, it is to be expected that catalysis may be effected by acids and bases other than H_3O^+ and OH^-. That this is the case has been found in a number of instances, and *general* acid-base catalysis is then said to occur. In other cases, catalysis by species other than H_3O^+ and OH^- has not been detected experimentally, and the catalysis is then said to be specific with respect to these two ions.

The idea that species other than the hydrogen and hydroxyl ions may be effective catalysts was first put forward in a concrete form by H. S. Taylor[1] and by Dawson.[2] There seemed, in particular, to be evidence that when certain reactions were occurring in the presence of weak acids, catalysis was effected by the undissociated acid as well as the H_3O^+ ions produced by the dissociation of the acid, and for this reason the hypothesis became known as the *dual theory*. Unfortunately, much of the evidence adduced by the early workers in the field now requires modification, because at the time information as to the degree of dissociation of acids was

[1] H. S. Taylor, *Medd. Vetensrapsakad. Nobelinst.*, **2**, Nos. 34–37 (1913); *Z. Elektrochem.*, **20**, 201 (1914); *J. Am. Chem. Soc.*, **37**, 551 (1915).

[2] H. M. Dawson and F. Powis, *J. Chem. Soc.*, **113**, 2135 (1913).

somewhat erroneous.[1] In particular, it was then thought that the degree of dissociation of strong acids can be calculated directly from the conductivity, while it is now known that such acids are almost completely dissociated. Some of the evidence obtained by Dawson and Powis[2] on the reaction between acetone and iodine remains valid, however, and will now be discussed.

The rate of this reaction is found to be proportional to the acetone concentration; the slow step is therefore the enolization of the acetone,

$$CH_3COCH_3 \rightarrow CH_3C(OH):CH_2$$

and this is followed by the addition of iodine. The enolization is catalyzed by acids, and the over-all reaction itself increases the acidity of the solution; consequently the reaction is studied by measuring initial rates. Some results obtained using monochloroacetic acid at a series of concentrations are shown in Table 42. The concentration of acid is shown in the

TABLE 42. IODINATION OF ACETONE CATALYZED BY MONOCHLOROACETIC ACID

$[CH_3COCH_3] = 0.273$ mole per liter $\quad K_{CH_2ClCOOH} = 1.55 \times 10^{-3}$

Acid concentration	$k \times 10^6$	$\alpha = \frac{\Lambda}{\Lambda_0}$	$\frac{k \times 10^6}{[H_3O^+]}$
0.05	4.6	0.161	571
0.10	7.6	0.117	650
0.20	11.9	0.0842	708
0.50	23.8	0.0542	878
1.00	40.1	0.0386	1,039

first column, and the corresponding rates in column two. The acid is sufficiently weak for the ratio of the conductivity at a given concentration to that at infinite dilution to give a fairly accurate value for the degree of dissociation, from which the value of $[H_3O^+]$ can be calculated. If the oxonium ion were the only catalyst, the ratio of the rate to its concentration, *i.e.*, $k/[H_3O^+]$, would be constant, but the figures in the last column show that the ratio increases as the acid concentration is increased. This rise is attributed to the fact that the concentration of the undissociated acid increases as the total concentration increases, and the catalytic constant for the undissociated acid can be calculated from the figures by plotting $k/[H_3O^+]$ against [acid]/$[H_3O^+]$. The catalytic constant for H_3O^+ can, moreover, be calculated by extrapolating k back to zero concentration, when the acid is completely dissociated. The values obtained in this

[1] For a detailed discussion of the early evidence, see R. P. Bell, "Acid-Base Catalysis," p. 48, Oxford University Press, New York, 1941.

[2] Dawson and Powis, *loc. cit.*

way were

$$k_{H^+} = 4.48 \times 10^{-4}$$

and

$$k_{CH_2ClCOOH} = 2.37 \times 10^{-5}$$

so that the specific rate of the over-all process can be written as

$$k = k_{H^+}[H_3O^+] + k_{CH_2ClCOOH}[CH_2ClCOOH] \quad (38)$$

$$= 4.48 \times 10^{-4}[H_3O^+] + 2.37 \times 10^{-5}[CH_2ClCOOH] \quad (39)$$

A similar treatment was applied by Dawson to a number of other acids, but the values obtained in some cases need revision, and the evidence for catalysis by the undissociated acid is then less strong.

If general acid-base catalysis is occurring in a system containing an acid HA, the over-all reaction rate is given by an equation of the form

$$v = k_0[S] + k_{H^+}[H_3O^+][S] + k_{OH^-}[OH^-][S] + k_{HA}[HA][S] + k_{A^-}[A^-][S] \quad (40)$$

The first term represents the spontaneous reaction. The first-order specific rate of the process is similarly

$$k = k_0 + k_{H^+}[H_3O^+] + k_{OH^-}[OH^-] + k_{HA}[HA] + k_{A^-}[A^-] \quad (41)$$

In an experimental study of such a system there are therefore five constants to be evaluated, and this requires judicious planning of the investigation. The problem is simplified if there is a range of pH values over which the reaction is not appreciably catalyzed by free oxonium or hydroxyl ions, as in curve a of Fig. 28. When this is the case, it is possible, by the use of buffers, to maintain the pH constant within this range, and to evaluate the constant for one constituent of the buffer by varying its concentration. Thus if an acetic acid–acetate buffer were used, the constant for the acid could be obtained by working with buffers having various acid concentrations but constant acetate-ion concentrations, all the buffers corresponding to pH values within the range of negligible catalysis by H_3O^+ and OH^-. When there is no such range for the reaction, a similar procedure is used in a region in which there is catalysis by H_3O^+ and OH^- ions, and a correction is made for the catalysis by these ions.

Mechanism of Acid-Base Catalysis. The idea that one step in a reaction catalyzed by an acid or a base is always the transfer of a proton between the substrate and the catalyst has already been referred to. In a previous section the mechanism of catalysis was considered with reference to the scheme

$$C + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + Y$$

$$X + W \xrightarrow{k_2} P + Z$$

and it may be seen that if C is an acidic catalyst, which transfers a proton to the substrate, Y is the base conjugate to C. Similarly, if C is a base, Y is its conjugate acid. The species W may be either the solvent or a solute, and the kinetics are, in general, different according to which plays the dominating role. In the former case, *i.e.*, if W is the solvent, Z is the lyonium ion in the case that C is acidic (*e.g.*, Z is H_3O^+ in the case of water as the solvent). On the other hand, Z is the lyate ion (*e.g.*, OH^- in the case of water as the solvent) when C is a basic catalyst. The species W may also be a basic substance present in solution, if C is acidic, or an acidic solute if C is basic; in the former case, Y is the acid conjugate to C, in the latter case the base conjugate to C. These various possibilities

TABLE 43. NATURE OF REACTING SPECIES IN ACID-BASE CATALYSIS

Type of catalysis	C	Y	W	Z
Acid	HA	A^-	H_2O	H_3O^+
Acid	H_2O	OH^-	B	BH^+
Base	B	BH^+	H_2O	OH^-
Base	H_2O	H_3O^+	HA	A^-

are summarized in Table 43, in which HA represents an acidic solute and B a basic one, the solvent, taken here to be water, may act as either an acid or a base. A valid mechanism corresponds to taking any pair of C and Y and combining that pair with any pair of W and Z, subject to the condition that if C is acting as an acid, W must act as a base, and vice versa; the former will be referred to as acid catalysis, and the latter, when C is basic and W acidic, as basic catalysis. It is seen that eight different possibilities exist, and the theoretical treatment is further complicated by the fact that the intermediate X may be either a stable or an unstable complex. The former possibility will be considered first, and the kinetic equations will be developed in detail only for the cases of acid catalysis.

Equilibrium Treatment. It was seen in the discussion given earlier that if the rate of decomposition of the intermediate complex X is small compared with the rates of its formation and reaction to give C and S, the concentration of the complex can be calculated assuming equilibrium between C and S and X and Y. This gave rise to Eqs. (11) and (15), according to the relative magnitudes of the concentrations of catalyst and substrate. In the case of acid-base catalysis. however, the kinetic laws take a somewhat different form, owing to the establishment of solution equilibria, particularly those involving the solvent and the various acidic and basic species present. The equilibrium that influences the kinetics may be written in the general form as

$$C + W \rightleftharpoons Y + Z$$

and this might, for example, represent

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

The equilibrium constant for the general equation, K', is given by

$$K' = \frac{[Y][Z]}{[C][W]} \tag{42}$$

and since $[C]$ is equal to $[C]_0 - [X]$,

$$K' = \frac{[Y][Z]}{([C]_0 - [X])[W]} \tag{43}$$

The equilibrium between the reactants and the intermediate complex,

$$C + S \rightleftharpoons X + Y$$

is given by Eq. (7), *viz.*,

$$\frac{[X][Y]}{([C]_0 - [X])([S]_0 - [X])} = K. \tag{44}$$

Elimination of $([C]_0 - [X])$ between Eqs. (43) and (44) gives

$$\frac{[X][W]}{[Z]([S]_0 - [X])} = \frac{K}{K'} \tag{45}$$

so that the concentration of intermediate complex is given by

$$[X] = \frac{K[Z][S]_0}{K[Z] + K'[W]} \tag{46}$$

The rate of reaction is therefore equal to

$$-\frac{d[S]}{dt} = k_2[X][W] \tag{47}$$

$$= \frac{k_2K[Z][S]_0[W]}{K[Z] + K'[W]} \tag{48}$$

It may be noted that the treatment has led to the result that the rate is always directly proportional to the concentration of the substrate $[S]_0$; this is in contrast to the situation with surface and enzyme catalysis, in which the rate becomes independent of the substrate concentration when this becomes large.

With regard to the influence of the catalyst concentration, two cases are to be distinguished. In the first case, $K[Z]$ is much greater than $K'[W]$, and the rate is therefore given by

$$-\frac{d[S]}{dt} = k_2[S]_0[W] \tag{49}$$

This implies that the second step, the reaction between the complex and W, is slow and rate determining. In acid catalysis, W may be either the solvent or a basic species B, and in the former case the rate is independent of the concentration of the catalyzing species present in solution. It will be seen later that this case will arise at sufficiently high catalyst concentrations.

In the second case $K'[W] \gg K[Z]$, and the rate is given by

$$-\frac{d[S]}{dt} = k_2 \frac{K}{K'} [Z][S]_0 \tag{50}$$

The species Z may be either the oxonium ion H_3O^+ or the acidic solute species BH^+, depending upon whether, in stage 2, the complex gives up its proton to a water molecule or to a basic solute. In the former case there is clearly specific hydrogen-ion catalysis; in the latter, general acid catalysis by the various acidic solutes that are present in the solution.

The fact that case 1 [Eq. (49)] applies at high catalyst concentrations, and case 2 [Eq. (50)] at low concentrations, may be shown as follows: Equations (4) and (42) combine to give

$$K[Z][S] = K'[W][X] \tag{51}$$

At low concentrations of catalyst, $[S] \gg [X]$, since X cannot be greater than $[C]$, which by hypothesis is small; it therefore follows that $K'[W] \gg K[Z]$, so that Eq. (50) applies. At high concentrations of catalyst, on the other hand, $[X] \gg [S]$, since most of the substrate is used up in forming the complex, and it then follows from Eq. (51) that $K[Z] \gg K'[W]$, so that Eq. (49) applies.

The conclusions arrived at above may be summarized as follows, the remarks applying to the equilibrium case and to acid catalysis only:

1. At low concentrations of acid catalyst, the reaction rate either is proportional to the hydrogen-ion concentration or is related linearly to the concentrations of the acidic species that may be present in the solution. Which is the case depends upon whether the complex gives up its proton to water or to basic solutes.

2. At high catalyst concentrations, the rate either becomes independent of the catalyst concentration (if the solvent is the acceptor) or, if a basic solute is the acceptor, varies linearly with the concentration of this solute. However, since in acid solutions the concentrations of basic substances are proportional to those of the conjugate acids, the effect is that if a solute is the acceptor, the rate continues to vary with the first power of the acid concentration.

These results may be further summed up in the statement that there may be either specific hydrogen-ion catalysis, in which case the rate be-

comes independent of the hydrogen-ion concentration at high acid concentrations, or general acid catalysis, in which case there is no limiting rate at high concentrations. The attainment of a limiting rate is therefore evidence against general acid catalysis in any particular reaction. The extension of the conclusions to basic catalysis will be evident: If the complex X chiefly accepts a proton from the solvent, there is specific basic catalysis with a limiting rate. Otherwise, if a solute is the proton donor in the second step, there is general catalysis but no attainment of a limiting rate.

The idea that the complex X is in equilibrium with the reactants was first suggested by Euler,[1] who proposed it as a universal explanation of acid-base catalysis. Evidence that the mechanism is valid for the acid-catalyzed hydrolysis of acetamide has been obtained, the apparent catalytic constant decreasing with increasing hydrogen-ion concentration until, at a sufficiently high concentration, there is no further influence of acid concentration on the rate. Since the attainment of a limiting rate is not found when the steady-state treatment is applied, this result appears to indicate unequivocally that the complex is a stable one. In no other case, however, has good evidence been obtained for the attainment of a limiting rate, and the general consensus of opinion appears to be that the steady-state treatment is more generally applicable.

Steady-state Treatment. The alternative hypothesis that the initial proton transfer may be slow and rate controlling was proposed by Brønsted,[2] who showed that the resulting kinetic laws would fit the experimental data in the majority of cases. Again, it is found that there may be specific or general catalysis, but the attainment of a limiting law is no longer found to be possible.

The general steady-state expression for the rate of a catalyzed reaction was seen on page 281 to be Eq. (20),

$$-\frac{d[S]}{dt} = \frac{k_1 k_2 [C]_0 [S]_0 [W]}{k_1([C]_0 + [S]_0) + k_{-1}[Y] + k_2[W]} \tag{52}$$

Since by hypothesis the rate of formation of the complex is slow and rate determining, the term $k_1([C]_0 + [S]_0)$ in the denominator may be neglected in comparison with the other terms; the rate equation then becomes

$$-\frac{d[S]}{dt} = \frac{k_1 k_2 [C]_0 [S]_0 [W]}{k_{-1}[Y] + k_2[W]} \tag{53}$$

Two special cases are important.

[1] H. von Euler, *Svensk. Vet. Akad. Forh.*, No. 4 (1899); *Z. physik. Chem.*, **28**, 619 (1899); **32**, 384 (1900); **36**, 641 (1901).

[2] J. N. Brønsted, *Chem. Revs.*, **5**, 321 (1928).

Case 1. If $k_2[W] \gg k_{-1}[Y]$, the rate becomes

$$-\frac{d[S]}{dt} = k_1[C]_0[S]_0 \tag{54}$$

The rate is thus completely controlled by the first step, and there is general acid catalysis.

Case 2. If $k_{-1}[Y] \gg k_2[W]$, the rate is equal to

$$-\frac{d[S]}{dt} = \frac{k_1 k_2}{k_{-1}} \frac{[C]_0[S]_0[W]}{[Y]} \tag{55}$$

However, all the acidic and basic species present in solution are at equilibrium, and in particular [*cf.* Eq. (42)]

$$\frac{[C]_0[W]}{[Y]} = \frac{[Z]}{K'} \tag{56}$$

since $[C]_0$ is in this case approximately equal to $[C]$. The rate equation therefore becomes

$$-\frac{d[S]}{dt} = \frac{k_1 k_2}{k_{-1}} \frac{[Z][S]_0}{K'} \tag{57}$$

Since in acid catalysis Z may be either the oxonium ion H_3O^+ or a solute acid, it is clear that this case corresponds to either specific or general acid catalysis according to the nature of Z.

It is convenient to distinguish between the cases in which W is the solvent and those in which it is a solute; reactions in which the former is the case are frequently referred to as protolytic reactions, while the latter are known as prototropic reactions. The above analysis has shown that protolytic reactions may show either general or specific catalysis according to the relative magnitudes of $k_2[W]$ and $k_{-1}[Y]$, while a prototropic reaction always exhibits general catalysis whatever the relative magnitudes. It is difficult to distinguish on the experimental side between the two types of reaction, however, since failure to detect general catalysis, which might be taken as evidence for a protolytic mechanism, does not imply that acids other than the hydrogen ion have absolutely no catalytic effect.

Whether the equilibrium or the steady-state treatment is the valid one, the conclusions may be summarized by the statement that if the mechanism is a prototropic one, *i.e.*, if the proton transfer in the second step involves a solute species, there will be general catalysis, and the reaction rate will always be linear in the concentration of the catalyst. For a protolytic mechanism, on the other hand, the catalysis may be either general or specific, and in the latter case only the rate at high catalyst concentrations may become independent of the catalyst concentration.

A number of examples of catalyzed reactions will now be considered.

Halogenation of Acetone. The reaction between acetone and iodine has already been referred to as being the reaction for which general acid catalysis was first established. The rate of the reaction is found to be independent of the concentration of the iodine and is unchanged by the substitution of bromine for iodine; the rate-controlling step therefore does not involve the addition of the halogen and involves only the ketone and the catalyst molecule. Dawson has published catalytic constants for a wide variety of undissociated acids,[1] and values for some bases[2, 3] have been obtained.

The reaction mechanism proposed for acid catalysis is that in the initial step the acetone accepts a proton from the acid, which may be represented as HA,

$$HA + CH_3COCH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3C(=^+OH)CH_3 + A^-$$

and that the resulting ion gives up its proton to a solute base B, at the same time changing over into the enol form:

$$CH_3C(=^+OH)CH_3 + B \xrightarrow{k_2} CH_2{=}C(OH)CH_3 + BH^+$$

The rate of formation of the enol is given by [*cf.* Eq. (53)]

$$\frac{d[\text{enol}]}{dt} = \frac{k_1k_2[HA][\text{ketone}][B]}{k_{-1}[A^-] + k_2[B]} \tag{58}$$

the assumption being made that the steady-state treatment is applicable, the intermediate ion being unstable. This rate of formation of the enol should be the rate of halogenation and also the rate of racemization in the case of an optically active ketone; it should also be the rate of exchange with heavy hydrogen. The identity of the rates of halogenation and racemization has been demonstrated in the case of two optically active ketones,[4] while the rates of bromination and of deuterium exchange have been shown to be the same for acetone.[5]

[1] H. M. Dawson and F. Powis, *J. Chem. Soc.*, **103**, 2135 (1913); H. M. Dawson and J. S. Carter, *ibid.*, **129**, 2872 (1926); H. M. Dawson and C. R. Hoskins, *ibid.*, 3166; H. M. Dawson *ibid.*, **130**, 213, 756, 1146 (1927); H. M. Dawson and A. Key, *ibid.*, **131**, 543, 1239, 1248 (1928); H. M. Dawson, G. V. Hall, and A. Key, *ibid.*, 2844; H. M. Dawson, C. R. Hoskins, and J. E. Smith, *ibid.*, **132**, 1884 (1929); see also J. N. Brønsted, *Trans. Faraday Soc.*, **24**, 728 (1928).

[2] *Ibid.*

[3] O. M. Lidwell and R. P. Bell, *Proc. Roy. Soc.* (*London*), **A, 176**, 88 (1940).

[4] C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 773 (1934); P. D. Bartlett and C. H. Stauffer, *J. Am. Chem. Soc.*, **57**, 2580 (1935).

[5] O. Reitz, *Z. physik. Chem.*, **179**, 119 (1937).

It may be seen that if $k_{-1}[A^-] \gg k_2[B]$, the rate is given by

$$\frac{d[\text{enol}]}{dt} = \frac{k_1 k_2 K'}{k_{-1}} [BH^+][\text{ketone}] \tag{59}$$

[*cf.* Eq. (57)], where the equilibrium constant K' refers to the equilibrium $BH^+ + A^- \rightleftharpoons HA + B$. This rate equation is consistent with the fact that general acid catalysis is observed; it also implies that the reaction is a prototropic one, for if the second step had not involved the solute base B, specific hydrogen-ion catalysis would have been found. Two pieces of evidence are available to show that Eq. (59) is in fact the rate law obeyed. The first is that with optically active ketones the addition of acid causes an instantaneous change in the rotation, followed by a slow racemization.[1] This may be explained as due to instantaneous reaction between the acid and the ketone to give the ion, which has a different rotation from the ketone, followed by the slow transfer of the proton from the ion to give the racemic mixture. The second piece of evidence is that the rates of halogenations of a series of ketones show no relationship to the basic strengths of the ketones.[2] If the rate were controlled by the addition of the proton, such a relationship would be expected, but otherwise not.

The mechanism proposed for the base-catalyzed reaction is that the ketone reacts with the base B to form a negative ion, to which two alternative electronic structures can be assigned:

$$CH_3COCH_3 + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \left\{ \begin{matrix} {}^-CH_2COCH_3 \\ CH_2{:}CCH_3 \\ \quad\quad O_- \end{matrix} \right\} + BH^+$$

The ion then reacts with the halogen, the enol not being formed in this case; the reason that this occurs instead of reaction with the unchanged enol is that the halogen is electron-attracting and therefore reacts more readily with the negative ion than with the molecule; the positive ion formed in the acid catalysis will, on the other hand, react less readily than the uncharged molecule.

Decomposition of Nitramide. The decomposition of nitramide,

$$NH_2NO_2 = N_2O + H_2O$$

[1] R. P. Bell and E. F. Caldin, *J. Chem. Soc.*, 382 (1938); R. P. Bell, O. M. Lidwell, and J. Wright, *ibid.*, 1861.

[2] L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935); L. A. Flexser and L. P. Hammett, *ibid.*, **60**, 885 (1938); L. Zucker and L. P. Hammett, *ibid.*, **61**, 2785 (1939).

is of importance as being the first reaction for which general *basic* catalysis was demonstrated. It was studied by Brønsted and Pederson,[1] who found it to be of the first order; it is uncatalyzed by acids but is strongly catalyzed by the hydroxyl ion, being an example of the behavior depicted in curve *c* of Fig. 28 (p. 284); the rate in acid solution is the rate of the spontaneous reaction. Using a solution containing sodium acetate and enough acetic acid to diminish the hydrogen-ion concentration until its effect was insignificant, it was found that the rate was greater than the spontaneous rate, a result attributed to catalysis by acetate ions; the rate was found, in agreement with this, to be proportional to the concentration of acetate ions but independent of the ratio of acid to salt. Similar catalytic behavior was found with the anions of several other weak acids[2, 3] and with aniline and substituted anilides.[4] A number of complex aquo ions were also found to have a catalytic influence.[5] The reaction has also been studied in nonaqueous solvents.[6]

Mutarotation of Glucose. The conversion of α-glucose into an equilibrium mixture of the α and β forms involves an opening and reclosing of the ring. The reaction is conveniently followed by making use of the change in optical rotation or in the volume or refractive index of the solution; the dilatometric procedure has been described in Chap. 2, where it was pointed out that the first-order constant obtained is the sum of the constants for the forward and reverse reactions.

The existence of catalysis by hydrogen and hydroxyl ions was demonstrated by Hudson and others.[7] There is a range of pH from about 4 to 6 within which catalysis by these species is negligible, so that the occurrence of general catalysis can be studied within it. General catalysis was demonstrated by Lowry and Smith,[8] using a polarimetric method, and by Brønsted and Guggenheim,[9] using the dilatometric procedure (p. 30). Undissociated acids such as acetic acid and cation acids such as NH_4^+ were found to be effective as acid catalysts, while uncharged bases (*e.g.*, NH_3), anion bases (*e.g.*, SO_4^{--}), and cation bases (*e.g.*, $[Co(NH_3)_5OH]^{++}$) were

[1] J. N. Brønsted and K. J. Pederson, *Z. physik. Chem.*, **108**, 185 (1923).

[2] *Ibid.*

[3] E. C. Baughan and R. P. Bell, *Proc. Roy. Soc. (London)*, **A, 158**, 464 (1937).

[4] J. N. Brønsted and H. C. Duus, *Z. physik. Chem.*, **117**, 299 (1925).

[5] J. N. Brønsted and K. Volqvartz, *ibid.*, **A, 155**, 211 (1931).

[6] J. N. Brønsted and J. E. Vance, *ibid.*, **A, 163**, 240 (1933); J. N. Brønsted, A. L. Nicholson, and A. Delbanco, *ibid*, **A, 169**, 379 (1934).

[7] C. S. Hudson, *J. Am. Chem. Soc*, **29**, 1571 (1907); **32**, 889 (1910); R. Kuhn and P. Jacob, *Z. physik. Chem.*, **113**, 389 (1924); H. von Euler, A. Olander, and E. Rudberg, *Z. anorg. Chem.*, **146**, 45 (1925).

[8] T. M. Lowry and G. F. Smith, *J. Chem. Soc.*, **130**, 2539 (1927).

[9] J. N. Brønsted and E. A. Guggenheim, *J. Am. Chem. Soc.*, **49**, 2554 (1927).

also catalysts. Catalysis by amino acids, existing as zwitter ions, has also been found,[1] the action being brought about by the carboxylate-ion part of the molecule.

Inversion of Sucrose. The rate of the inversion of cane sugar is found to be directly proportional to the hydrogen-ion concentration.[2] The reaction was one for which evidence was adduced in favor of the dual theory,[3] and it was believed that undissociated acids have a catalytic effect. It now appears,[4] however, that the influences observed are due to salt effects (see p. 303). There is no catalysis by the hydroxyl ion or by other bases and no appreciable spontaneous reaction at ordinary temperatures, so that the reaction may be regarded as an example of specific hydrogen-ion catalysis (curve *d*, Fig. 28).

Hydrolysis of Ordinary Esters. The kinetics of the hydrolysis of esters has been studied in great detail; the reactions are examples of case *b* in Fig. 28, there being no spontaneous reaction but catalysis by both hydrogen and hydroxyl ions. Both H. S. Taylor[5] and Dawson[6] have argued that the evidence is in favor of the existence of catalysis by undissociated acids, but a reconsideration of the data in the light of possible salt effects has indicated that this is not true.[7] Further evidence has been brought forward, but on the whole it seems to be very doubtful that there is catalysis by any species except the oxonium and hydroxyl ions.

Hydrolysis of Ortho Esters. The ortho esters, *e.g.*, ethyl orthoacetate, ethyl orthopropionate, and ethyl orthocarbonate, are exceptional in this respect; catalysis by some undissociated acids has been established. The reactions have been studied by Brønsted and Wynne-Jones,[8] using a dilatometric method. The hydrolyses are not catalyzed by hydroxyl ions or other bases but are very strongly affected by hydrogen ions (case *c*, Fig. 28), so much so that noticeable catalysis by these ions is found even in strongly basic solution; as a result, only the effects of weak acids could be investigated.

The reason why the ortho esters are not catalyzed by bases, while the

[1] F. H. Westheimer, *J. Org. Chem* , **2**, 431 (1938).

[2] S. Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889); W. Palmaer, *ibid.*, **22**, 492 (1897); H. von Euler, *ibid.*, **32**, 348 (1900); L. Bowe, *J. Phys. Chem* , **31**, 290 (1927).

[3] H. C S. Snethlage, *Z. Elektrochem.*, **18**, 539 (1912); *Z. physik. Chem.*, **85**, 252 (1913); J. W. McBain and F. C. Coleman, *J. Chem Soc.*, **105**, 1517 (1914).

[4] *Cf.* R. P. Bell, "Acid-Base Catalysis," pp. 51–52, Oxford University Press, New York, 1941.

[5] H. S. Taylor, *Medd Nobelinst.*, **2**, Nos 34–37 (1913); *Z. Elektrochem.*, **20**, 201 (1914); *J. Am. Chem. Soc.*, **37**, 551 (1915).

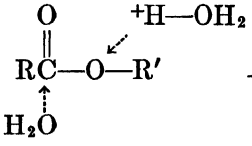
[6] H. M. Dawson and F. Powis, *J. Chem. Soc* , **113**, 2135 (1913).

[7] Bell, *loc. cit*

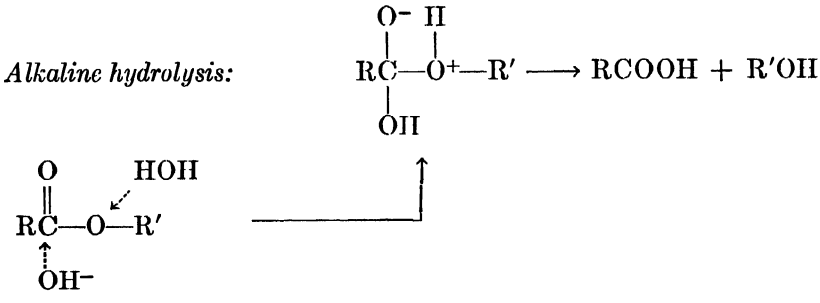
[8] J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 58 (1929).

ordinary esters are, is suggested when the mechanism of ester hydrolysis is considered. According to Lowry,[1] the intermediate complex in the hydrolysis of ordinary esters is the same for both hydrogen- and hydroxyl ion catalysis, the mechanisms being

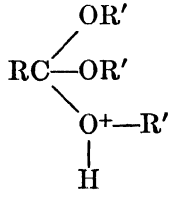
Acid hydrolysis:



Alkaline hydrolysis:



In the case of an ortho ester $RC(OR')_3$, the addition of a proton from H_3O^+ to an oxygen atom can still occur, the resulting complex being



but the addition of a hydroxyl ion to the carbon atom is now impossible, as carbon cannot expand its valence shell beyond eight. The influence of substituents on the rates of hydrolysis of esters was discussed on page 140.

Hydrolysis of Amides. The first kinetic work on the hydrolysis of amides was carried out by Remsen[2] and by Emmet Reid,[3] who found that the alkaline hydrolysis was of the second order. The reaction is of special interest in being the only one for which there is any evidence for the existence of an Arrhenius intermediate complex; thus Euler and Olander[4]

[1] *Cf.* W. A. Waters, "Physical Aspects of Organic Chemistry," D Van Nostrand Company, Inc., New York, 1936.

[2] I. Remsen, *J. Am. Chem. Soc.*, **21**, 71 (1899).

[3] E. Emmet Reid, *ibid.*, 284.

[4] H. von Euler and A. Olander, *Z. physik. Chem.*, **131**, 107 (1927).

found that in the acid hydrolysis the catalytic constant decreased significantly with increase of acid concentration from 0.1 N to 3 N, and it has been seen that such behavior is not expected when the steady-state treatment is applicable. It has been objected that the change in the catalytic constant might be due to a salt effect, the acid concentrations being rather large, but the salt effect has been observed[1] and is actually found to be positive, *i.e.*, to bring about an apparent increase in the catalytic constant. There is therefore good evidence for Euler's explanation in this case, although only a qualitative interpretation of the results is possible. It has been found that the activation energy varies somewhat with the change in catalyst concentration.[2] This effect is to be expected, since at low concentrations the rate is given by Eq. (50) and at sufficiently high concentrations by Eq. (49).

Catalytic Activity and Acid-base Strength. Since acid-base catalysis always involves the transfer of a proton from the acid catalyst or to the basic catalyst, it is natural to seek a correlation between the effectiveness of a catalyst and its strength as an acid or base. This strength is a measure of the ease with which the catalyst transfers a proton to or from a water molecule; thus the strength of the acid HA is given by the equilibrium constant of the process

$$HA + H_2O \leftrightharpoons H_3O^+ + A^-$$

the acid constant being defined by [*cf.* Eq. (35)]

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{60}$$

The first suggestion of a connection between the catalytic constant k_a and the acid constant K_a was made in 1914 by Taylor,[3] who proposed the relationship

$$k_a = k_{H^+}K_a^{1/2} \tag{61}$$

where k_{H^+} is the catalytic coefficient of the hydrogen ion. This equation agreed only in a very approximate manner with the data, and a more satisfactory relationship, *viz.*,

$$k_a = G_aK_a^{\alpha} \tag{62}$$

was proposed in 1924 by Brønsted and Pederson;[4] here G_a and α are constants, the latter being less than unity. The analogous equation for basic catalysis is

$$k_b = G_bK_b^{\beta} \tag{63}$$

[1] T. W. J. Taylor, *J. Chem. Soc.*, **133**, 2741 (1930).
[2] B. S. Rabinovitch and C. A. Winkler, *Can. J. Research*, **B, 20,** 73 (1942).
[3] H. S. Taylor, *Z. Elektrochem.*, **20,** 201 (1914).
[4] **Brønsted and Pederson,** ***loc. cit.***

The relationship between the catalytic constant of a base and the acid strength of the conjugate acid may similarly be expressed as

$$k_b = G_b' \left(\frac{1}{K_a}\right)^{\beta} \tag{64}$$

β is again always less than unity. These equations [(62), (63), and (64)] are commonly spoken of as Brønsted relations.

The equations require a slight modification if they are to be applied to an acid which has more than one ionizable proton or to a base which can accept more than one proton. Thus if a long-chain fatty acid, $CH_3(CH_2)_nCOOH$, is compared with the dibasic acid $HOOC(CH_2)(CH_2)_n$ $COOH$, and if there is negligible interaction between the two carboxyl groups, the acid strength of the dicarboxylic acid will be twice that of the monocarboxylic acid, since in the former molecule the ion can be formed by the loss of either of the two protons. For the same reason the catalytic strength of the dicarboxylic acid will be twice that of the monocarboxylic acid. These two facts are, however, inconsistent with the Brønsted relationship (62) as it stands, since a ratio of two in the acid strengths would lead to a ratio of 2^{α} in the catalytic constants, and this is generally different from (less than) two. This anomaly is avoided if both the acid strength and the catalytic constant are divided by the number of protons involved in the dissociation; in the example given, the modified catalytic constants of the two acids would be equal, as would be the modified acid strengths, and the relationship (62) would therefore be obeyed. This, however, is still not completely satisfactory; thus in the case of the two acids $HOOC(CH_2)_nCOOR$ and $HOOC(CH_2)_nCOO^-$, both of which have one dissociable proton, the catalytic strengths are the same; on the other hand the acid strength of the second is only one-half that of the first since the ion $^-OOC(CH_2)_nCOO^-$ into which the second dissociates has two points at which a proton may be added, whereas the ion of the first acid has only one. These results are again inconsistent with Eq. (62), and to remove the difficulty, it is necessary to multiply the dissociation constant of $HOOC(CH_2)_nCOO^-$ by two before inserting it into the equation.

The conclusions may be generalized by means of the relationships[1]

$$\frac{k_a}{p} = G_a \left(\frac{qK_a}{p}\right)^{\alpha} \tag{65}$$

and

$$\frac{k_b}{q} = G_b \left(\frac{p}{qK_a}\right)^{\beta} \tag{66}$$

[1] J. N. Brønsted, *Chem. Revs.*, **5**, 322 (1928).

In Eq. (65) p is the number of dissociable protons bound equally strongly in the acid while q is the number of equivalent positions in the conjugate base to which a proton may be attached; similarly, in Eq. (66) q is the number of positions in the catalyzing base to which a proton may be attached, while p is the number of equivalent dissociable protons in the conjugate acid. These statistical factors are customarily used only when the protons or positions under consideration are attached to different atoms; thus it is unnecessary to apply the correction to NH_4^+, for which p may be taken as unity.

TABLE 44. DECOMPOSITION OF NITRAMIDE

Uncharged bases: $k_b = \dfrac{1.70 \times 10^{-4}}{K_A^{0.75}}$

$(p = q = 1)$

Catalyst	K_a	k_b	
		Observed	Calculated
Water	55.5	6.8×10^{-6}	8.2×10^{-6}
p-Chloroaniline	9.1×10^{-5}	0.21	0.18
Aniline	2.0×10^{-5}	0.54	0.57
p-Toluidine	7.0×10^{-6}	1.16	1.24

TABLE 45. DECOMPOSITION OF NITRAMIDE

Bases with one negative charge: $k_b/q = 7.2 \times 10^{-5} \left(\dfrac{p}{qK_a}\right)^{0.80}$

Catalyst	p	q	K_a	k_b	
				Observed	Calculated
Hydroxyl ion	1	2	1.1×10^{-16}	1×10^{6}	1×10^{9}
Propionate ion	1	2	9.4×10^{-6}	0.822	0.90
Acetate ion	1	2	1.3×10^{-5}	0.649	0.66
Primary phosphate ion	3	2	7.6×10^{-3}	0.0079	0.0096

The equations (65) and (66) have been applied to a large number of experimental data, particularly relating to the base-catalyzed decomposition of nitramide and the acid-base-catalyzed mutarotation of glucose. In the former case it was found that very good agreement could be obtained if the bases were classified according to the number of charges on them, different values of G_b and β being taken for each class. Some results for uncharged bases are shown in Table 44 and for bases having one negative charge in Table 45; the agreement is very satisfactory, although

G_B and β are appreciably different in the two cases. For the mutarotation of glucose it is no longer advantageous to classify the catalysts, except into acids and bases. For the bases the best agreement was obtained with β equal to 0.4, while with the acids the best value of the index was 0.3.

Salt Effects in Acid-Base Catalysis. In Chap. 5 the question of the influence of neutral salts on the rates of reactions in solution has been discussed. This matter is of particular importance in connection with acid-base catalysis, since in addition to its possible catalytic action, a salt may exert an influence by virtue of changing the activity coefficients of other species in solution. It is for this reason that much of the early evidence regarding catalysis by species other than hydrogen and hydroxyl ions must be discounted, much of the apparent catalytic action being due to a salt effect.

In the study of acid-base catalysis it is particularly convenient to classify salt effects as "primary" and "secondary." The primary effect arises from the fact that the rate of a bimolecular interaction in solution between A and B is given by (*cf.* p. 124)

$$v = k[A][B]\frac{f_A f_B}{f_\ddagger} \tag{67}$$

where the f's are the activity coefficients. Since salts influence the f's, they affect the velocity v and the specific rate, equal to $kf_Af_B/f_\ddagger$, following the laws discussed in Chap. 5.

The secondary salt effect is not concerned with the direct influence of a salt on the rate of reaction, but with its influence on the concentrations of the reactants; it is thus operative even when no reaction is occurring. The equilibrium constant for the dissociation of a weak acid HA can be written as

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}\frac{f_{H_3O^+}f_{A^-}}{f_{HA}} \tag{68}$$

where K_a is a true constant at a given temperature and in a given solvent. Since salts influence the activity coefficients f, they also influence the concentrations of H_3O^+, A^-, and HA, and in this way indirectly influence the rate of a reaction involving one of these species. The activity coefficient f_{HA} for a neutral molecule is only slightly influenced by the ionic strength, while $f_{H_3O^+}$ and f_{A^-} are both decreased by increasing the ionic strength u (at low ionic strengths) according to the Debye-Hückel law

$$-\log_{10} f_i = Qz_i^2 u^{1/2} \tag{69}$$

The net result is therefore an increase in the degree of dissociation of HA *i.e.*, a increase in $[H_3O^+]$ and $[A^-]$ and a decrease in $[HA]$. Salt effects of

this kind are, of course, given not only by foreign salts but by salts which are playing a part in the reaction.

The work on both primary and secondary salt effects in chemical kinetics has been done largely by Brønsted and his coworkers.[1] Positive secondary salt effects have been observed in acid-catalyzed reactions involving weak uncharged acids, since salts, as has already been described, increase the degree of dissociation and hence the hydrogen-ion concentration; the effect is similar to a purely catalytic action, with which it is apt to be confused. The same type of result is found in cases of hydroxyl-ion catalysis in the presence of weak uncharged bases, the concentration of hydroxyl ions being increased by the addition of the salt. Different results are, however, found if the acid or base is charged. In the case of strong acids and bases the secondary salt effects are small, since the species are almost completely dissociated under all conditions.

Catalysis by enzymes

A considerable amount of work has been done on reactions catalyzed by enzymes, but only a small number of adequate kinetic studies have been carried out.[2] The present brief account will be confined to a consideration of those investigations in which the order, the reaction mechanism, and the temperature dependence have been studied in detail, since totally wrong conclusions can be drawn if this is not done.

Since the hydrogen-ion concentration has a very marked effect on the rates of enzyme-catalyzed reaction, it is of the utmost importance to work with well-buffered solutions whose pH is known. The usual type of variation of the reaction rate with the pH is shown in Fig. 29, there being a pH at which the rate is at a maximum. Since this pH is usually close to the isoelectric point of the enzyme, the behavior strongly suggests that the most active catalyzing species is the zwitter ion of the enzyme, the concentration of this being a maximum at the isoelectric point.

Influence of Concentrations. The rates of enzyme-catalyzed reactions are usually found to vary in a complex manner with initial concentrations and with the time, and the elucidation of the laws obeyed in a given case is a matter of some difficulty. Since the products of the reactions some-

[1] J. N. Brønsted and K. J. Pederson, *Z. physik. Chem.*, **108**, 185 (1924); J. N. Brønsted and C. E. Teeter, *J. Phys. Chem.*, **28**, 579 (1924); J. N. Brønsted and C. V. King, *J. Am. Chem. Soc.*, **47**, 2523 (1925); Brønsted and Wynne-Jones, *loc. cit.; cf.* M. Kilpatrick, *J. Am. Chem. Soc.*, **48**, 2091 (1926).

[2] For previous reviews of enzyme kinetics, see I. W. Sizer, "Advances in Enzymology," Vol. 3, p. 35, Interscience Publishers, Inc., New York, 1943; E. A. Moelwyn-Hughes, "Handbuch der Enzymologie," Leipzig, 1940 (Edwards Bros., Inc., Ann Arbor, Mich., 1943), p. 220; A. E. Stearn, "Advances in Enzymology," Vol. 9, p. 35, Interscience Publishers, Inc., New York.

times interfere with the rates, it is better to study only initial rates and to investigate the influence of the initial concentration on the initial rate; the additional study of the progress of the reaction with time, however, gives valuable information as to the influence of products. When measurements are made of initial rates, it has usually been found that the rate is strictly proportional to the enzyme concentration. In a few cases this has also been found to be the case for the dependence on the substrate concentration, but more often the behavior is of the type shown in Fig. 26. In the case of reactions involving a single substrate, this behavior has been explained by Michaelis and Menten,[1] using a treatment practically equivalent to that given on page 279; their final equation was [*cf.* Eq. (13)]

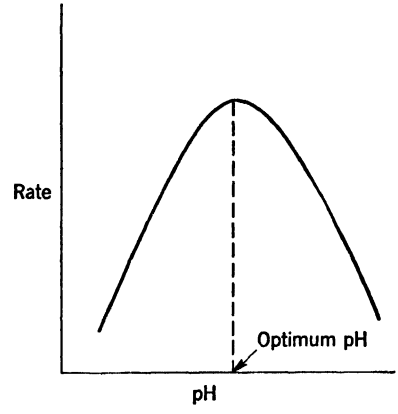


FIG. 29 The variation of the rate of an enzyme-catalyzed reaction with the pH of the solution.

$$-\frac{d[S]}{dt} = \frac{k_2[C]_0[S]_0}{[S]_0 + K_m} \qquad (70)$$

where K_m is the equilibrium constant for the dissociation of the enzyme-substrate complex, and k_2 is the rate constant for its decomposition into the products of the reaction. This equation was seen to have been derived on the basis of the equilibrium law, but the steady-state assumption gives a very similar equation [Eq. (21), p. 281). It has been seen that at sufficiently high catalyst concentrations a limiting rate is to be expected but that the required concentrations would generally be very much higher than could be attained in practice.

The Michaelis-Menten law may be derived in an alternative, but equivalent manner, as follows: Let θ be the fraction of the enzyme molecules that are associated with a substrate molecule with the formation of a complex; the fraction that are not so associated is then $1 - \theta$, and if the complex formation may be likened to an adsorption process, for which the Langmuir isotherm is applicable, it is clear that [*cf.* Eq. (3), p. 149)

$$\frac{\theta}{1 - \theta} = K[S]_0 \qquad (71)$$

where K is the equilibrium constant for the process. From this it follows that

$$\theta = \frac{K[S]_0}{1 + K[S]_0} \qquad (72)$$

[1] L. Michaelis and M. L. Menten, *Biochem. Z.*, **49**, 333 (1913).

so that the number of complexes, *i.e.*, the number of enzyme molecules associated with a substrate molecule, is

$$\theta[C]_0 = \frac{K[S]_0[C]_0}{1 + K[S]_0} \tag{73}$$

If k_2 is the specific rate of decomposition of the complexes, the over-all rate of reaction is

$$-\frac{d[S]}{dt} = \frac{k_2K[S]_0[C]_0}{1 + K[S]_0} \tag{74}$$

which is of the same form as Eq. (70), to which it reduces if K is written as $1/K_m$.

The validity of the Michaelis-Menten law has been established for a wide variety of enzyme-catalyzed reactions involving a single substrate, and values for the Michaelis constant K_m have been obtained from an analysis of the rate-concentration curves; it may be seen from Eq. (70) that the rate is one-half of the limiting rate when the substrate concentration is equal to the Michaelis constant. More direct evidence has also been obtained[1] for the existence of the postulated enzyme-substrate complexes.

When the reaction involves two substrates, an extension of the treatment is necessary.[2] Dehydrogenation reactions are of this type; an example is the reaction between lactic acid and coenzyme I (CoI) to give pyruvic acid and dihydrocoenzyme I (H_2-CoI),

$$CH_3CHOHCOOH + CoI \rightarrow CH_3COCOOH + H_2\text{-}CoI$$

the process being catalyzed by the enzyme lactic dehydrogenase. In such a case the enzyme must be regarded as presenting pairs of neighboring sites, on one of which substrate 1 (S_1) may be adsorbed, and on the other substrate 2 (S_2). The adsorption isotherms are then, for site 1,

$$\frac{\theta_1}{1 - \theta_1} = K_1[S_1]_0 \tag{75}$$

and, for site 2,

$$\frac{\theta_2}{1 - \theta_2} = K_2[S_2]_0 \tag{76}$$

Therefore

$$\theta_1 = \frac{K_1[S_1]_0}{1 + K_1[S_1]_0} \tag{77}$$

[1] K. G. Stern, *J. Biol. Chem.*, **114**, 473 (1936); B. Chance, *ibid.*, **151**, 553 (1943); *Science*, **109**, 204 (1949).

[2] I. M. Socquet and K. J. Laidler, *Arch. Biochem.*, **25**, 171 (1950); Laidler and Socquet, *J. Phys. & Colloid Chem.*, **54**, 530 (1950).

and

$$\theta_2 = \frac{K_2[S_2]_0}{1 + K_2[S_2]_0} \tag{78}$$

The rate of reaction is proportional to the number of dual sites which are occupied simultaneously by S_1 and S_2; if each enzyme has one pair of sites, the concentration of enzyme-substrate complexes involving both substrates is $[C]_0\theta_1\theta_2$. The rate of reaction is, therefore, if k_2 is the rate of decomposition of the complex,

$$-\frac{d[S]}{dt} = k_2\theta_1\theta_2[C]_0 \tag{79}$$

$$= \frac{k_2K_1K_2[C]_0[S_1]_0[S_2]_0}{(1 + K_1[S_1]_0)(1 + K_2[S_2]_0)} \tag{80}$$

In special cases this law reduced to simpler forms, of which the following may be mentioned:

Case 1. When $[S_1]_0$ and $[S_2]_0$ are both sufficiently small,

$$-\frac{d[S]}{dt} = k_2K_1K_2[C]_0[S_1]_0[S_2]_0 \tag{81}$$

so that the reaction is of the first order with respect to the enzyme and each of the substrates.

Case 2. When $[S_1]_0$ and $[S_2]_0$ are both sufficiently large,

$$-\frac{d[S]}{dt} = k_2[C]_0 \tag{82}$$

and the reaction is of zero order with respect to the substrates but still of the first order with respect to the enzyme.

Case 3. If $[S_1]_0$ is large but $(S_2)_0$ is of intermediate magnitude,

$$-\frac{d[S]}{dt} = \frac{k_2K_2[C]_0[S_2]_0}{1 + K_2[S_2]_0} \tag{83}$$

and an analogous law applies to the case of $[S_2]_0$ large.

By a judicious choice of initial conditions it is clearly possible to evaluate the constants k_2, K_1, and K_2.

The above formulation does not take into account the possibility that S_1 may be adsorbed on the sites of the second kind, and vice versa. This would constitute a type of inhibition, and the equations can readily be modified to allow for this.[1] Another limitation of the treatment that has been given is that the assumption is tacitly made [in Eqs. (75) and (76)] that the enzyme concentration is so low that the fraction of the substrate

[1] Socquet and Laidler, *loc. cit.*

adsorbed on the enzyme is very small. If this is not the case, it can be shown that the rate is no longer linear with respect to the enzyme concentration, but rather reaches a maximum value at a certain enzyme concentration and subsequently falls. The existence of such a maximum is typical of all two-substrate-catalyzed systems; when there is only one substrate, the rate may reach a limiting value with increase in catalyst concentration but will not show a maximum.

Another variation is shown in the hydrolysis of urea, catalyzed by urease, where there is a maximum in the curve relating the rate to the urea concentration.[1] This behavior has been explained quantitatively[2] in terms of the existence of two neighboring active sites on the urease molecule: for reaction to occur, a urea molecule must be adsorbed on one site and a water molecule on the other. The urea may, however, be adsorbed on the second type of site, and owing to this the rate will fall at high urea concentrations.

Influence of Temperature. The study of the influence of temperature on the rates of enzyme-catalyzed reactions is somewhat complicated by the fact that the deactivation of the enzyme itself is markedly influenced by the temperature. At sufficiently low temperatures this effect is unimportant, and an increase in temperature then increases the rate of reaction in accordance with the Arrhenius law. At high temperatures, on the other hand, the enzyme is very rapidly deactivated, and the apparent net rate of reaction is very low. The apparent rate therefore passes through a maximum at a certain temperature; this is sometimes known as the optimum temperature for the enzyme, although it is not very well defined and, in particular, varies with the concentrations of enzyme and substrate.

The two temperature effects can be distinguished by carrying out an independent study of the rate of deactivation of the enzyme and making a correction to the apparent rate of the substrate reaction to allow for the deactivation that occurs simultaneously. Enzyme denaturations are sometimes found to be of the first order with respect to the enzyme[3] and to obey the Arrhenius law; some values for the heats and entropies are given in Table 46.[4] It is to be noted that the values are very much higher than are found with most other reactions; this has been attributed to the breaking of hydrogen bonds during the process, there being a corresponding loosening of the structure.

When allowance is made for the deactivation of the enzyme, it is still frequently found that enzyme-catalyzed reactions show some deviations

[1] S. F. Howell and J. B. Sumner, *J. Biol. Chem* , **104**, 619 (1934).
[2] K. J. Laidler and J. P. Hoare, *J. Am. Chem. Soc.*, **71**, 2699 (1949).
[3] See, however, E. J. Casey and K. J. Laidler, *Science*, **111**, 110 (1950).
[4] *Cf.* A. E. Stearn, *Ergeb. Enzymforsch.*, **7**, 1 (1938).

from the simple Arrhenius law. This is to be expected from the fact that the reactions obey such kinetic laws as [Eq. (74)]

$$-\frac{d[S]}{dt} = \frac{k_2K[S]_0[C]_0}{1 + K[S]_0} \tag{84}$$

in which both k_2 and K vary exponentially with the reciprocal of the absolute temperature; the rate itself will not, however, obey the Arrhenius law except when $K[S]_0$ is very small compared with unity, or when it is very large compared with unity. If K decreases with the temperature, *i.e.*, if the heat of formation of the complex is positive, it is clear that $K[S]_0$ may be small compared with unity at high temperatures and large at low ones; at low temperatures the temperature coefficient will therefore be that of k_2, and at high that of k_2K. Since k_2 increases with temperature according to the Arrhenius law, and since by hypothesis K decreases,

TABLE 46. HEATS AND ENTROPIES OF ACTIVATION FOR THE DEACTIVATION OF ENZYMES

Enzymes	pH	$\Delta H\ddagger$	ΔS^*
Pepsin	6.4	55.6	113.3
Trypsin .	6.5	40 2	44.7
Invertase	5 7	52 3	84.7
Invertase	4.0	110.3	262.5

the effect will be that the activation energy of the reaction, obtained by plotting the logarithm of the rate against $1/T$, will decrease with increasing temperature. Exactly the same type of behavior will be found if K increases with the temperature, *i.e.*, if there is a negative heat of formation of the enzyme-substrate complex. The apparent activation energy will, of course, not change sharply at a certain temperature (as has frequently been supposed) but will change smoothly, usually over a considerable temperature range; an example of the behavior found is shown in Fig. 30, which refers to the urea hydrolysis, for which the kinetic laws are somewhat more complicated than usual.

Energies and Entropies of Activation. The energies of activation for some enzyme-catalyzed reactions are given in Table 47, together with some values for the corresponding uncatalyzed reactions, or for the reactions catalyzed by inorganic catalysts. In most of the examples given it is not clear whether the activation energy quoted applies to the case of low or high concentration of substrate, but the important point is that in all cases the activation energy for the enzyme-catalyzed reaction is con-

siderably smaller than that for the uncatalyzed reaction, or for the reaction catalyzed by an inorganic catalyst.

Very little information is available relative to the entropies of activation of enzyme-catalyzed reactions. This is partly due to the fact that the majority of the investigations have been carried out using enzyme preparations whose molar concentrations were not known. A second reason is that insufficient consideration has been given to the basic kinetic laws which are obeyed in these reactions.

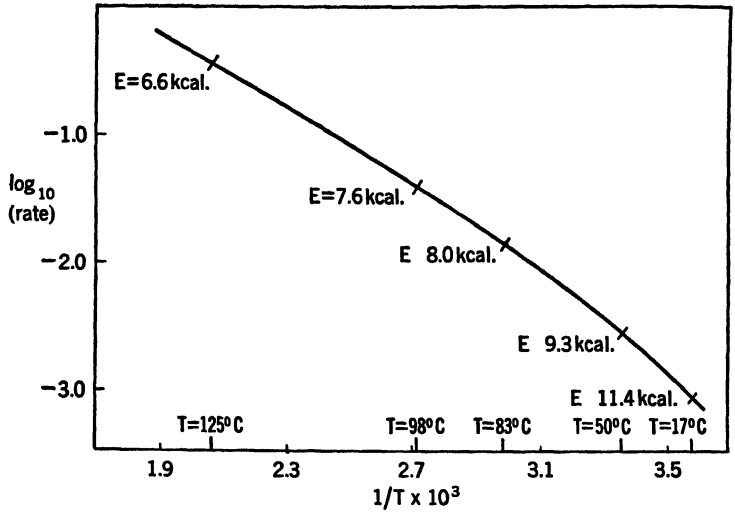


FIG. 30. A plot of $\log_{10}$ (rate) vs. $1/T$ for the urease-catalyzed hydrolysis of urea; the activation energy varies with the temperature, some of the values being noted.

TABLE 47. ACTIVATION ENERGIES FOR CATALYZED REACTIONS

Reaction	Catalyst	$E_{a\,(kcal)}$
Inversion of sucrose	Yeast invertase	11 5
	Malt invertase	13.0
	Trypsin-kinase	14.4
	H_3O^+	20 6
Hydrolysis of ethyl butyrate	Pancreatic lipase	4.2
	H_3O^+	13.2
Hydrogen peroxide decomposition	Liver catalase	5.5
	Platinum	11.7
	Fe^{++}	10.1, 8.5
	No catalyst	17–18
Hydrolysis of urea	Urease	12.5–6.5
	H_3O^+	24.5

If a reaction obeys the simple Michaelis-Menten equation, the experimental data can be analyzed as follows: The kinetic law is then

$$v = \frac{k_2 K[S]_0[C]_0}{1 + K[S]_0} \tag{85}$$

and k_2 and K may be expressed as

$$k_2 = \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S_2^*/R} e^{-\Delta H_2^\ddagger/RT} \tag{86}$$

and

$$K = e^{\Delta S/R} e^{-\Delta H/RT} \tag{87}$$

The rate of reaction at low substrate concentrations is therefore given by

$$v = [S]_0[C]_0 \frac{\mathbf{k}T}{\mathbf{h}} e^{(\Delta S_2^* + \Delta S)/R} e^{-(\Delta H_2^\ddagger + \Delta H)/RT} \tag{88}$$

The entropy of activation is therefore equal to $\Delta S_2^* + \Delta S$, and the heat of activation to $\Delta H_2^\ddagger + \Delta H$. At high concentrations on the other hand, $K[S] \gg 1$, so that the rate is given by

$$v = k_2[C]_0 \tag{89}$$

$$= [C]_0 \frac{\mathbf{k}T}{h} e^{\Delta S_2^*/R} e^{-\Delta H_2^\ddagger/RT} \tag{90}$$

the results therefore give directly ΔS_2^* and $\Delta H_2^\ddagger$, which are the heats and entropies of activation for the decomposition of the complex into the reaction products. The difference between the entropies and heats of activation at low and high concentrations moreover gives the entropies and heats corresponding to the formation of the complex. The situation is closely analogous to that for a surface reaction, for which the difference between the heats of activation for sparsely and fully covered surfaces is the heat of adsorption of the reactant.

Unfortunately this type of procedure has rarely been applied to enzyme-catalyzed reactions. It has been done for certain pepsin-catalyzed reactions[1] and for the urease-catalyzed hydrolysis of urea[2] (the results for this reaction being analyzed on the basis of a somewhat more complicated enzyme model); the values obtained for $\Delta H_2^\ddagger + \Delta H$ and $\Delta S_2^* + \Delta S$ are given in Table 48. The table also includes values obtained by Butler[3] for the trypsin-catalyzed hydrolysis of chymotrypsinogen, the substrate

[1] E. J. Casey and K. J. Laidler, *J. Am. Chem. Soc.*, **72**, 2159 (1950).

[2] Laidler and Hoare, *loc. cit.*; J. P. Hoare and K. J. Laidler, *J. Am. Chem. Soc.*, **72**, 2489 (1950).

[3] J. A. V. Butler, *ibid.*, **63**, 2971 (1941).

concentration in which was probably so low that Eq. (88) is applicable. It is to be noted that the values of the entropy differences $\Delta S_2^* + \Delta S$ between the reactants and the activated complex are all positive, in contrast to those for the acid-catalyzed reaction quoted. It therefore appears that enzymes act not only by lowering the energy of activation but also by increasing the entropy of activation.

TABLE 48. HEATS AND ENTROPIES OF REACTION FOR ENZYME-CATALYZED REACTION

Catalyst	Substrate	$\Delta H_2^\ddagger + \Delta H$, kcal	$\Delta S_2^* + \Delta S$, entropy units
Pepsin	Carbobenzoxy-l-glutamyl-l-tyrosine	20·2	4·6
Pepsin	Carbobenzoxy-l-glutamyl-l-tyrosine ethyl ester	23·1	16·1
Urease	Urea	12·5	7·5
Trypsin	Chymotrypsinogen	16·3	8·5
(H_3O^+)	Acetylglycine	21·2	−21·5

In the cases of the pepsin- and urease-catalyzed reactions the data permit the evaluation of ΔH and ΔS, the heat and entropy changes involved in the formation of the intermediate complexes from the reactants. It was found that there is an increase in both S and H in forming the complex, and in order to explain the entropy increase, it is proposed that the enzyme undergoes a change in structure when the complex is formed. In agreement with this idea, there was a negative entropy of activation for the decomposition of the complex into the reaction products.

Catalysis in chain reactions

The previous discussion of the present chapter has been concerned with catalyzed reactions which proceed in only two stages, in the first of which the intermediate complex is formed, and in the second of which it decomposes or otherwise reacts to give the final products. In addition, a number of catalyzed reactions, particularly those occurring in the gas phase, involve chain mechanisms, the function of the catalyst often being to initiate chains by producing free radicals. Some examples of free-radical mechanisms in catalyzed reactions will now be considered.

Decomposition of Ozone Catalyzed by Chlorine. Chlorine is found to have a marked influence on the homogeneous thermal decomposition of ozone, the rate following the law[1]

[1] M. Bodenstein, E. Padelt, and H. J. Schumacher, *Z. physik. Chem.*, **B, 5, 209 (1929)**; A. Hamann and H. J. Schumacher, *ibid.*, **B, 17, 293 (1932)**.

$$-\frac{d[O_3]}{dt} = k[O_3]^{3/2}[Cl_2]^{1/2} \tag{91}$$

This has been interpreted in terms of the mechanism

(1) $Cl_2 + O_3 \rightarrow ClO + ClO_2$
(2) $ClO_2 + O_3 \rightarrow ClO_3 + O_2$
(3) $ClO_3 + O_3 \rightarrow ClO_2 + 2O_2$
(4) $ClO_3 + ClO_3 \rightarrow Cl_2 + 3O_2$

In this scheme ClO_2 and ClO_3 are chain carriers, the ClO decomposing into the elements without initiating chains. The steady-state expression for ClO_3 is

$$k_2[ClO_2][O_3] - k_3[ClO_3][O_3] - k_4[ClO_3]^2 = 0 \tag{92}$$

and that for ClO_2 is

$$k_1[Cl_2][O_3] + k_3[ClO_3][O_3] - k_2[ClO_2][O_3] = 0 \tag{93}$$

Addition of these expressions gives

$$k_1[Cl_2][O_3] - k_4[ClO_3]^2 = 0 \tag{94}$$

whence

$$[ClO_3] = (k_1[Cl_2][O_3]/k_4)^{1/2} \tag{95}$$

Also

$$[ClO_2] = k_3(k_1[Cl_2][O_3]/k_4)^{1/2}/k_2 + k_1[Cl_2]/k_2 \tag{96}$$

The over-all rate of decomposition is given by

$$-\frac{d[O_3]}{dt} = k_1[Cl_2][O_3] + k_2[ClO_2][O_3] + k_3[ClO_3][O_3] \tag{97}$$

Introduction of Eqs. (95) and (96) gives

$$-\frac{d[O_3]}{dt} = 2k_3\left(\frac{k_1}{k_4}\right)^{1/2}[Cl_2]^{1/2}[O_3]^{1/2} + 2k_1[Cl_2][O_3] \tag{98}$$

If reaction (1) can be assumed to be unimportant, *i.e.*, if the chains are long, this equation reduces to

$$-\frac{d[O_3]}{dt} = 2k_3\left(\frac{k_1}{k_4}\right)^{1/2}[O_3]^{3/2}[Cl_2]^{1/2} \tag{99}$$

in agreement with the experimental law.

Catalyzed Decomposition of Hydrogen Peroxide. The decomposition of hydrogen peroxide in aqueous solution in glass vessels is partly heterogeneous, occurring to some extent on the surface of the vessel and also on

particles of dust liberated from the glass walls.[1] In quartz vessels the reaction is largely homogeneous[2] but is catalyzed markedly by ferrous and other ions. The activation energy of the uncatalyzed homogeneous reaction[3] is 17 to 18 kcal, and the frequency factor is about 10^6, the low value probably being due to a low transmission coefficient for the initial formation of free radicals by the process

$$H_2O_2 \rightarrow 2OH$$

The catalytic effect of ferrous ions was attributed by Haber and Weiss[4] to the initial production of free hydroxyl radicals by the reaction

$$Fe^{++} + HOOH \rightarrow Fe^{+++} + OH + OH^-$$

The decomposition is explained as due to the chain-propagating processes

$$OH + HOOH \rightarrow HOH + OOH$$
$$OOH + HOOH \rightarrow O_2 + H_2O + OH$$

the chains being broken by reactions such as

$$Fe^{++} + OH \rightarrow Fe^{+++} + OH^-$$

Haber and Weiss confirmed this scheme by flow experiments in which the rates of disappearance of hydrogen peroxide and ferrous ions were determined. By working at very low concentrations and using a colorimetric method for the determination of iron, Baxendale, Evans, and Park[5] were able to avoid the necessity for flow methods. They found the energy of activation for the initial step to be 10.1 kcal (as compared with 8.5 kcal found by Haber and Weiss) and the frequency factor to be 1.78×10^9.

Catalysis by the ferric ion is also found, and this is attributed to the initial reaction

$$Fe^{+++} + HOOH \rightarrow Fe^{++} + H^+ + OOH$$

The presence of free radicals in this reaction system was confirmed by Baxendale, Evans, and Park, who showed that polymerization was catalyzed by the ion (*cf.* p. 360).

[1] F. O. Rice, *J. Am. Chem. Soc.*, **48**, 2099 (1926); *J. Phys. Chem.*, **31**, 1507 (1927).

[2] A. C. Robertson, *J. Am. Chem. Soc.*, **53**, 382 (1931).

[3] J. Williams, *Trans. Faraday Soc.*, **24**, 245 (1928); C. Pana, *ibid.*, 486.

[4] F. Haber and J. Weiss, *Proc. Roy. Soc.* (*London*), A, **147**, 333 (1934); *cf.* F. Haber and R. Willstatter, *Ber.*, **64**, 2844 (1931).

[5] J. H. Baxendale, M. G. Evans, and G. S. Park. *Trans. Faraday Soc.*, **42**, 155 (1946).

The catalysis of this decomposition by surfaces such as platinum and charcoal, and by the enzyme catalase, is attributed by Weiss[1] to initiation of the same reaction mechanism.

PROBLEMS

***1.** A catalyzed reaction obeys the law

$$v = \frac{k_2 K[S]_0[C]_0}{1 + K[S]_0}$$

The activation energy corresponding to k_2 is 10.0 kcal, and the heat evolved in the formation of the intermediate complex is 4.0 kcal per mole. Calculate the experimental energy of activation corresponding to 0, 25, and 50°C, if K has the value 100 liters per mole at 25°C and the substrate concentration is 0.01 mole per liter at the three temperatures.

2. The first-order rate constant for an enzyme-catalyzed reaction is 3.0×10^{-4} sec^{-1}. If the enzyme concentration is 4.5×10^{-3} g per liter and molecular weight of the enzyme is 350,000, calculate the second-order constant for the reaction.

[1] J. Weiss, *J. Phys. Chem.*, **41**, 1107 (1937).

CHAPTER 11

OXIDATION

According to modern concepts, a substance is said to be oxidized if electrons are removed from it, and conversely, reduction implies the addition of electrons to a molecule. A simple type of oxidation is therefore the elimination of an electron, as in the process

$$Fe^{++} \rightarrow Fe^{+++} + e$$

but various other types of processes are included in the definition. Since most atoms and free radicals (exceptions are atomic hydrogen and free metallic atoms) have deficient electron shells, they are capable of acting as oxidizing agents by removing electrons from other species, themselves becoming ions. From this point of view it is possible to consider that the oxidizing ability of molecular oxygen is due to its tendency to behave as the diradical —O—O—, and therefore to abstract electrons from other substances. Oxidations involving molecular oxygen are commonly known as autoxidations.

Oxidative reactions, and reactions involving oxygen in particular, show a number of special characteristics, and for this reason it is convenient to treat them in a separate chapter from other complex reactions. Gas-phase reactions involving oxygen itself will be considered first; these processes will be seen to proceed by free-radical mechanisms and, because of a special feature of the mechanisms, to be capable in many cases of giving rise to an explosion.

Gas-phase autoxidations

Branching Chains.[1] The special feature just mentioned is that in reactions involving oxygen in the gas phase, it frequently happens that in one or more of the elementary processes occurring there is an increase in the number of free radicals in the system; an example of such a process is

$$H + O_2 \rightarrow HO + O$$

in which the single hydrogen atom has given rise to the two radicals OH and O. When reactions of this type occur to a sufficient extent, the total

[1] *Cf.* N. Semenoff, *Z. Physik.*, **46**, 109 (1927), "Chemical Kinetics and Chain Reactions," Oxford University Press, New York, 1935; C. N. Hinshelwood, "Kinetics of Chemical Change," *ibid.*, 1940.

number of free radicals in the system may increase rapidly, so that steady-state conditions no longer hold; the reaction therefore occurs almost instantaneously, and an explosion is said to occur, although it may be noted that these explosions are sometimes very mild. When explosion occurs, there is usually an appreciable emission of light; this is partly black-body radiation arising as a result of the rapidity of the exothermic process, and is frequently also due to radiation by electronically excited species produced in some of the elementary processes occurring (*cf.* p. 382).

An elementary reaction involving an increase in the total number of free radicals is known as a "branching" reaction, and the over-all process is known as a branching chain process. That such processes may give rise to explosion may be seen by consideration of the following set of schematic reactions which represents the types of processes which occur in a reaction involving oxygen:

(1)	$M \rightarrow \mathrm{R}$	Chain initiation
(2)	$\mathrm{R} + M \rightarrow \alpha\mathrm{R} + M'$	Chain branching
(3)	$\mathrm{R} + M \rightarrow$ products	Reaction to give final products
(4)	$\mathrm{R} \rightarrow ?$	Destruction at surface
(5)	$\mathrm{R} \rightarrow ?$	Destruction in the gas phase

The first reaction is the initial production of free radicals; an example is the process $H_2 \rightarrow 2H$, which has been postulated as the chain-initiating process in the hydrogen-oxygen reaction. Reaction (2) represents a chain-branching mechanism in which R, by collision with another molecule (here the reactant M), gives rise to α radicals. Reaction (3) denotes a reaction to give final products together with the removal of the radicals, while reactions (4) and (5) represent the two general methods by which the radical R may be destroyed, at the surface and in the gas phase, respectively.

The steady-state expression for R is

$$\frac{d[\mathrm{R}]}{dt} = k_1[M] + k_2(\alpha - 1)[\mathrm{R}][M] - k_3[\mathrm{R}][M] - (k_4 + k_5)[\mathrm{R}] = 0 \quad (1)$$

whence

$$[\mathrm{R}] = \frac{k_1[M]}{k_3[M] + (k_4 + k_5) - k_2(\alpha - 1)[M]} \quad (2)$$

The rate of reaction is therefore given by

$$v = k_3[\mathrm{R}][M] \quad (3)$$

$$= \frac{k_1k_3[M]^2}{k_3[M] + k_4 + k_5 - k_2(\alpha - 1)[M]} \quad (4)$$

This expression has been written by Hinshelwood[1] in the more general form

$$v = \frac{F}{f_s + f_g + A(1 - \alpha)} \tag{5}$$

where F represents the rate of chain initiation, f_s and f_g are the rates of destruction of the radicals at the surface and in the gas phase, respectively, and A is a function related to the rate of the chain-branching process.

If there is chain branching, α is greater than unity, so that the term $A(1 - \alpha)$ in the denominator of this expression is negative; if it is sufficiently negative to balance the term $f_s + f_g$, the rate becomes infinite, *i.e.*, explosion occurs. The physical meaning of this is that the total number of free radicals produced in the chain-branching process is greater than the number destroyed, so that no stationary state is possible.

The relative magnitudes of $f_s + f_g$ and of $A(1 - \alpha)$ depend upon the concentrations of the various molecules; the denominator of Eq. (5) may therefore be positive for certain concentrations and negative for others. At any set of concentrations for which $f_s + f_g + A(1 - \alpha)$ is equal to zero, there is therefore an explosion threshold or limit; as the concentration is changed across this limit, a steady reaction may change into an explosion. Many examples of such a critical explosion limit are known, as will now be considered for the hydrogen-oxygen reaction.

Upper and Lower Explosion Limits. Reaction between hydrogen and oxygen[2] takes place with measurable speed between 450 and 600°C; below this range the rate is extremely slow, and above it all mixtures explode. If a mixture of hydrogen and oxygen, in the stoichiometric ratio $2H_2 : O_2$, is maintained at a pressure of 200 mm at 550°C, a steady homogeneous reaction occurs. On reducing the pressure gradually, it is found that the rate diminishes somewhat, but at a certain critical pressure in the neighborhood of 100 mm, the mixture explodes with the emission of light; the limit at which this occurs is known as the upper, or second, explosion limit. If the pressure is reduced to below a lower, or first, explosion limit (at a few millimeters' pressure), explosion again fails to occur, the rate of reaction being quite slow. The variation of the rate of reaction with the pressure is shown schematically in Fig. 31, while the manner in which the explosion limits vary with the temperature is shown in Fig. 32. It is seen that at 550°C explosion (the "low-pressure" explosion) occurs provided that the pressure is between two well-defined explosion limits; above about 600°C explosion occurs at all pressures, while below about 460°C it will not occur at all. If at, for example, 550°C the pressure is increased

[1] *Ibid.*

[2] C. N. Hinshelwood and A. T. Williamson, "The Reaction between Hydrogen and Oxygen," Oxford University Press, New York, 1934.

beyond the second limit, the reaction gradually accelerates, and explosion again occurs above a third explosion limit.

The existence of the first and second limits may be explained as follows: The removal of radicals may occur primarily at the surface or primarily in the gas phase. The greater the pressure, the less important is the surface recombination; when surface recombination is more important than gas-phase removal, there may therefore be a transition from slow reaction to explosion on increasing the pressure. If, on the other hand, radicals are principally removed in the gas phase, there may be a transition to explosion as the pressure is decreased. Some reactions exhibit only a

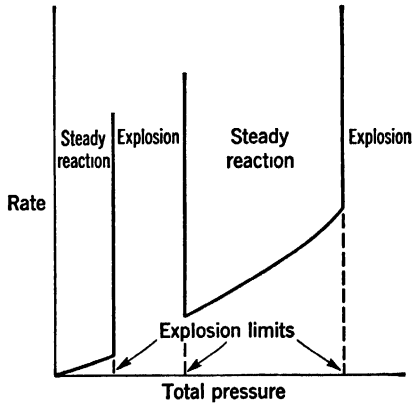


FIG. 31.

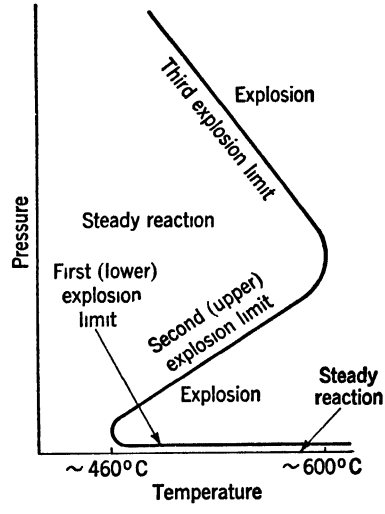


FIG. 32.

FIG. 31. The rate of the hydrogen-oxygen reaction as a function of the total pressure.
FIG. 32. Pressure-temperature explosion limits; the temperatures indicated apply approximately to the hydrogen-oxygen reaction.

lower limit, some only an upper; others, such as the hydrogen-oxygen and carbon monoxide–oxygen reactions, show both limits.

Lower Explosion Limit.[1] The lower explosion limit can be treated quantitatively without specifying the nature of the atoms or radicals which propagate the reaction chains; this is a great advantage, since several chain carriers are frequently present, and the situation would otherwise be very complex. Considering again the hydrogen-oxygen reaction, it will be supposed that there are two chain carriers, X and Y, which react as follows:

$$X + O_2 \rightarrow Y + ?$$
$$Y + H_2 \rightarrow X + ?$$

[1] Semenoff, *loc. cit.*

i.e., X reacts with an oxygen molecule to give a radical Y, and Y reacts with a hydrogen and regenerates X. Combination of these processes with an initiating reaction (1), which produces X, a chain-branching process (4), which gives rise to α radicals of the type Y, and two surface chain-ending processes (5) and (6), gives the scheme

(1)	$? \rightarrow X$	rate $= F$
(2)	$X + O_2 \rightarrow Y + ?$	rate $= k_2[X][O_2]$
(3)	$Y + H_2 \rightarrow X + ?$	rate $= k_3[Y][H_2]$
(4)	$X + O_2 \rightarrow \alpha Y + ?$	rate $= k_4[X][O_2]$
(5)	$X \rightarrow ?$	rate $= k_5[X]$
(6)	$Y \rightarrow ?$	rate $= k_6[Y]$

The steady-state expression for X is

$$\frac{d[X]}{dt} = F - k_2[X][O_2] + k_3[Y][H_2] - k_4[X][O_2] - k_5[X] = 0 \qquad (6)$$

and that for Y is

$$\frac{d[Y]}{dt} = k_2[X][O_2] - k_3[Y][H_2] + \alpha k_4[X][O_2] - k_6[Y] = 0 \qquad (7)$$

Solving for $[X]$ gives

$$[X] = \frac{F(k_6 + k_3[H_2])}{(k_2 + k_4)k_6[O_2] + k_3k_5[H_2] + k_5k_6 - (\alpha - 1)k_3k_4[H_2][O_2]} \qquad (8)$$

The condition that this becomes infinite, *i.e.*, the condition for the lower explosion limit, is therefore given by

$$(k_2 + k_4)k_6[O_2] + k_3k_5[H_2] + k_5k_6 - (\alpha - 1)k_3k_4[H_2][O_2] = 0 \qquad (9)$$

This expression may be simplified by making certain approximations; thus, neglecting k_4 in comparison with k_2, neglecting the term k_5k_6 (since both k_5 and k_6 are small), equating k_2 and k_3 (which is justified if both reactions occur at every collision), and equating k_5 and k_6 gives

$$k_5([O_2] + [H_2]) = (\alpha - 1)k_4[H_2][O_2] \qquad (10)$$

The constant k_5 depends upon the rate with which X reaches the wall and is therefore inversely proportional to the total pressure, so that one may write

$$k_5 = \frac{k_5'}{[H_2] + [O_2]} \qquad (11)$$

substances other than hydrogen and oxygen being assumed to be absent. The explosion limit is therefore given by

$$k_5' = (\alpha - 1)k_4[H_2][O_2] \tag{12}$$

which may be written as

$$[H_2][O_2] = \text{const.} \tag{13}$$

In the presence of a foreign gas M, k_5 may be written as

$$k_5 = \frac{k_5'}{[H_2] + [O_2] + [M]} \tag{14}$$

and the condition becomes

$$\frac{[H_2] + [O_2]}{[H_2] + [O_2] + [M]} k_5' = (\alpha - 1)k_4[H_2][O_2] \tag{15}$$

This may be written as

$$[H_2][O_2]\left(1 + \frac{[M]}{[H_2] + [O_2]}\right) = \text{const.} \tag{16}$$

Since concentrations are proportional to partial pressures, this condition may be written as

$$p_{H_2}p_{O_2}\left(1 + \frac{p_M}{p_{H_2} + p_{O_2}}\right) = \text{const.} \tag{17}$$

If the reaction occurs in a cylindrical tube of diameter d, it is found that the condition becomes

$$p_{H_2}p_{O_2}\left(1 + \frac{p_M}{p_{H_2} + p_{O_2}}\right)d^2 = \text{const.} \tag{18}$$

This expression, and equivalent expressions derived for other reactions, have been tested against the experimental data by plotting $1/p_{H_2}p_{O_2}$ against $1 + p_M/(p_{H_2} + p_{O_2})$, and straight lines have been obtained.

Satisfactory agreement between this simple theory and experiment has been found for the reaction between hydrogen and oxygen,[1] oxygen and carbon monoxide,[2] phosphorus and oxygen,[3] phosphine and oxygen,[4] and many other reactions. Deviations from exact agreement are attributed to the fact that there is some variation in the effectiveness of various gases in inhibiting the diffusion of free radicals to the surface, an effect

[1] C. N. Hinshelwood and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A, 138,** 311 (1932).

[2] G. Hadman, H. W. Thompson, and C. N. Hinshelwood, *ibid.*, 297.

[3] Semenoff, *loc. cit.*, H. W. Melville and E. B. Ludlam, *Proc. Roy. Soc.* (*London*), **A, 132,** 108 (1931).

[4] R. H. Dalton and C. N. Hinshelwood, *ibid.*, **A, 125,** 294 (1929).

that has been investigated by Melville and Ludlam.[1] In addition, the effectiveness of the surface in removing radicals varies with the nature of the adsorbed gas films on the surface, and this depends somewhat on the composition of the gas mixture.

The influence of the vessel diameter on the position of the lower limit is very marked, as is seen from its occurrence as a square in the expression [Eq. (18)] for the limit; the lower limit differs markedly in this respect from the upper, which is practically independent of the diameter. Roughly speaking, the product of the pressures of the reacting gases at the lower limit varies inversely with the square of the diameter. At the lower limit, foreign gases, by hindering diffusion to the surface, facilitate explosion; at the upper limit they contribute to deactivation and inhibit explosion.

Upper (Second) Explosion Limit. The fact that the upper explosion limit is practically independent of the vessel diameter, and also of the state of the vessel surface, suggests that the limit is determined by deactivation in the gas phase and not at the surface. This conclusion is supported by the result that foreign gases inhibit explosion, lowering the partial pressures of the reacting gases corresponding to the limit. As is seen in Fig. 32 the upper limit varies considerably with the temperature, being displaced to higher pressures as the temperature rises.

As with the lower limit, the upper limit is determined by the balancing of radical production by chain branching and radical removal, but here the most important removal mechanism is in the gas phase. For there to be an upper limit, it is necessary for the rate of the deactivation process to increase with pressure more rapidly than that of the branching process; one obvious way for this to happen is for the former to occur in a ternary collision and the latter in a binary collision.

The upper limit in the hydrogen-oxygen reaction has been interpreted along these lines in the following simple way:[2] Suppose that X and Y are two species which collide in the course of the chain process, with the possibility of chain branching. If a ternary collision occurs, however, involving in addition a third body which may be H_2, O_2, or a foreign molecule M, deactivation is assumed to occur. If the rates of branching and deactivation are equated, the result is

$$\nu[X][Y] = k_1[X][Y][H_2] + k_2[X][Y][O_2] + k_3[X][Y][M] \qquad (19)$$

Here the k's are proportional to the specific rate constants of the ternary process, and ν is proportional to the probability of branching. This condition defines the upper limit, where it may be seen that

[1] Melville and Ludlam, *loc. cit.*

[2] G. H. Grant and C. N. Hinshelwood, *ibid.*, **A, 141,** 29 (1933); L. S. Kassel and H. H. Storch, *J. Am. Chem. Soc.*, **57,** 672 (1935).

$$\nu = k_1[H_2] + k_2[O_2] + k_3[M] \tag{20}$$

which is consistent with experiment. In the absence of foreign gases, the limit is found to vary according to the relationship

$$k_1[H_2] + k_2[O_2] = \nu \tag{21}$$

where k_2/k_1 is equal to 0.325. On the basis of the molecular diameters of hydrogen and oxygen, it has been calculated that the ratio should have the value of 0.39, in satisfactory agreement with experiment. This implies that the relative speeds of the different molecules have the dominant influence on the deactivation process. In accordance with Eq. (20) the addition of inert gases brings about a linear decrease in the partial pressures of hydrogen and oxygen at the limit, the specific influence depending upon the molecular velocity of the substance added; helium, on account of its low weight and correspondingly high speed, has a marked effect.

In view of the above equations for the upper limit, it is clear that the limit will vary with the temperature in the same way as ν, since the temperature variation of the k is quite small. The temperature variation of ν obeys the Arrhenius law, the energy of activation being that of the branching reaction; this energy of activation can therefore be determined by investigating the variation of the upper limit with the temperature.

Third Explosion Limit. It has already been mentioned that at high pressures the steady reaction between hydrogen and oxygen again occurs explosively. It was originally thought that the explosion was of the purely thermal type, the reaction being very rapidly accelerated as a result of the heat liberated in the system, but Hinshelwood[1] has recently shown that the transition to explosion can again be explained as due to an increase in the number of free radicals. This is due to the formation of the radical HO_2, produced in the three-body reaction

$$H + O_2 + M \rightarrow HO_2 + M$$

At lower pressures this species plays no part in chain propagation or branching and is destroyed at the walls; at the second limit there is a balance between this reaction, which effectively removes radicals, and the branching processes. At higher pressures on the other hand, the reaction

$$HO_2 + H_2 \rightarrow H_2O + OH$$

which is a nonbranching chain process, occurs. As the pressure is increased, this reaction becomes relatively more important than the destruction of HO_2 at the walls, and at a certain critical pressure there is therefore a rapid increase in the number of radicals. It is not certain whether the situation is similar in other reactions.

[1] C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 188,** 1 (1946).

The reaction mechanisms for a few reactions involving oxygen will now be considered.

Hydrogen-Oxygen Reaction.[1] Several features of the reaction between hydrogen and oxygen have already been discussed, and it now remains to consider the reaction mechanism in more detail.

One plausible mechanism, which has evolved as a result of the work of many investigators, is that recently discussed by Hinshelwood:[2]

(1) $H_2 \rightarrow 2H$
(2) $H + O_2 \rightarrow OH + O$
(3) $O + H_2 \rightarrow OH + H$
(4) $H + O_2 + M \rightarrow M + HO_2$
(5) $HO_2 \rightarrow$ destruction at surface
(6) $HO_2 + H_2 \rightarrow H_2O + OH$
(7) $H \rightarrow$ destruction at surface
(8) $OH \rightarrow$ destruction at surface

At the lower limit the most important radical-removing processes are reactions (7) and (8), and it is the balancing of the rates of these processes with those of the chain-branching processes that determines the limit. At pressures above the lower limit reactions (7) and (8) become unimportant, as the radicals are prevented from reaching the walls, but (5) is assumed to play a significant role. Under these conditions application of the steady-state treatment gives, for the rate of reaction,

$$\frac{d[H_2O]}{dt} = \frac{F\left(\dfrac{1.5k_5 + 2k_6[H_2]}{k_5 + k_6[H_2]}\right)}{1 - \dfrac{2k_2}{\Sigma k_4[M]} - \dfrac{k_6[H_2]}{k_5 + k_6[H_2]}} \tag{22}$$

The denominator of this expression becomes zero, *i.e.*, the rate becomes infinite, at two different pressures. At the lower pressure, corresponding to the second limit, the ternary collision process (4), which removes radicals, balances the branching process; at the upper pressure, corresponding to the third limit, the chain process (6) is sufficiently important to compete with diffusion of HO_2 to the surface.

The nature of the chain-initiating reaction has been a matter of considerable discussion and cannot be regarded as settled. Reaction (1) above, the thermal dissociation of hydrogen, was originally favored by

[1] Hinshelwood and Williamson, *loc. cit.*; Hinshelwood, *loc. cit.*
[2] Hinshelwood, *ibid.*; *cf.* G. von Elbe and B. Lewis, *J. Chem. Phys.*, **10**, 366 (1942).

Lewis and von Elbe,[1] who, however, have now abandoned this reaction[2] on the grounds that its activation energy is too high to be consistent with the observed rate of reaction and the observed over-all activation energy. As an alternative these authors propose that chain initiation is brought about by the dissociation of hydrogen peroxide,

$$H_2O_2 \rightarrow 2OH$$

the hydrogen peroxide being supposed to be produced by processes which have little influence on the rate of reaction or the explosion limits. On the other hand, Willbourn and Hinshelwood,[3] on the basis of a further experimental study of the reaction at and below the third limit, have concluded that the activation energy of the chain-initiating step is about 103 kcal, and they consequently favor the process $H_2 + M \rightarrow 2H + M$. A somewhat higher value for the activation energy of the initial step was determined by Ashmore and Dainton,[4] who also favor hydrogen dissociation. The possibility must be considered that reactions such as

$$H_2 + O_2 \rightarrow 2OH - 20 \text{ kcal}$$

and

$$H_2 + O_2 \rightarrow HO_2 + H - 40 \text{ kcal}$$

also contribute to the initiation process.

Carbon Monoxide–Oxygen Reaction. The carbon monoxide autoxidation in the gas phase exhibits the same type of behavior as does the hydrogen-oxygen reaction, there being an explosive region confined between two pressure limits. The lower limit was first observed by Sagulin[5] and the upper limit by Kopp, Kowalsky, Sagulin, and Semenoff;[6] the variation of the pressure limits with the temperature was investigated by Hadman, Thompson, and Hinshelwood.[7] The upper limit varies exponentially with the reciprocal of the absolute temperature, the variation corresponding to

[1] B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," p. 39, Cambridge University Press, New York, 1938.

[2] G. von Elbe and B. Lewis, *J. Chem. Phys.*, **10**, 366 (1942); Lewis and von Elbe, "Third Symposium on Combustion and Flame and Explosion Phenomena," p. 484, The Williams & Wilkins Company, Baltimore, 1949.

[3] A. H. Willbourn and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 185,** 353 (1946).

[4] P. G. Ashmore and F. S. Dainton, *Nature*, **158,** 416 (1946).

[5] A. B. Sagulin, *Z. physik. Chem.*, **B, 1,** 275 (1928); *cf.* N. Semenoff, *Z. Physik*, **48,** 571 (1928); W. E. Garner and A. S. Gomm, *Trans. Faraday Soc.*, **24,** 470 (1928).

[6] D. Kopp, A. Kowalsky, A. B. Sagulin, and N. Semenoff, *Z. physik. Chem* , **B, 6,** 307 (1930).

[7] G. Hadman, H. W. Thompson, and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 138,** 297 (1932).

an activation energy of 35 kcal per mole. Semenoff and his coworkers[1] found that carbon monoxide and oxygen could be replaced by equivalent amounts of nitrogen without there being much change in the upper limit, and a similar result was found by Hinshelwood and his associates[2] for argon; the significance of this will be discussed later.

The combustion of carbon monoxide is very much influenced by the presence of water or hydrogen.[3] It appears that the effect of these substances is largely due to their efficacy in helping to initiate chains by producing free radicals; thus the drier the mixture, the more energetic must be the ignition for combustion to be initiated. The amount of water or hydrogen present has very little influence on the position of the upper explosion limit, indicating that the chain-propagating reactions involve only carbon monoxide, oxygen, and species which are derived from these two molecules (such as O and O_3).

The carbon monoxide–oxygen reaction is of special interest in that the flame associated with it is one of the most luminous of all flames, and Kondratjew and Kondratjewa[4] have shown that one quantum of radiation is emitted for every 125 molecules of carbon dioxide formed in the reaction. This is much too large a proportion to be due to thermal excitation and indicates that in at least one of the elementary processes occurring a molecule is produced in an electronically excited state. The emitting species was formerly thought[5] to be electronically excited carbon dioxide, but Hornbeck[6] has recently shown that the luminescence is due largely to radiation by excited oxygen.

To account for these facts, the following reaction scheme has been proposed:[7]

[1] Kopp, Kowalsky, Sagulin, and Semenoff, *loc. cit.*

[2] Hadman, Thompson, and Hinshelwood, *loc. cit.*

[3] Cf. W. A. Bone, *J. Chem. Soc.*, 338 (1931); W. A. Bone and D. T. A. Townend, "Flame and Combustion in Gases," Longmans, Roberts and Green, London, 1927; A. R. Ubbelohde, *J. Chem. Soc.*, 972 (1933).

[4] V. Kondratjew, *Acta Physicochim. U.R.S.S.*, **2**, 126 (1935); E. Kondratjewa and V. Kondratjew, *ibid.*, **6**, 748 (1937); *J. Phys. Chem.* (*U.S.S.R.*), **9**, 736, 747 (1937); H. Kondratjewa and V. Kondratjew, *Acta Physicochim. U.R.S.S.*, **4**, 547 (1936); **6**, 625 (1937).

[5] V. Kondratjew, *Z. Physik*, **63**, 322 (1930); A. Fowler and A. G. Gaydon, *Proc. Roy. Soc.* (*London*), **A**, **142**, 362 (1933); A. G. Gaydon, "Spectroscopy and Combustion Theory," Chap. VI, Chapman & Hall, Ltd., London, 1948.

[6] G. A. Hornbeck, *J. Chem. Phys.*, **16**, 1005 (1948); R. C. Herman, H. S. Hopfield, G. A. Hornbeck, and S. Silverman, *ibid.*, **17**, 220 (1949).

[7] V. F. Griffing and K. J. Laidler, "Third Symposium on Combustion and Flame and Explosion Phenomena," p. 432, The Williams & Wilkins Company, Baltimore, 1949; K. J. Laidler, *ibid.*, p. 441; *J. Chem. Phys.*, **17**, 221 (1949); *cf.* G. von Elbe and B. Lewis, *J. Am. Chem. Soc.*, **59**, 2025 (1937).

(1) $$CO + O_2 \rightarrow CO_2 + O$$
(2) $$O + CO + M \rightarrow CO_2^* + M$$
(3) $$O + O_2 + M \rightarrow O_3 + M$$
(4) $$O_3 + CO \rightarrow CO_2 + 2O$$
(5) $$O_3 + CO + M \rightarrow CO_2 + O_2 + M$$
(6) $$CO_2^* + M \rightarrow O + CO + M$$
(7) $$CO_2^* + O_2 \rightarrow CO_2 + 2O$$
(8) $$CO_2^* \rightarrow CO_2 + h\nu$$
(9) $$CO_2^* + O_2 \rightarrow CO_2 + O_2^*$$
(10) $$O_2^* \rightarrow O_2 + h\nu$$

The chain carriers postulated in this scheme are O and O_3. That oxygen atoms are in fact involved in the reaction has been shown by Gaydon,[1] who found a yellow-green emission on adding nitric oxide to the flame. von Elbe and Lewis[2] showed that it is not possible to explain the kinetics if oxygen atoms alone are assumed to act as chain carriers, and they have postulated that O_3 and CO_3 also play a role; in view of the lack of evidence for CO_3, however, and since it is not essential to explain the results, it has been omitted in the above scheme.

The reactions postulated as occurring may now be discussed very briefly. Reaction (1) is by far the most likely chain-initiating step for the dry reaction; it is exothermic by 9 kcal, whereas most other possible reactions are endothermic. In connection with reaction (2), it can be shown theoretically that the carbon dioxide produced when a normal oxygen atom reacts with a normal carbon monoxide molecule must be in an electronically excited state; this is indicated by means of the asterisk. The activation energy of this reaction has been shown directly[3] to be about 2 kcal. Reaction (3) has also been investigated directly and shown[4] to have a very small, or zero, energy of activation. Reaction (4) is endothermic by 11.4 kcal, but its occurrence must be postulated as it is the only plausible chain-branching process. The activation energy is obtained from the variation of the upper limit with the temperature and is 35 kcal. Reaction (5) accounts for chain ending and is exothermic. Reactions (6), (7), (8), and (9) are all probable reactions involving excited carbon dioxide. The transition from CO_2^* to CO_2 is a "forbidden" one, so that the radiative life of CO_2^* is quite high. Most of the CO_2^* molecules probably undergo reaction (9), *i.e.*, produce excited oxygen, which radiates.

[1] A. G. Gaydon, *Proc. Roy. Soc (London)*, **A, 183,** 111 (1944); *Trans. Faraday Soc.*, **42,** 292 (1946).

[2] G. von Elbe and B. Lewis, *J. Am. Chem. Soc.*, **59,** 2025 (1937).

[3] W. F. Jackson, *J. Am. Chem Soc* , **56,** 2631 (1934); W. Groth, *Z. physik. Chem.*, B, **37,** 307 (1937).

[4] U. Beretta and H. J. Schumacher, *ibid.*, **B, 17,** 417 (1932).

In addition to these reactions, there are various wall reactions, which it is necessary to postulate to account for the lower explosion limit.

The equation for the upper explosion limit may be obtained by writing down the steady-state expressions for O, O_3, CO_2^*, and O_2^*, solving for [O], and equating to zero the denominator of the factor multiplying [O] in the final expression; this gives the condition that [O] becomes infinite. The equation obtained is

$$k_5[M][k_3[O_2](k_6[M] + k_7[O_2] + k_8) + k_2k_8[CO]] = k_3k_4[O_2](k_6[M] + k_7[O_2] + k_8) - k_2k_4k_7[CO] \quad (23)$$

and this, when account is taken of the fact that $k_3[O_2] \gg k_2[CO]$, reduces approximately to

$$k_5[M] = k_4 \quad (24)$$

The term $k_5[M]$ is in reality the sum of a number of terms, *viz.*,

$$k_5[M] = k_{CO}[CO] + k_{O_2}[O_2] + k_X[X] \quad (25)$$

where X represents molecules other than CO and O_2. The upper limit is therefore given by

$$k_{CO}[CO] + k_{O_2}[O_2] + k_X[X] = k_4 \quad (26)$$

This explains why carbon monoxide and oxygen do not have very specific influences on the limit; they can be replaced, for example, by nitrogen, which in weight and diameter is very similar to carbon monoxide and oxygen, without any appreciable effect on the limit.

Since k_{CO}, k_{O_2}, and k_X do not vary much with the temperature, it is clear that the activation energy of 35 kcal, obtained from the variation of the upper limit with the temperature, corresponds to that of the chain-branching process (4), *viz.*, $O_3 + CO \rightarrow CO_2 + 2O$.

On the basis of the above reaction scheme, the light yield, *i.e.*, the number of protons emitted divided by the number of carbon dioxide molecules produced, has been shown[1] to be equal to

$$\frac{k_2[CO]}{2k_2[CO] + k_3[O_2]} \quad (27)$$

and since $k_3[O_2] \gg k_2[CO]$, this is approximately

$$\frac{k_2[CO]}{k_3[O_2]} \quad (28)$$

[1] Griffing and Laidler, *loc. cit.*; *cf.* G. von Elbe and B. Lewis, *J. Am. Chem. Soc.*, **59**, 2025 (1937).

This ratio is the ratio of the rates of reactions (2) and (3) and has been given variously as $\frac{1}{150}$ and $\frac{1}{40}$. The experimental figure of $\frac{1}{125}$ for the light yield is therefore consistent with the kinetic results on the basis of the proposed reaction scheme.

Oxidation of Phosphorus. The combustion of phosphorus vapor shows somewhat the same features as the hydrogen-oxygen and carbon monoxide–oxygen reactions, although the quantitative relations are very different. The existence of the upper and lower explosion limits was first demonstrated by Semenoff,[1] and a tendency of foreign gases to promote inflammation of certain mixtures of phosphorus vapor and oxygen was noticed by Chariton and Walta,[2] such gases exerting an effect on the lower limit. The influence of foreign gases on the lower limit was investigated in detail by Melville and Ludlam,[3] who found the equation

$$[O_2][P_4]\left(1 + \frac{a[M]}{[H_2]+[O_2]}\right)d^2 = \text{const.} \qquad (29)$$

to be obeyed; the constant a is an empirical quantity which depends upon the nature of the gas added. The value of a was found to vary inversely with the coefficient of diffusion of oxygen in the particular gas added and to decrease slightly with rise in temperature in the manner of a diffusion constant. These facts are clearly consistent with the interpretation of the lower limit given earlier.

The upper limit was investigated by a number of workers,[4] some of whom determined the influence of foreign gases upon it; these were found to lower the limit, *i.e.*, to decrease the tendency to inflammation. The steady reaction above the upper limit is accompanied by a cold flame (*cf.* p. 331), and on the basis of a spectroscopic study Ouellet[5] attributed the radiation to emission by P_4O_{10} formed in an electronically excited state.

A reaction scheme has been proposed by Semenoff.[6] The first step is the production of oxygen atoms, perhaps on the walls of the vessel. These then react according to the scheme

(1) $$O + P_4 \rightarrow P_4O$$

(2) $$P_4O + O_2 \rightarrow P_4O_2 + O$$

[1] N. Semenoff, *Z. Physik.*, **46**, 109 (1927).

[2] J. Chariton and Z Walta, *ibid.*, **39**, 547 (1926).

[3] H. W. Melville and E. B. Ludlam, *Proc. Roy. Soc* (*London*), **A, 132**, 108 (1931).

[4] A. Kowalsky, *Z. physik. Chem.*, **B, 4**, 188 (1929); J. Tausz and H. Gorlacher, *Z. anorg. Chem.*, **190**, 95 (1930).

[5] C. Ouellet, *Trans. Faraday Soc.*, **29**, 486 (1933).

[6] Semenoff, *loc. cit.; Chem. Revs.*, **6**, 347 (1929).

Oxidation of P_4O_2 to P_4O_{10} then occurs by a number of steps, the over-all process being sufficiently exothermic to leave the P_4O_{10} in an electronically excited state. Chain branching is supposed to involve the mechanism

$$P_4O_{10}^* + O_2 \rightarrow P_4O_{10} + 2O$$

which is analogous to reaction (7) in the carbon monoxide–oxygen reaction. Dainton[1] has suggested that the stages in the oxidation of P_4O_2 to P_4O_{10} are analogous to process (2) and can therefore be represented by

$$P_4O_m + O_2 \rightarrow P_4O_{m+1} + O$$

The thermochemical data[2] indicate that the reactions with $m = 1, 2, 3, 4$, and 5 will be almost thermoneutral, while those with $m = 6, 7, 8$, and 9 are exothermic by about 44 kcal.

Oxidation of Hydrocarbons. The study of the oxidation of hydrocarbons is of special practical importance in view of their use as engine fuels. From the fundamental standpoint the reactions are of great interest in that the data for the various reactions can be coordinated into a consistent theoretical scheme, and because a special type of explosion, the cool flame, plays a prominent part.

On oxidation the hydrocarbons give rise to a wide variety of products, including water, carbon monoxide, carbon dioxide, acids, alcohols, aldehydes, peroxides, and olefins. The characteristics of the reactions have been explained on the basis of a considerable number of theories; among earlier ones may be mentioned the hydroxylation theory of Bone,[3] according to which the oxygen atoms are successively introduced between carbon and hydrogen atoms. Pope, Dykstra, and Edgar[4] supposed that the hydrocarbons oxidize by way of higher aldehydes, which are degraded step by step to lower aldehydes, but this theory is inconsistent with a number of facts.[5] The importance of aldehydes in the over-all reactions is, however, very great.

The hydrocarbon oxidations frequently show an induction period, followed by very rapid reaction. In the case of the oxidation of methane it has been found[6] that traces of formaldehyde are formed in the induction period and that the addition of formaldehyde shortens or eliminates the period.

[1] F. S. Dainton, *Trans. Faraday Soc.*, **42**, 365 (1946).

[2] H. A. Skinner, *ibid.*, **41**, 646 (1945.)

[3] *Cf.* Bone and Townend, *loc cit*

[4] J. C. Pope, F. J. Dykstra, and G Edgar, *J. Am. Chem. Soc.*, **51**, 1875, 2203, 2213 (1929).

[5] *Cf.* A. D. Walsh, *Trans. Faraday Soc.*, **42**, 269 (1946).

[6] W. Bone and J. B. Gardner, *Proc. Roy. Soc.* (*London*), **A, 154**, 297 (1937); W. Bone and R. E. Allum, *ibid.*, **A, 134**, 578 (1931).

Another important feature of the reactions is the fact that they are very strongly inhibited by increase of surface. Coating the surface of the vessel with potassium chloride, which suppresses the hydrogen-oxygen reaction to a marked degree, has little effect on the rates of hydrocarbon oxidations but prevents almost completely the formation of peroxides.[1]

A characteristic of special interest in hydrocarbon oxidations is the occurrence of cool flames under certain conditions of temperature and pressure. These are detected on the basis of jumps in the pressure and by the appearance of the luminescence. The flames are usually pale in color, travel slowly, and reveal peroxides and aldehydes on analysis. Their propagation through cold mixtures has been extensively studied by Townend and his coworkers.[2] Cool flames do not occur in the oxidation of methane or ethane but are found with all the other paraffins and with the olefins from propylene upward. Benzene does not give a cool flame,[3] but its monoalkyl derivatives from *n*-propylbenzene upward do. Emeléus[4] recorded the spectra of the cool flames of diethyl ether, acetaldehyde, propionaldehyde, and hexane and found all of them identical. The spectra have now been found[5] to be identical with the fluorescence spectrum of formaldehyde, so that the emitter in the flames is known to be electronically excited formaldehyde.

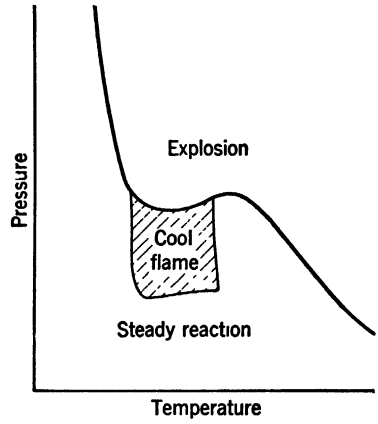


FIG. 33. Pressure-temperature explosion and cool-flame limits for a typical hydrocarbon-oxygen mixture.

The temperature and pressure limits for the occurrence of cool flames, and of explosions, have been studied carefully by Townend and his coworkers;[6] the limits for a typical reaction are shown in Fig. 33. For all of the hydrocarbons the temperature limits for the cool flames are at about 280 and 410°C. A region of explosion exists at higher temperatures and pressures, and it is seen in Fig. 33 that there is an explosion peninsula

[1] R. N. Pease, *J. Am. Chem. Soc.*, **51**, 1839 (1929); **57**, 2296 (1935); R. N. Pease and W. P. Munro, *ibid.*, *J. Am. Chem. Soc.*, **56**, 2034 (1934).

[2] *Cf.* M. Maccormac and D. T. A. Townend, *J. Chem. Soc.*, 143 (1940).

[3] R. Fort and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A, 127**, 218 (1930).

[4] H. J. Emeléus, *J. Chem. Soc.*, 2948 (1926), 1733 (1929).

[5] *Cf.* A. G. Gaydon, "Spectroscopy and Combustion Theory," p. 49, Chapman & Hall, Ltd., London, 1948; *Quart. Rev.*, **4**, 1 (1950).

[6] D. T. A. Townend, *Chem. Revs.*, **21**, 259 (1937); M. Maccormac and D. T. A. Townend, *J. Chem. Soc.*, 238 (1938).

between two temperature limits; this behavior is to be contrasted with that found in the hydrogen-oxygen reaction, where the explosion peninsula is defined by two pressure limits.

Some of the usual features of the reactions are explained by Semenoff's hypothesis[1] of "degenerate branching" chains, which was put forward primarily to interpret the long induction periods found in the reactions. That chain branching actually occurs is indicated by the fact that the reactions accelerate without any rise in temperature; however, the branching must be of such a nature that it occurs infrequently. Semenoff's proposal was that there is some process which gives rise to an intermediate product M, which may remain inert but which sometimes undergoes reaction to produce a free radical; such a process may be represented by

$$A \rightarrow M \begin{cases} \longrightarrow \text{stable molecule} \\ \longrightarrow \text{free radical} \end{cases}$$

A being a hydrocarbon molecule. The intermediate M is supposed to have a fairly long life so that branching is delayed; this explains the slow increase in the number of radicals, which gives rise to an induction period. In the case of hydrogen-oxygen mixtures, branching chains give rise, under isothermal conditions, to infinite velocity; with hydrocarbons, on the other hand, the number of radicals grows so slowly with time that before the rate becomes infinite the effect of the removal of the reactants is significant and the rate is slowed down. The cool flames are explosions of this degenerate type, the reaction velocity being high but not infinite. When true explosions occur, it is supposed, if the only branching that occurs is degenerate, that they are of the thermal type, due to self-heating of the mixture. It appears probable that this is usually the case with the hydrocarbons;[2] only degenerate branching occurs, so that the explosions are thermal and therefore of an entirely different character from the hydrogen-oxygen explosions, which according to Hinshelwood are isothermal. In the case of methane, the kinetics are consistent with the fact that the intermediate product M is formaldehyde;[3] this may, sometimes a considerable time after the ending of the primary chains, give rise to new free radicals.

It is now necessary to consider how the hypothesis of degenerate branching explains the existence of lower and upper temperature limits of explosion. The lower temperature limit is easily explained as due to the

[1] N. Semenoff, *Z. physik. Chem.*, **B, 11,** 464 (1930); *cf.* N. Semenoff, "Chemical Kinetics and Chain Reactions," p. 68, Oxford University Press, New York, 1935.

[2] R. G. W. Norrish and S. G. Foord, *Proc. Roy. Soc.* (*London*), **A, 157,** 503 (1936).

[3] *Ibid.*

fact that degenerate branching becomes less important as the temperature is lowered and eventually becomes too slow to allow the number of radicals to increase. Evidence with regard to the upper limit is provided by the fact that under certain conditions, particularly at lower pressures, the rate of oxidation has a negative temperature coefficient over a certain range of temperatures. This suggests that there is some chain-breaking process which competes with the delayed branching and becomes relatively more important as the temperature rises.

A plausible mechanism[1] for the oxidation of a straight-chain hydrocarbon RCH_2CH_3 may be represented by the following scheme:

(1) $$RCH_2CH_3 + O_2 \rightarrow RCHCH_3 + HO_2$$

(2) $$RCHCH_3 + O_2 \rightarrow R(CH_3)CHOO$$

(3) $$R(CH_3)CHOO + RCH_2CH_3 \rightarrow R(CH_3)CHOOH + RCHCH_3$$

(4) $$R(CH_3)CHOOH \rightarrow R(CH_3)CO + H_2O$$

(5) $$R(CH_3)CHOOH \rightarrow R + CH_3CHO + OH$$

(6) $$R'CH_2 + O_2 \rightarrow R'CH_2OO \quad [R'CH_2 = R]$$

(7) $$R'CH_2OO \rightarrow R'CHO + OH$$

(8) $$R'CHO \rightarrow R'H + CO$$

According to this mechanism, the hydroperoxide $R(CH_3)CHOOH$ is an important intermediate, and is responsible for the formation of the aldehydes. The radical R produced in reaction (5) can undergo a further series of reactions, (6), (7), and (8), similar to (2) to (5), until all the C-C bonds are severed. Several features of this reaction scheme may now be discussed.

According to the reaction (1), the oxygen attacks the hydrocarbon not at the end of the chain but at the α carbon atom. This has been concluded on the basis of the products obtained from the oxidation of various types of hydrocarbons, in particular from the oxidation of substituted benzenes.[2] In the latter work it was found that ethyl- and *n*-propylbenzenes gave rise, respectively, to acetophenone and propiophenone. Tertiary-butylbenzene was not oxidized under the same conditions, showing that for oxidation to occur there must be a hydrogen atom on an α carbon atom; this result is evidence also for the fact that the initial step involves the removal of a hydrogen atom. Further evidence for the same

[1] *Cf.* Walsh, *loc. cit.*; *Trans. Faraday Soc* , **43**, 297, 305 (1947).

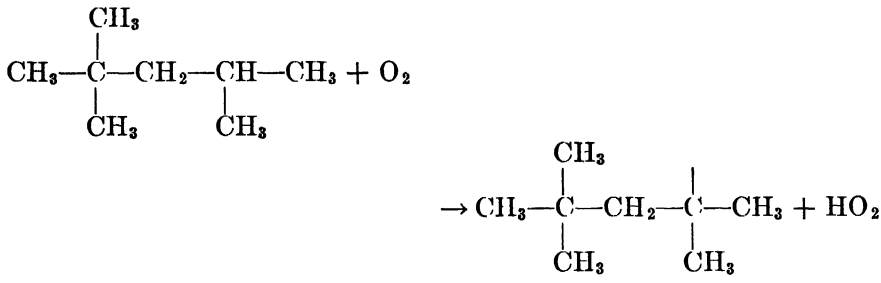
[2] A. Grum, *Ber.*, **53**, 987 (1920); H. N. Stephens, *J. Am. Chem. Soc.*, **48**, 2920 (1926); A. W. Burwell, *Ind. Eng. Chem* , **26**, 204 (1934); H. N. Stephens and F. L. Roduta, *J. Am. Chem. Soc.*, **57**, 2380 (1935).

point of view is that methylcyclopentanone is found to form a peroxide exclusively at the tertiary carbon atom in the molecule.[1]

These and other results are all consistent with the generalization that the reactivity of C-H bonds toward oxygen (and other electrophilic reagents) diminishes in the order

$$\text{tertiary} > \text{secondary} > \text{primary}$$

In a straight-chain hydrocarbon the oxygen will therefore avoid the hydrogen atoms attached to the end carbon atoms and will prefer to react with the secondary hydrogen atoms; the choice of the α carbon atoms is probably a steric effect. In a branched-chain hydrocarbon the oxygen will initially remove a tertiary hydrogen atom if one is available; thus with isooctane the primary step is probably



This postulated order of reactivity of the various types of C-H bonds with oxygen is consistent with the fact that the probability of attack of a methyl radical during the thermal decomposition of a hydrocarbon decreases in the same order.[2] It is to be noted that according to the above reaction scheme, not all the hydrocarbon molecules are initially attacked by an oxygen molecule, some having their hydrogen atoms removed by free radicals; such reactions are not represented in the mechanism given above.

The fact that an alkyl hydroperoxide is an important intermediate in the oxidation of hydrocarbons has been supported by much direct and indirect evidence. The most direct is the fact[3] that peroxides and, in particular, substances behaving like alkyl hydroperoxides are found as early products of the partial combustion of hydrocarbons; supporting evidence is provided by the result that there is often an initial pressure drop in a

[1] P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

[2] *Cf.* F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, 1935.

[3] A. Egerton, F. L. Smith, and A. R. Ubbelohde, *Trans. Roy. Soc.* (*London*), **A**, **234**, 433 (1935).

hydrocarbon oxidation[1] and by the fact that the addition of alkyl hydroperoxides to a hydrocarbon undergoing combustion may bring about explosion ("knock"). It is to be noted that the peroxidic substances are present only in low concentrations, which explains why they were not detected in many of the investigations.

The most likely process for the alkyl radical produced in reaction (1) to undergo would appear to be a direct association with an oxygen molecule, which behaves in many ways like a diradical [reaction (2)]. The resulting peroxide radical $R(CH_3)CHOO$ then removes a hydrogen atom from another hydrocarbon molecule, as indicated in reaction (3). The hydroperoxide formed in this way is not stable under the usual experimental conditions and decomposes in the manner now to be considered.

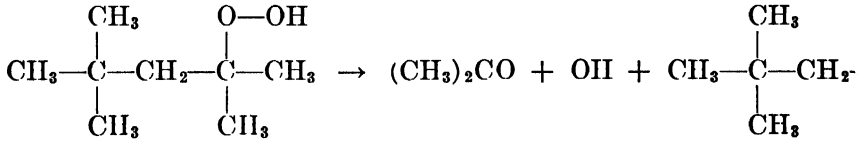
The alkyl hydroperoxides formed from all the straight-chain hydrocarbons except ethane are secondary hydroperoxides, $R(CH_3)CHOOH$; in the case of ethane CH_3CH_2OOH is formed. The secondary compounds may undergo decomposition to the ketone [reaction (4)], the primary compound formed in the ethane oxidation decomposing to acetaldehyde

$$CH_3CH_2OOH \rightarrow CH_3CHO + H_2O$$

These processes probably occur on the surface.[2] The peroxides may also undergo an explosive decomposition in the gas phase, involving the splitting of an O-O bond and of an adjacent C-C bond:[3]

$$R(CH_3)CHOOH \rightarrow CH_3CHO + R + OH$$

In the case of tertiary hydroperoxides, which are formed from branched-chain hydrocarbons having a tertiary hydrogen atom, decomposition occurs by fission at the O-O bond followed by splitting of the weakest C-C bond on the α carbon atom,[4] *e.g.*,



Besides the above unimolecular decompositions of peroxides, various bimolecular reactions are possible;[5] again the tendency is toward splitting

[1] E. W. J. Mardles, *J. Chem. Soc.*, 226 (1928); S. S. Madvedev, *Acta Physicochim. U.R.S.S.*, **9**, 395 (1938); V. A. Avramenko and M. B. Neumann, *ibid.*, **10**, 601 (1939); B. V. Aivazov, N. P. Keier, and M. B. Neumann, *ibid.*, **14**, 201 (1941).

[2] E. J. Harris, *Proc Roy. Soc.* (*London*), **A, 173,** 126 (1939).

[3] A. R. Ubbelohde, *ibid.*, **A, 152,** 378 (1935).

[4] Harris, *loc. cit.*

[5] *Ibid.*

of the O-O bond and of an adjacent C-C bond. These modes of decomposition have been shown to be catalyzed by formaldehyde.

The radical R (which may now be written as $R'CH_2$) produced in reaction (5) also forms a peroxide radical [reaction (6)] and this also undergoes decomposition. The manner in which this occurs is suggested by the evidence found by Bates[1] with regard to the combustion of methyl and ethyl radicals, which appear to react as follows:

$$CH_3 + O_2 \rightarrow CH_3OO \rightarrow HCHO + OH$$
$$C_2H_5 + O_2 \rightarrow CH_3CH_2OO \rightarrow CH_3CHO + OH$$

These reactions are highly exothermic, and the C-O distance shortens considerably from RCH_2OO to RCHO; the aldehyde molecules are therefore probably highly excited vibrationally and readily decompose to the paraffin and carbon monoxide,

$$RCHO \rightarrow RH + CO$$

The radical R produced in reaction (5) therefore probably undergoes reactions (6), (7), and (8), which are similar to the reactions mentioned above. The occurrence of these processes explains the fact that the number of moles of carbon monoxide produced in the low-temperature oxidation of 1 mole of a straight-chain paraffin is one less than the number of moles of oxygen consumed;[2] according to the above scheme, two molecules of oxygen are involved in the formation of one $R'CH_2$ radical, while one molecule of carbon monoxide is produced [in reaction (8)].

It is to be noted that in the above reaction scheme the peroxide radical $R(CH_3)CHOO$ does not undergo direct decomposition but forms the hydroperoxide $R(CH_3)CHOOH$, which subsequently decomposes according to reactions (4) and (5). This is true because (except with methane and ethane) the radical $R(CH_3)CHOO$ is a secondary radical, which is expected to be more stable than the primary ones produced subsequently. At lower temperatures (about 300 to 400°C) it is supposed that the decomposition of the secondary radical is unimportant, the decomposition via the hydroperoxide being dominant. As the temperature is raised, the decomposition of the secondary radical becomes relatively more important, and that of the hydroperoxide molecule less so. The fact that the decomposition of the molecule can be a branching chain process [reaction (5)] explains the fact that the temperature coefficient of the rate is often found to be negative in the temperature range from 400 to 450°C. At still higher temperatures the rate of the radical decomposition may have

[1] J. R. Bates and R. Spence, *J. Am. Chem. Soc.*, **53**, 1689 (1931); L. T. Jones and J. R. Bates, *ibid.*, **56**, 2285 (1934).

[2] Pope, Dykstra, and Edgar, *loc cit.*

increased so much that thermal explosion can take place. This scheme of reactions therefore represents a specific mechanism for the degenerate branching postulated by Semenoff (p. 332); the role of the intermediate M is played by the secondary hydroperoxide $R(CH_3)CHOOH$, which can give rise to branching [reaction (5)] but which can also decompose without the occurrence of branching [reaction(4)].

The spectra of cool hydrocarbon flames have been seen (p. 331) to involve emission by electronically excited formaldehyde. The light yield is very small; the ratio of the number of photons emitted to the number of molecules oxidized has been given variously as 10^{-16} (Day and Pease[1]) and as 10^{-6} (Topps and Townend[2]). In either case, in view of the fact that formaldehyde is an important reaction product, it is clear that the fraction of formaldehyde molecules which are formed in the excited state is very small. This is consistent with the fact that none of the reactions playing a part in the chain process and producing formaldehyde is sufficiently exothermic to cause excitation with a high efficiency, about 77 kcal being required for the excitation.

Two types of explanation are possible. The first is that a small fraction of the formaldehyde molecules produced by processes such as

$$CH_3 + O_2 \rightarrow HCHO + OH + 47.2 \text{ kcal}$$
$$CH_3CO + O_2 \rightarrow HCHO + OH + CO + 39 \text{ kcal}$$

may be electronically excited, the additional energy required for excitation to 77 kcal being available as thermal energy in a small fraction of the collisions. An alternative explanation[3] is that the excited formaldehyde is formed in a radical-radical reaction such as

$$RCH_2O + OH \rightarrow ROH + HCHO + 91 \text{ kcal}$$

Such a process will occur infrequently owing to the low concentration of radicals but may give rise to excited formaldehyde at every collision.

Liquid-phase oxidation

Oxidation reactions in the liquid phase are found to have characteristics somewhat similar to those occurring in the gas phase, and it has been found that they can be interpreted by means of analogous free-radical mechanisms. This will be illustrated by a few typical and well-known examples.

Oxidation of Liquid Aldehydes. A great deal of work has been done on the oxidation of liquid aldehydes by molecular oxygen. The oxidation

[1] R. A. Day and R. N. Pease, *J. Am. Chem. Soc.*, **62**, 2234 (1940).
[2] J. E. C. Topps and D. T. A Townend, *Trans. Faraday Soc.*, **42**, 345 (1946).
[3] A. D. Walsh, *ibid.*, **43**, 297 (1947)

of liquid benzaldehyde, which has been studied in particular by Bäckstrom and his coworkers,[1] is found to be extremely sensitive to light, one quantum of absorbed radiation sometimes leading to the oxidation of 10,000 or more molecules of the aldehyde; this clearly establishes that the reaction proceeds by a free-radical mechanism. That the dark reaction is also a chain reaction is indicated by its having an induction period and being inhibited by small traces of substances such as phenols, amines, and alcohols. Catalysis of the dark reaction by traces of many salts, particularly those of iron, copper, nickel, manganese, and chromium, has also been observed. The rate of the reaction is found to be practically independent of the oxygen concentration, a similar result being found with the gas-phase oxidation.[2]

The influence of inhibitors was found to be the same for both the thermal and the photochemical reactions, indicating that similar chain mechanisms occur in the two cases: the difference between the two reactions lies only in the initiating process. The photochemical yield is a measure of the chain length, and the latter was found to decrease with increasing inhibitor concentration $[I]$ in accordance with the law

$$\text{Length} = \frac{k_1}{1 + k_2[I]} \tag{30}$$

where k_1 and k_2 are constants. By comparing the influence of inhibitors on the thermal and photochemical reactions, Bäckstrom was able to establish that the chain lengths are the same.

Perbenzoic acid, $C_6H_5CO \cdot OOH$, can be isolated as an intermediate product of the benzaldehyde oxidation, and this substances has been shown to oxidize benzaldehyde to benzoic acid. By analogy with the mechanism for hydrocarbon oxidation (p. 333), the following mechanism[3] seems plausible:

(1) $$C_6H_5CHO + O_2 \rightarrow C_6H_5CO + HO_2$$

(2) $$C_6H_5CO + O_2 \rightarrow C_6H_5CO \cdot OO$$

(3) $$C_6H_5CHO + C_6H_5CO \cdot OO \rightarrow C_6H_5CO + C_6H_5CO \cdot OOH$$

Here reaction (1) accounts for chain initiation, and (2) and (3) for propagation. Subsequently the perbenzoic acid oxidizes benzaldehyde to benzoic acid,

$$C_6H_5CO \cdot OOH + C_6H_5CHO \rightarrow 2C_6H_5COOH$$

by a chain process the details of which have not been elucidated. In the

[1] H. Bäckstrom, *J Am. Chem. Soc.*, **49**, 1460 (1927); H. Bäckstrom and H. N. Alyea, *ibid.*, **51**, 90 (1929).

[2] M. Bodenstein, *Sitzber. preuss. Akad. Wiss., Physik.-Math. Klasse*, **III**, 73 (1931).

[3] H. Bäckstrom, *Z. physik. Chem.*, **B, 25**, 99 (1934).

photochemical reaction, it is postulated that a diradical is produced initially,

$$C_6H_5CHO + h\nu \rightarrow C_6H_5\overset{\displaystyle H}{\underset{\displaystyle |}{C}}\!-\!O$$

and that this reacts with another benzaldehyde molecule to give the radical C_6H_5CO, which is the principal chain carrier:

$$C_6H_5\overset{|}{\underset{|}{C}}\!H\!-\!O + C_6H_5CHO \rightarrow C_6H_5\underset{|}{C}H\!-\!OH + C_6H_5\underset{|}{C}\!=\!O$$

In agreement with this mechanism, it is found that photochemically activated aldehydes can dehydrogenate alcohols.[1] The catalysis of the reaction by salts of variable valence is probably due[2] to chain-initiating reactions of the type

$$Fe^{+++} + C_6H_5CHO \rightarrow Fe^{++} + H^+ + C_6H_5\underset{|}{C}O$$

Inhibitors appear to act by donating a hydrogen atom or an electron to a free radical, rendering it inactive.

Oxidation of Sodium Sulfite. The autoxidation of sodium sulfite in solution,

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

has been studied in great detail[3] and found to have many of the characteristics of the oxidation of liquid benzaldehyde. The rate is proportional to the concentration of sodium sulfite but independent of that of oxygen, the reaction can be accelerated by radiation and by traces of heavy-metal ions. It is strongly inhibited by a number of organic substances, the inhibition law being

$$\text{Rate} = \frac{k_1}{1 + k_2[I]} \tag{31}$$

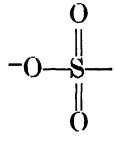
where k_1 and k_2 are constants for given concentrations of sulfite and oxygen. Chain lengths for the reaction, in the presence of various amounts of inhibitors, have been determined by comparing the photochemical and thermal rates.

[1] C. Weizmann, E. Bergmann, and Y. Hirschberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938).

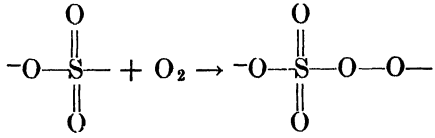
[2] H. Wieland and D. Richter, *Ann.*, **486**, 226 (1931).

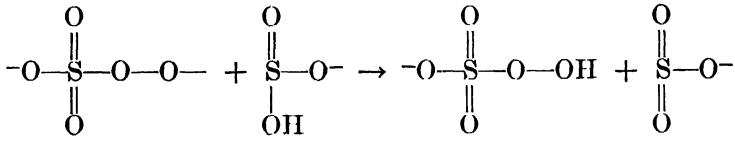
[3] See especially H. Backstrom, *J. Am. Chem Soc.*, **49**, 1460 (1927); Bäckstrom and Alyea, *loc. cit.*; H. N. Alyea, *J. Am. Chem. Soc.*, **52**, 2743 (1930); K. K. Jeu and H. N. Alyea, *ibid.*, **55**, 575 (1933).

The reaction has been interpreted[1] as involving the radical-ion

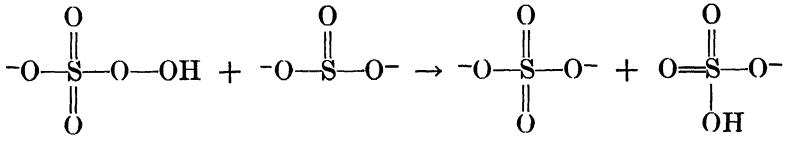


which plays a part in the following reaction chain:

(1) 

(2) 

The HSO_5^- ion produced in reaction (2) is the univalent anion of Caro's acid, H_2SO_5, and is a sufficiently strong oxidizing agent to convert sulfites directly to sulfates:



In the photochemical reaction the radical-ion $—SO_3^-$ is supposed to be produced by the reaction

$$SO_3^{--} + h\nu \rightarrow —SO_3^- + e$$

while in the presence of metals, reactions such as

$$Fe^{+++} + SO_3^{--} \rightarrow Fe^{++} + —SO_3^-$$

probably occur. The hypothesis that the mechanism involves the $—SO_3^-$ radical-ion is supported by the fact that the photochemical decomposition of sodium sulfite (in the absence of oxygen) gives sodium dithionate and oxygen, the dithionate ions presumably being formed by the association of two $—SO_3^-$ radical-ions:

$$2\,—SO_3^- \rightarrow S_2O_6^{--}$$

The radical-ion $—SO_3^-$ has also been postulated[2] as playing a part in the peroxide-catalyzed addition of bisulfites to olefins.

[1] F. Haber and R. Willstätter, *Ber.*, **64**, 2844 (1931); H. Bäckstrom, *Z. physik. Chem.*, **B, 25**, 122 (1934)

[2] M. S. Kharasch, E. M. May, and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1938).

The inhibiting effect of alcohols has been attributed by Bäckstrom to reaction between the alcohol and the radical-ion $—SO_3^-$; the alcohols are in fact found to be oxidized to aldehydes. Similar reactions probably occur with other inhibitors.

Oxidation by Hydrogen Peroxide. It has been seen that hydroperoxides play important parts in the oxidation of organic compounds by molecular oxygen. Hydrogen peroxide, the simplest molecule of this type, also brings about a number of characteristic oxidation processes, some of the mechanisms of which may be discussed briefly.

In the presence of a small concentration of ferrous ions, hydrogen peroxide will rapidly oxidize at 0°C a number of α-hydroxy acids;[1] lactic acid, for example, is oxidized to pyruvic acid. In the absence of ferrous ions, higher temperatures are required for oxidation to be effected, while ferric ions do not very readily bring about reaction.

It was suggested by Haber and Willstätter[2] that the type of initiation mechanism proposed for the oxidation of sulfites (*cf.* p. 340) might be applicable to this process, the reaction in this case being

$$Fe^{+++} + HOOH \rightarrow Fe^{++} + H^+ + —OOH$$

However, to account for the fact that ferrous ions are the more effective catalysts, Haber and Weiss[3] later suggested the initiation reaction

$$Fe^{++} + HOOH \rightarrow Fe^{+++} + HO + (H—O—)^-$$

the products being the hydroxyl radical and the radical-ion $(H—O—)^-$. The effective species is the hydroxyl radical, which may react with an α-hydroxy acid as follows:

$$OH + RCHOHCOOH \rightarrow \underset{\displaystyle O—}{RCHCOOH} + H_2O$$

$$\underset{\displaystyle O—}{RCHCOOH} + HOOH \rightarrow RCOCOOH + H_2O + OH$$

the hydroxyl radical being regenerated in the second step. Reactions of this type, in which the oxidation ceases when all the iron is oxidized to the ferric state, have been discussed in detail by Weiss,[4] who refers to them as type A oxidations.

In certain other reactions involving hydrogen peroxide and iron salts,

[1] H. J. H. Fenton, *J. Chem. Soc.*, **65**, 899 (1894).
[2] Haber and Willstätter, *loc. cit.*
[3] F. Haber and J. Weiss, *Proc. Roy Soc.* (*London*), **A, 147**, 333 (1934).
[4] J. Weiss, *J. Phys. Chem.*, **41**, 1107 (1934)

the ferric ion alone is effective; these are called type B reactions. In them the effective oxidizing agent is the ferric ion, the function of the hydrogen peroxide being to reoxidize the ferrous ions formed. An example is the oxidation of iodides: the iodide ion is oxidized to the atom by the ferric ion,

$$Fe^{+++} + I^- = Fe^{++} + I$$

and two iodine atoms combine to form molecular iodine; the ferrous ions formed in the reaction are reoxidized to the ferric state by hydrogen peroxide. Quinols are oxidized in a similar manner. In general, type A oxidations occur with substances which are oxidized with difficulty and which therefore allow the hydroxyl radical to accumulate; type B oxidations on the other hand occur with substances that are readily oxidized and which would therefore react with, and destroy, free hydroxyl radicals.

Reaction between Ferric and Stannous Salts. The reduction of ferric chloride by stannous salts, a well-known analytical reaction, can be represented by the stoichiometric equation

$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}$$

It was first studied from the kinetic standpoint by Noyes,[1] and subsequently by other workers including Gorin,[2] who investigated the reaction between ferric and stannous perchlorates in perchloric acid solution. The reaction was regarded by Noyes as of the third order, although the third-order specific rates were not particularly constant; this has been attributed to salt effects. Gorin found that the perchlorates reacted very much more slowly than the chlorides and concluded that the reaction could not be interpreted as a direct reaction between the ferric and stannous ions.

The results have more recently been interpreted by Weiss[3] on the basis of the following reaction mechanism, involving the complex ion $SnCl_4^{--}$, which is known to be formed in solutions of stannous chloride:

$$(1) \qquad SnCl_2 + 2Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SnCl_4^{--}$$

$$(2) \qquad Fe^{+++} + SnCl_4^{--} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe^{++} + SnCl_4^{-}$$

$$(3) \qquad Fe^{+++} + SnCl_4^{-} \xrightarrow{k_3} Fe^{++} + SnCl_4$$

This scheme is consistent with the well-known fact that oxidation and reduction processes usually proceed by single steps in which one electron is

[1] W. A. Noyes, *Z. physik. Chem.*, **16**, 576 (1895).
[2] M. H. Gorin, *J. Am. Chem. Soc.*, **58**, 1787 (1936).
[3] J. Weiss, *J. Chem. Soc.*, 309 (1944).

transferred at a time;[1] in the ion $SnCl_4^-$, formed in the second reaction, the tin is in the intermediate trivalent state. The intermediate formation of such compounds in the oxidation of stannous salts has been demonstrated.[2]

The steady-state expression for $SnCl_4^-$ is

$$k_2[Fe^{+++}][SnCl_4^{--}] - k_{-2}[Fe^{++}][SnCl_4^-] - k_3[Fe^{+++}][SnCl_4^-] = 0 \quad (32)$$

whence

$$[SnCl_4^-] = \frac{k_2[Fe^{+++}][SnCl_4^{--}]}{k_{-2}[Fe^{++}] + k_3[Fe^{+++}]} \quad (33)$$

The rate of reaction is thus given by

$$-\frac{d[Fe^{+++}]}{dt} = k_2[Fe^{+++}][SnCl_4^{--}] + k_3[Fe^{+++}][SnCl_4^-] - k_{-2}[Fe^{++}][SnCl_4^-] \quad (34)$$

$$= 2k_3[Fe^{+++}][SnCl_4^-] \quad (35)$$

by subtraction of Eq. (32), and

$$-\frac{d[Fe^{+++}]}{dt} = \frac{2k_2k_3[Fe^{+++}]^2[SnCl_4^{--}]}{k_{-2}[Fe^{++}] + k_3[Fe^{+++}]} \quad (36)$$

In neutral or slightly acid solution, the concentration of ferric ions will be small, owing to partial hydrolysis; as an approximation one can therefore assume that $k_3[Fe^{+++}] \ll k_2[Fe^{++}]$, except at the beginning of the reaction. When this is the case, the rate equation simplifies to

$$-\frac{d[Fe^{+++}]}{dt} = \frac{2k_2k_3}{k_{-2}}\frac{[Fe^{+++}]^2[SnCl_4^{--}]}{[Fe^{++}]} \quad (37)$$

This kinetic equation explains the observation of Noyes that the third-order rate constants were greatly improved by the addition of a quantity of ferrous salt to the mixture; this keeps approximately constant the value of the denominator in the above rate expression.

In more acid solutions, the ferric salt is less hydrolyzed, and the alternative condition $k_3[Fe^{+++}] \gg k_{-2}[Fe^{++}]$ may be obeyed, especially at the beginning of the reaction. The rate expression then becomes

$$-\frac{d[Fe^{+++}]}{dt} = 2k_2[Fe^{+++}][SnCl_4^{--}] \quad (38)$$

[1] *Cf* Haber and Weiss, *op cit* 332; J. Weiss, *Nature*, **135**, 648 (1934); *Naturwissenschaften*, **23**, 64 (1935); L. Michaelis and M. P. Schubert, *Chem. Revs.*, **22**, 437 (1938).

[2] T. R. Bell, W. Wulfkuehler, and R. E. Wingard, *J. Am. Chem. Soc.*, **57**, 1729 (1935).

$$= \frac{2k_1k_2}{k_{-1}} [Fe^{+++}][SnCl_2][Cl^-]^2 \qquad (39)$$

using the equilibrium relationship for reaction (1). This is in agreement with the results of Noyes under these conditions, and Weiss has shown that the ordinary second-order constants determined by Noyes are actually directly proportional to the square of the concentration of chloride ions. The effect of these ions therefore cannot be considered to be a salt effect.

CHAPTER 12

POLYMERIZATION

It is convenient to classify polymers into two types, in accordance with their mechanisms of formation. The first of these types comprises the condensation polymers, which are formed by the elimination of water between monomer molecules; examples include the polyesters, such as that obtained by the condensation of ω-hydroxydecanoic acid molecules,

$$n\mathrm{HO(CH_2)_9COOH} = \mathrm{HO[(CH_2)_9COO]}_n\mathrm{H} + (n - 1)\mathrm{H_2O}$$

The second class consists of the addition polymers, formed without the elimination of water or any other substance; an example is polystyrene, formed by the addition of a large number of styrene molecules:

$$n\mathrm{C_6H_5CH{=}CH_2} = -[\mathrm{C_6H_5CH{-}CH_2}]_n-$$

This type of polymer can be formed only from molecules containing a double bond.

Various other classifications are also convenient for special purposes; thus the question of whether the polymer consists of straight chains or is in the form of a three-dimensional network is of great importance, particularly in connection with its physical properties. When the monomer contains only two reactive, or "functional," groups, long chains are formed; if there are more than two, polymerization may occur in three dimensions. Another possible type of classification depends upon whether one or more types of reacting molecules are incorporated in the chain; when there is more than one, the material is usually referred to as a copolymer.

In discussing the kinetics of polymerization, it is somewhat more convenient to classify polymers according to the type of kinetic mechanism found in their formation. It has been seen in previous chapters that chemical reactions can proceed by three distinct types of mechanisms: molecular, free radical, and ionic. All three types are found in polymerization processes. The formation of condensation polymers is usually found to proceed by a molecular mechanism, while addition polymers may be formed by chain reactions involving either free radicals or ions. These three types of mechanisms will be considered separately.

Molecular mechanisms

The molecular mechanisms occurring in polymerization processes are of the same type as those in such condensation reactions as esterifications; they involve electron transfers and depend upon molecular polarities but do not give rise to free ions: for this reason they are referred to as molecular. The results have established the important fact that the rates of the condensation reactions occurring in polymerization processes depend primarily on the functional groups and are practically independent of the chain length. This has the effect of simplifying the treatment considerably, as it can be assumed that, except in the very early stages of reaction, the rates of all the processes are the same. The evidence for this comes largely from the results of polyesterification studies, which may now be considered.

Polyesterification. One of the simplest cases to consider is the acid-catalyzed reaction between a glycol and a dicarboxylic acid, with the formation of a copolymer; an example is the hydrogen-ion–catalyzed reaction between diethylene glycol, $HOCH_2CH_2OH$, and adipic acid, $HOOC(CH_2)_4COOH$. Such a reaction proceeds by the mechanism

(1) $HO(CH_2)_2OH + HOOC(CH_2)_4COOH \rightarrow HO(CH_2)_2OOC(CH_2)_4COOH$

(2) $HO(CH_2)_2OOC(CH_2)_4COOH + HO(CH_2)_2OH \rightarrow HO(CH_2)_2OOC(CH_2)_4COO(CH_2)_2OH$

(3) $HO(CH_2)_2OOC(CH_2)_4COO(CH_2)_2OH + HOOC(CH_2)_4COOH \rightarrow HO(CH_2)_2OOC(CH_2)_4COO(CH_2)_2OOC(CH_2)_4COOH$

etc. If equivalent amounts of the glycol and acid are taken, the initial concentration of the functional groups being c_0, the rate of change of the concentration c of functional groups is given by

$$-\frac{dc}{dt} = kc^2 \tag{1}$$

where k is the specific rate constant; the reaction is of the second order since the catalyst concentration remains constant, and it is tentatively assumed that each reaction has the same specific rate. This equation integrates to

$$\frac{c_0 - c}{cc_0} = kt \tag{2}$$

since $c = c_0$ when $t = 0$. It is convenient to express this relationship in terms of the fraction f of functional groups which are esterified at time t, *i.e.*,

$$f = \frac{c_0 - c}{c_0} \tag{3}$$

Elimination of c between these expressions gives

$$\frac{1}{1-f} - 1 = c_0 kt \tag{4}$$

If the assumption of constant f is correct, therefore, a plot of $1/(1-f)$ against t should be linear. A number of reactions of this type have been studied by Flory,[1] who has established the linearity of the plot and has determined values for the characteristic reaction constant k for each example.

Similar studies have been carried out in the absence of added catalyst, in which case the treatment is slightly different. The esterifications are now catalyzed by the dicarboxylic acid itself, so that the rate of the reaction is proportional to the cube of the concentration of functional groups,

$$-\frac{dc}{dt} = kc^3 \tag{5}$$

A procedure similar to the above leads to

$$\frac{1}{(1-f)^2} - 1 = 2ktc_0^2 \tag{6}$$

so that in this case a plot of $1/(1-f)^2$ against t should be linear if k does not vary. This has been confirmed by Flory[2] for the polymerization of ω-hydroxyundecanoic acid, and the polyesterification of a number of glycols with adipic acid. Only a limited amount of work has been done on polycondensations in which three-dimensional products are formed.[3]

General Treatment of Molecular Polymerization. The treatment of the previous section has been generalized by Dostal and Raff,[4] as follows: The reactions occurring may all be expressed as

$$M_m + M_n = M_{m+n}$$

where M_m represents a chain of m monomers; m and n can assume all values from unity upward. The monomer M_1 may be removed by reaction with itself and with all other molecules present; its net rate of disappearance is thus given by

$$-\frac{d[M_1]}{dt} = k[M_1][M_1] + k[M_1][M_2] + \cdots + k[M_1][M_n] \tag{7}$$

[1] P. J. Flory, *J. Am. Chem Soc.*, **61**, 3334 (1939).

[2] *Ibid*, **61**, 3334 (1939); **62**, 2261 (1940); *cf.* W. O. Baker, C. S. Fuller, and J. H. Heiss, *ibid.*, **63**, 2142 (1911).

[3] R. H. Kienle, P. A. Van der Meulen, and F. E. Petke, *ibid.*, **61**, 2258, 2268 (1939); R. H. Kienle and F. E. Petke, *ibid.*, **62**, 1053 (1940); **63**, 481 (1941); T. T. Jones, *J. Soc. Chem. Ind.*, **65**, 264 (1946).

[4] H. Dostal and R. Raff, *Monatsh.*, **68**, 188 (1936); *Z. physik. Chem.*, **B, 32**, 117 (1936).

In accordance with the results discussed previously, the same specific rate is assigned to each reaction. Equation (7) may be written as

$$\frac{d[M_1]}{dt} = -k[M_1] \sum_{n=1}^{\infty} [M_n] \tag{8}$$

Dimers can be produced by reaction between two monomers and can be removed by reaction with molecules of all lengths; the net rate of production of dimers is therefore

$$\frac{d[M_2]}{dt} = \frac{1}{2} k[M_1]^2 - k[M_2] \sum_{n=1}^{\infty} [M_n] \tag{9}$$

the factor ½ being required because the formation of one dimer requires the reaction of two monomers. In general, the net rate of formation of n-mers is given by

$$\frac{d[M_n]}{dt} = \frac{1}{2} k \sum_{s=1}^{s=n-1} [M_s][M_{n-s}] - k[M_n] \sum_{n=1}^{\infty} [M_n] \tag{10}$$

The first term expresses the rate of formation of n-mers from the combination of two smaller molecules, the sum of whose number of monomers adds up to n; the second term is the rate of removal of n-mers by reaction with any other molecule. The fraction of reaction that has occurred at any time may be defined by

$$f = \frac{[M_1]_0 - \sum_{n=1}^{\infty} [M_n]}{[M_1]_0} \tag{11}$$

wher $[M_1]_0$ represents the total concentration of monomers at the beginning of the reaction, and $\sum_{n=0}^{\infty} [M_n]$ represents that of all the molecules at time t. The solution of Eq. (10) is

$$-\frac{d \sum_{n=1}^{\infty} [M_n]}{dt} = \frac{1}{2} k(\sum_{n=1}^{\infty} [M_n])^2 \tag{12}$$

and this with Eq. (11) gives

$$\frac{df}{dt} = \frac{1}{2}[M_1]_0 \, k(1 - f)^2 \tag{13}$$

This equation integrates to

$$f = \frac{[M_1]_0 kt}{2 + [M_1]_0 kt} \tag{14}$$

which expresses the extent of reaction as a function of the time. The equations also give rise to an expression for the concentration of n-mers as a function of the extent of the reaction, f:

$$[M_n] = [M_1]_0 f^{n-1}(1 - f)^2 \tag{15}$$

This expression is of importance in that it gives the distribution of polymers corresponding to any extent of reaction; it has also been derived by purely statistical methods.[1]

Free-radical mechanisms

Certain olefinic substances, such as styrene and some of its derivatives, will polymerize slowly at ordinary temperatures when pure; the polymerization of all such substances, however, is facilitated by certain agents which are known to produce free radicals. The photolysis of vinyl acetate, for example, causes it to polymerize at ordinary temperatures,[2] and this is assumed to be due to activation of the double bond with the formation of a diradical. The direct introduction of free radicals into olefins is also found to induce polymerization; hydrogen atoms and methyl radicals, for example, bring about the polymerization of vinyl acetate.[3] Moreover, a number of substances which are known to favor free-radical mechanisms are found to catalyze addition polymerizations of this type; examples are oxygen and peroxides. Addition polymerization may also be catalyzed by acidic substances, but, as will be seen later, the process then occurs by an ionic rather than a free-radical mechanism.

The general scheme of reactions which occur in a free-radical polymerization will be discussed first, and this will be followed by a detailed discussion of the individual processes which occur.

Reaction Mechanism. The most plausible assumption to make regarding the processes which occur after free-radical initiation is that a free radical adds on to the olefin, opening up the double bond and producing a second radical; thus in the case of a methyl radical and the olefin $RCH{=}CH_2$,

$$CH_3 + RCH{=}CH_2 \rightarrow R(CH_3)CH{-}CH_2{-}$$

This new radical can then add on to another olefin, the process continuing until terminated by radical-recombination processes. This reaction scheme

[1] P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936); **64**, 2205 (1942); *J. Chem. Phys.*, **12**, 125 (1944).

[2] H. W Melville, *J. Chem. Soc.*, 274 (1947).

[3] T. T. Jones and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A, 187**, 19 (1946); see also G. W. Schultz and G. Wittig, *Naturwissenschaften*, **27**, 156, 387, 659 (1939).

can be represented as follows:

(1)	$? \rightarrow R_1$	Initiation
(2)	$R_1 + M \rightarrow R_2$	
(3)	$R_2 + M \rightarrow R_3$	
(4)	$R_3 + M \rightarrow R_4$	Chain propagation
	.....	
(5)	$R_{n-1} + M \rightarrow R_n$	
(6)	$R_n + R_m \rightarrow M_{m+n}$	Chain termination

Here M represents a monomer molecule, R_1 an initiating free radical, and R_n a free radical consisting of an R_1 radical attached to a chain of $n - 1$ monomer molecules. In this simple scheme, complications such as branching of the polymer chain are not considered.

The rate of polymerization can readily be expressed, using the usual steady-state treatment, in terms of the rate constants for the individual reactions. The rate of the initiation will be expressed as v_i, and its form in special cases will be considered later. All the propagation processes [reactions (2) to (5)] will be assumed to occur with the same specific rate k_p, and the specific rates of the various terminating reactions will be written as k_t.

Application of the steady-state treatment to the radical R_1 gives

$$v_i - k_p[R_1][M] - k_t[R_1] \sum_{n=1}^{\infty} [R_n] = 0 \tag{16}$$

the third term accounting for the fact that the radicals R_1 can be removed by reaction with any radical, including another R_1. Similarly for R_2,

$$k_p[R_1][M] - k_p[R_2][M] - k_t[R_2] \sum_{n=1}^{\infty} [R_n] = 0 \tag{17}$$

and for R_3,

$$k_p[R_2][M] - k_p[R_3][M] - k_t[R_3] \sum_{n=1}^{\infty} [R_n] = 0 \tag{18}$$

in general, for R_n,

$$k_p[R_{n-1}][M] - k_p[R_n][M] - k_t[R_n] \sum_{n=1}^{\infty} [R_n] = 0 \tag{19}$$

There is an infinite number of such equations, corresponding to values of n from unity to infinity, but it is easily seen that the sum of all of the equations is simply

$$v_i - k_t \sum_{n=1}^{\infty} [R_n] \sum_{n=1}^{\infty} [R_n] = 0 \tag{20}$$

whence

$$\sum_{n=1}^{\infty} [R_n] = \left(\frac{v_i}{k_t}\right)^{1/2} \tag{21}$$

The rate of disappearance of monomer is thus given by

$$-\frac{d[M]}{dt} = k_p[M] \sum_{n=1}^{\infty} [R_n] \tag{22}$$

$$= k_p \left(\frac{v_i}{k_t}\right)^{1/2} [M] \tag{23}$$

Various special cases of this equation, corresponding to different mechanisms of initiation, will now be considered and discussed with reference to the experimental data.

Thermal Initiation. In a purely thermal polymerization the initiation process is a second-order reaction between monomer molecules; in this case

$$v_i = k_i[M]^2 \tag{24}$$

where k_i is the specific rate of initiation. Equation (23) therefore becomes

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_i}{k_t}\right)^{1/2} [M]^2 \tag{25}$$

so that the over-all order is the second. This law is obeyed in the polymerization of styrene in the gas phase[1] and in various solvents.[2]

The law is also obeyed in the thermal polymerization of ethylene in the gas phase, a reaction which it is difficult to study quantitatively because decomposition occurs in addition to the polymerization. Pease[3] investigated the reaction at high pressures, under which conditions the decomposition is suppressed, and found an activation energy of 35 kcal; somewhat higher values have been given later,[4] however, and it appears that oxygen, which greatly accelerates the reaction, may have been present in Pease's experiments.

[1] *Cf.* H. M. Hulburt, R. A. Harman, A. V. Tobolsky, and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943).

[2] G. V. Schultz and E. Husemann, *Z. physik. Chem.*, B, **34**, 187 (1936); **43**, 385 (1939); H. Suess, K. Pilch, and A. Rudorfer, *ibid.*, **A, 179**, 361 (1937); H. Suess and A. Springer, *ibid.*, **A, 181**, 81 (1937); G. V. Schultz, A. Dingklinger, and E. Husemann, *ibid.*, **39**, 246 (1938); G. V. Schultz, *Z. Elektrochem.*, **47**, 265 (1941).

[3] R. N. Pease, *J. Am. Chem. Soc.*, **52**, 1158 (1930); **53**, 513 (1931); R. N. Pease and P. R. Cheesebro, *Proc. Natl. Acad. Sci. U. S.*, **14**, 472 (1928).

[4] H. H. Storch, *J. Am. Chem. Soc.*, **56**, 374 (1934); **57**, 2598 (1935); S. Lenher, *ibid.*, **53**, 3752 (1931); M. V. Krause, M. S. Nemtzov, and E. A. Soskina, *Compt. rend. acad. sci. U.R.S.S.*, **2**, 301 (1934); *J. Gen. Chem.* (*U.S.S.R.*), **5**, 343 (1935).

The precise nature of the initiation process in thermal reactions of this kind is a matter of considerable interest. It has been suggested that in the case of ethylene there is dissociation into methylene radicals,

$$C_2H_4 \rightarrow 2CH_2$$

but this seems unlikely both on energetic grounds and in view of failure to detect the radical. The frequency factor for the thermal polymerization is low, and this suggests that the initial step is the formation of the diradical,

$$C_2H_4 \rightarrow —CH_2—CH_2—$$

a process which is expected, on theoretical grounds, to have a low transmission coefficient (*cf.* p. 386).

Catalytic Initiation. If initiation involves a second-order reaction between a catalyst C and the monomer, the rate of initiation is

$$v_i = k_i[C][M] \tag{26}$$

Introduction of this into Eq. (23) gives for the rate of disappearance of the monomer,

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_i}{k_t}\right)^{\frac{1}{2}} [M]^{\frac{3}{2}}[C]^{\frac{1}{2}} \tag{27}$$

This law is obeyed accurately in the polymerization of styrene[1] and vinyl acetate,[2] catalyzed by benzoyl peroxide, and in that of ethylene catalyzed by azomethane.

The latter reaction may be considered in more detail. The function of the azomethane is to produce methyl radicals in the system, and Rice and Sickman[3] found that polymerization occurred at 300°C. The rate of polymerization was found to be given by

$$-\frac{d[C_2H_4]}{dt} = k[CH_3NNCH_3]^{\frac{1}{2}}[C_2H_4]^{\frac{3}{2}} \tag{28}$$

which is of the same form as Eq. (27).

The polymerization of ethylene has been brought about by free radicals produced in other ways. Sensitization by radicals produced in the thermal decomposition of ethylene oxide,[4] vinyl ethyl ether,[5] and mercury and lead

[1] Schultz and Husemann, *loc. cit.*; *Z. physik. Chem.*, **43**, 385 (1939).

[2] A. C. Cuthbertson, G. Gee, and E. K. Rideal, *Proc. Roy. Soc. (London)*, **A, 170,** 300 (1939).

[3] O. K. Rice and D. V. Sickman, *J. Am. Chem. Soc.*, **57**, 1384 (1935); D. V. Sickman and O. K. Rice, *J. Chem Phys.*, **4**, 608 (1936).

[4] C. J. M. Fletcher and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 2135 (1936).

[5] S. N. Wang and C. A. Winkler, *Can. J. Research*, **B, 21,** 97 (1943).

alkyls[1] has been achieved, and by working at high pressures, sensitization with lead tetraethyl was brought about in benzene solution.[2] Radicals produced photochemically have also been employed to induce the polymerization of ethylene; molecules photolyzed for this purpose include ammonia,[3] methyl- and ethylamines,[4] acetone,[5] acetaldehyde,[6] and alkyl iodides.[7] Polymerization has also been brought about by mercury photosensitization.[8]

In polymerizations brought about by free radicals, it is found that the over-all activation energy is low, generally only 1 or 2 kcal. This indicates that the higher activation energy found for the thermal polymerization (about 40 kcal) is largely for the primary production of free radicals.

Another possibility with respect to a catalytic or sensitized initiation is that the initiating reaction is first order with respect to the catalyst and zero order with respect to the monomer, *i.e.*, the initiation rate is

$$v_i = k_i[C] \tag{29}$$

The rate of polymerization is then

$$-\frac{d[M]}{dt} = k_p\left(\frac{k_i}{k_t}\right)^{1/2}[M][C]^{1/2} \tag{30}$$

This law is accurately followed by the polymerization of *d-sec*-butyl α-chloroacrylate, sensitized by benzoyl peroxide.[9]

Photochemical Initiation. In photochemical initiation the rate of the initiating step is given by

$$v_i = I \tag{31}$$

where I is the intensity of light absorbed in mole-quanta per second. The rate of polymerization is then

$$-\frac{d[M]}{dt} = k_p\left(\frac{I}{k_t}\right)^{1/2}[M] \tag{32}$$

[1] H. S. Taylor and W. H. Jones, *J Am. Chem. Soc.*, **52**, 1111 (1930); F. S. Romm, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1784 (1940); O. Beeck and F. F. Rust, *J. Chem. Phys.*, **9**, 480 (1941).

[2] P. L. Cramer, *J. Am. Chem. Soc.*, **56**, 1234 (1934).

[3] H. S. Taylor and H. J. Emeléus, *ibid.*, **52**, 2150 (1930).

[4] *Ibid.*, **53**, 3370 (1931).

[6] H. S. Taylor and J. C. Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937).

[5] J. G. Roof, and F. Daniels, *J. Am. Chem. Soc.*, **62**, 2912 (1940); C. J. Danby and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A, 179**, 169 (1941).

[7] G. C. Joris and J. C. Jungers, *Bull. soc. chim. Belges*, **47**, 135 (1938); J. C. Jungers and L. M. Yeddanapalli, *Trans. Faraday Soc.*, **36**, 483 (1940); R. v. Tassel, *Natuurw. Tijdschr.* (*Belg.*), **20**, 83 (1938); J. C. Jungers and G. C. Joris, *Bull. soc. chim. Belges*, **50**, 61 (1941).

[8] D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.*, **9**, 829 (1941).

[9] C. C. Price and R. W. Kell, *J. Am. Chem. Soc.*, **63**, 2798 (1941).

Such a law is obeyed in the polymerization of ethylene induced by wave lengths of about 1860 A.[1] The spectroscopic work on absorption in this region suggests[2] that the primary process is

$$C_2H_4 + h\nu \rightarrow 2CH_2$$

and the initial propagating step would then be

$$C_2H_4 + CH_2 \rightarrow C_3H_6$$

Alternatively, the photolysis of an ethylenic compound may produce a diradical —CH_2CH_2— by uncoupling the π electrons of the double bond, and photosensitization probably produces the same effect.

Rates of the Elementary Reactions. It is of great importance for an understanding of the mechanisms of polymerizations to have knowledge of the specific rates of the various elementary processes. This presents little difficulty as far as the initiation reaction is concerned, the procedure being somewhat similar to that used by Bodenstein (p. 204) for the hydrogen-bromine reaction. The quantities that have to be measured are the rate of the over-all process and the value of the kinetic chain length, γ, which, as previously, is defined as the ratio of the over-all rate to the rate of the initial step,

$$\gamma = \frac{-d[M]/dt}{v_i} \tag{33}$$

The kinetic chain length can, for the above mechanism, be identified with the number of repeating units in the polymer chain, a quantity that can be determined in various ways. The rate v_i of the initiating reaction, and hence its specific rate, can therefore be obtained using the above equation.

This procedure has been applied to some examples, and the results are of interest. The benzoyl peroxide–catalyzed polymerization of styrene has been seen to obey the law

$$-\frac{d[M]}{dt} = k[M]^{3/2}[C]^{1/2} \tag{34}$$

the over-all frequency factor being about 10^{11} and the activation energy between 23 and 25 kcal. The over-all constant k is equal to $k_p(k_i/k_t)^{1/2}$, and the chain length is therefore equal to

$$\gamma = \frac{k_p}{(k_i k_t)^{1/2}} \frac{[M]^{1/2}}{[C]^{1/2}} \tag{35}$$

[1] H. S. Taylor and H. J. Emeléus, *J. Am. Chem. Soc.*, **53**, 562, 3370 (1931); R. D. McDonald and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A, 157**, 480 (1936).

[2] H. J. Hilgendorf, *Z. Physik*, **95**, 781 (1935); W. C. Price, *Phys. Rev.*, **45**, 843 (1934); **47**, 444 (1935).

These relations lead to

$$\frac{1}{\gamma}\frac{d[M]}{dt} = k_i[M][C] = v_i \tag{36}$$

and proceeding in this way, the frequency factor corresponding to k_i is found to be 10^{12} and the activation energy to be about 29 kcal;[1] similar results have been found by an alternative method, employing benzoquinone as inhibitor.[2] The frequency factor obtained is seen to be of the order usually associated with a bimolecular reaction.

Application of the same procedure to the data of Schulz and Husemann,[3] and of Foord,[4] on the uncatalyzed polymerization of styrene gives the result that the activation energy is 23 to 28 kcal and the frequency factor between 10^4 and 10^6. This would imply that in the catalyzed reaction the catalyst has acted not by altering the energy of activation, which has remained practically constant, but by raising the frequency factor from an abnormally low value to a normal value. On the other hand, Bamford and Dewar[5] have recently obtained an activation energy of 37 kcal, and a frequency factor of 1.23×10^{10} for the initiation process; this frequency factor is not abnormally small, and the peroxide catalyst would be concluded to act by reducing the activation energy and not by increasing the frequency factor. Further work would appear to be required in connection with this important point.

The nature of the propagating reactions is not difficult to envisage; the uncoupling of the π electrons in the double bond of the monomer is again involved, together with the formation of a new bond employing one of these electrons and the lone electron in the free radical. Similarly, the terminating reactions involve the pairing of an electron from each of the radicals,

$$R_m + R_n \rightarrow M_{m+n}$$

or alternatively the transfer of a hydrogen atom with the formation of two molecules, by a disproportionation mechanism, *e.g.*,

$$RCH_2CH_2 + RCH_2CH_2 \rightarrow RCH_2CH_3 + RCH{=}CH_2$$

Whereas the determination of the individual specific rates for the initiation reaction presents no particular difficulty, the assignment of values to the rates of propagation and termination is considerably more difficult; some progress has, however, been made in this direction by following a

[1] Hulburt, Harman, Tobolsky, and Eyring, *loc. cit.*

[2] S. G. Foord, *J. Chem. Soc.*, 48 (1940).

[3] G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B, 43,** 385 (1939).

[4] S. G. Foord, *loc. cit.*

[5] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **A, 192,** 309 (1948).

procedure devised by Melville.[1] The over-all specific rate of a polymerization has been seen to be equal to $k_p(k_i/k_t)^{\frac{1}{2}}$; the evaluation of k_i, described previously, therefore gives the value of $k_p/k_t^{\frac{1}{2}}$ but does not allow a separation of the constants. Melville pointed out that a further relationship can be obtained if a measurement could be made of the total stationary concentration of the free radicals R_n which are concerned in the chain-propagating steps; thus the over-all rate of reaction is [*cf.* Eq. (22)]

$$-\frac{d[M]}{dt} = k_p[M]\sum_{n=1}^{\infty}[R_n] \tag{37}$$

so that if $\sum_{n=1}^{\infty}[R_n]$ is known, k_p can be determined at once from the over-all rate. The method used for determining this concentration was to measure the mean lifetime τ of the active radicals. The stationary-state expression for active radicals is

$$\text{Rate of formation of radicals} = \text{rate of removal of radicals} = \sum_{n=1}^{\infty}\frac{[R_n]}{\tau} \tag{38}$$

so that if τ and the rate of formation of radicals are known, the concentration $\sum_{n=1}^{\infty}[R_n]$ can be calculated. The rate of formation of radicals can be determined in various ways; one involves the use of inhibitors (*cf.* p. 357); and the rate can also be determined from the number of quanta absorbed in photochemical polymerizations, assuming that each absorbed photon starts a chain.

The determination of the mean life τ was achieved by a photochemical method involving the interruption of the excitation. By means of a rotating slotted disk placed between the source of radiation and the reaction system, the latter experiences equal periods of illumination and darkness. If I is the intensity of light absorbed in the absence of the disk, the effective intensity when the disk is present is $I/2$, provided that the period of illumination is short compared with the active life of the radicals; if the rate of reaction is proportional to the square root of the intensity [Eq. (32)], the rate under these conditions is $(I/2)^{\frac{1}{2}}$ as compared with $I^{\frac{1}{2}}$ in the absence of the disk. If the disk is then rotated so slowly that the radicals have disappeared before the next period of illumination, the system will essentially absorb I over only half the period of the experiment;

[1] H. W. Melville, *J. Chem. Soc.*, 274 (1947); G. M. Burnett and H. W. Melville, *Nature*, **156**, 661 (1945). The rotating sector method was apparently first used in kinetic studies by F. Briers, D. L. Chapman, and E. Walters, *J. Chem. Soc.*, 502 (1926).

the rate will now be proportional to $I^{1/2}/2$. At high speeds of rotation the rate will therefore be $2^{1/2}$ times that at lower speeds, and, from the variation of the reaction rate with the frequency of rotation, the mean life of the radicals can be calculated.

This procedure has been applied to the polymerization of vinyl acetate by Burnett and Melville[1] and by Bartlett and Swain;[2] unfortunately the results are somewhat in disagreement. By making measurements at a number of temperatures, the activation energy of the propagating reactions was found to be about 4 kcal and the frequency factor to be about 10^5; this again indicates that there is a restriction to reaction. The specific rate of the termination reaction was found from k_i, k_p, and the over-all rate; an activation energy of zero was found and a frequency factor of approximately 10^9. This value is about what would be expected, on entropy grounds, for a reaction between molecules of some complexity. It was also possible to show, by changing the experimental conditions so as to alter the chain length, that the specific rate of propagation is practically independent of the mean chain length, and therefore that the rate of propagation is independent of the size of the reacting molecules and radicals.

The rotating-sector method has recently been applied by Mackay and Melville[3] to the liquid-phase polymerization of methyl methacrylate. They find the activation energy for the propagating reactions to be 4.4 kcal., and the frequency factor 5×10^5 liters $mole^{-1}$ sec^{-1}. For the chain-ending step the activation energy was zero and the frequency factor $\sim 10^8$.

Inhibition of Polymerization. As with oxidation and other processes involving free radicals, inhibition of polymerization can be brought about by various substances. Inhibition by impurities was found[4] to be responsible for the variable induction periods noted by earlier investigators on the subject; the period of inhibition extends until the inhibitor has been removed by reaction with free radicals.

Studies on inhibition by known amounts of various substances give information regarding the initiating and chain-ending steps in the polymerization process, and a number of investigations of this kind have been carried out. Melville,[5] for example, has studied in a comprehensive manner the rate of the photochemical polymerization of vinyl acetate in the presence of various amounts of benzoquinone. The length of the induc-

[1] *Ibid.*

[2] P. D. Bartlett and C. G. Swain, *J. Am. Chem. Soc.*, **67**, 2273 (1945); **68**, 2381 (1946).

[3] M. H. Mackay and H. W. Melville, *Trans. Faraday Soc.*, **45**, 323 (1949).

[4] *Cf.* P. J. Flory, *ibid.*, **59**, 241 (1937); K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 2377 (1946).

[5] Melville, *loc. cit.*

tion period was found to be inversely proportional to the amount of benzoquinone, and on the assumption that one molecule of benzoquinone reacts with one photoactivated vinyl acetate molecule, the rate of removal of the quinone (which was determined colorimetrically) is a measure of the rate of activation of the monomers, *i.e.*, the rate of the initiation process.

Influence of Oxygen on Polymerization. The influence of oxygen on polymerization reactions is a somewhat complex one, in that both inhibition and catalysis may occur, in some cases the two competing in one reaction system. In the case of the photopolymerization of vinyl acetate and of acrylic acid and its esters, the inhibitory effect predominates,[1] but with the thermal polymerization of methyl methacrylate, vinyl acetate, and other substances, the catalytic effect was found to be more important.[2]

It has been shown that peroxides are always found when polymerization occurs in the presence of oxygen,[3] and it appears that these are formed by the interaction between oxygen and free radicals, as discussed in the previous chapter. The influence of the oxygen depends upon the stability of the peroxides formed: If they are stable, the net effect of their formation is to remove free radicals, and an inhibitory effect is therefore found. If they decompose into free radicals, on the other hand, they propagate the chains, and the net effect will therefore be catalysis. Whether oxygen inhibits or catalyzes therefore depends upon a delicate balance between various factors, the stability of the intermediate peroxides exerting an important effect.

When oxygen reacts with an olefinic molecule, two types of processes may occur. In the case of olefins which contain an α methylene group, it is found that the principal reaction is a removal of hydrogen from the methylene group with the formation of HO_2 and a free radical,[4]

$$\text{(1)}\quad \mathrm{R{-}CH{=}CH{-}CH_2{-}R' + O_2 \rightarrow R{-}CH{=}CH{-}\underset{|}{CH}{-}R' + HO_2}$$

This behavior is consistent with the low strength of the C-H bond in this position. In the absence of such a C-H bond, on the other hand, the most important reaction is a simple addition of the oxygen molecule to the double bond,

$$\text{(2)}\quad \mathrm{R{-}CH{=}CH{-}R' + O_2 \rightarrow R{-}\underset{|}{\overset{|}{CH}}{-}\underset{|}{\overset{|}{CH}}{-}R'} \quad \begin{matrix} & & \mathrm{O} & \\ & & & \diagdown \\ & & & \mathrm{O{-}} \end{matrix}$$

[1] H. Staudinger and A. Schwalbach, *Ann.*, **488**, 33 (1931); H. Staudinger and H. W. Kohlschuetter, *Helv. Chim. Acta*, **64**, 2091 (1931).

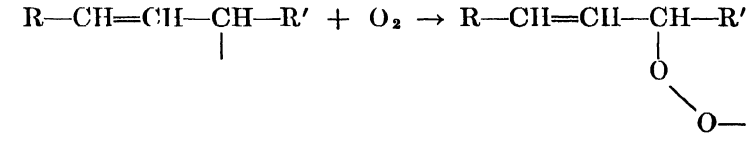
[2] H. Staudinger and E. Urich, *Helv. Chim. Acta*, **62**, 1127 (1929).

[3] *Cf.* C. E. Barnes, *J. Am. Chem. Soc.*, **67**, 217 (1945).

[4] E. H. Farmer, *Trans. Faraday Soc.*, **38**, 340 (1942).

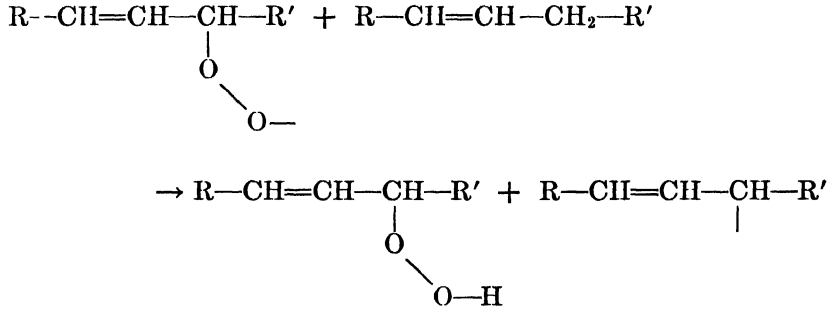
This type of process also occurs to a minor degree when the α methylene group is present.

The first type of reaction is succeeded by the addition to the radical of an oxygen molecule, with the formation of a peroxide molecule,



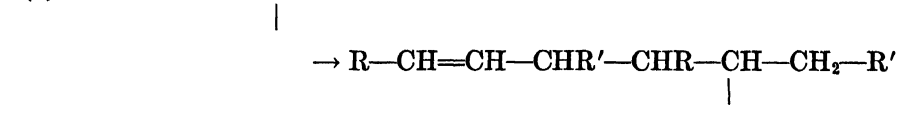
(3)

and the peroxide radical produced in either reaction (2) or reaction (3) may then abstract a hydrogen atom from another molecule with the formation of a hydroperoxide molecule and a second free radical, *e.g.*,



(4)

this reaction being chain propagating. Such hydroperoxides have been isolated[1] as intermediate products in the autoxidation of olefins, and their rates of decomposition have been studied. In some cases it has been possible to detect the hydroperoxides of polymerized olefins, some containing the repeated unit —CH(CH_2R′)—CHR—O—O—, in which the molecules are therefore held together by peroxide linkages. Alternatively, polymerization may occur by direct addition to olefin molecules of radicals formed by reactions such as



(5)

There are thus two alternative mechanisms for polymerization in the presence of oxygen, one leading to polymers connected by O—O linkages, and the other to those connected by C—C linkages; both may occur simultaneously, the nature of the product depending upon the conditions.

[1] E. H. Farmer, H. P. Koch, and D. A. Sutton, *J. Chem. Soc.*, 541 (1943); E. H. Farmer, *ibid.*, 121 (1942); E. H. Farmer and D. A. Sutton, *ibid.*, 139.

Since oxygen can attack any methylenic group in a polymer molecule with the ultimate formation of a free radical, its role in giving rise to branched polymer chains is readily understood.

Catalysis of Free-radical Polymerization in Solution. A type of kinetic behavior similar to that observed in the gas phase is found when polymerization is carried out in solution. In organic solvents the most usual catalysts are organic peroxides, while such peroxidic substances as hydrogen peroxide and persulfates are used in aqueous solution. The mechanism of the initiation reactions in these cases has not yet been studied in any detail, but mechanisms depending upon the formation of peroxides of the monomer have been put forward to account for the catalytic action.

It has recently been found[1] that catalysis in aqueous solution by peroxidic substances is enhanced by the addition of small amounts of reducing substances such as ferrous ions. This effect has been given the name "reduction activation," and its mechanism has been elucidated. The catalysis of polymerization by the ferrous-ion–hydrogen peroxide system has been carefully studied by Evans and his collaborators,[2] who have worked with acrylonitrile, methyl methacrylate, methacrylic acid, styrene, and methyl acrylate; in all cases polymerization occurred much more rapidly than in the presence of hydrogen peroxide alone. As has been seen in Chap. 11, hydrogen peroxide decomposes in the presence of ferrous ions by the Weiss-Haber mechanism, the initial step of which is

$$\text{(1)} \qquad Fe^{++} + H_2O_2 \rightarrow HO^- + OH + Fe^{+++}$$

On the addition of the monomer the oxygen production ceases and polymerization occurs; this is attributed to reaction between the hydroxyl radicals and the monomer,

$$\text{(2)} \qquad OH + RCH{=}CH_2 \rightarrow RCH(OH){-}CH_2OH$$

The radical produced in this way then adds on to another monomer molecule, and the chain continues until it is terminated by reactions such as

$$\text{(3)} \qquad HO(M)_n{-} + {-}(M)_mOH \rightarrow HO(M)_{m+n}OH$$

$$\text{(4)} \qquad HO(M)_n{-} + OH \rightarrow HO(M)_nOH$$

In fact, the kinetic laws obeyed indicate that the first process is more important. By observing the rate of formation of ferrous ions by the initiation reaction (1), the value of its frequency factor was found to be

[1] R. G. K. Bacon, *Trans. Faraday Soc.*, **42**, 141 (1946); J. H. Baxendale, M. G. Evans, and G. S. Park, *ibid.*, 155; L. B. Morgan, *ibid.*, 169.

[2] Baxendale, Evans, and Park, *loc. cit.*; J. H. Baxendale, J. Bywaters, and M. G. Evans, *Trans. Faraday Soc.*, **42**, 675 (1946); M. G. Evans, *J. Chem. Soc.*, 266 (1947).

given by 1.78×10^9, and the activation energy proved to be 10 kcal. This value is to be compared with 30 kcal for the formation of benzoyl radicals from benzoyl peroxide; this accounts for the high efficiency of this type of reduction activation. The low frequency factor has been attributed to the increase in ionic character in the activated state, the situation being compared to that found in the formation of quaternary ammonium salts.

Catalysis of polymerizations by persulfate ions activated by various reducing agents, such as heavy metals, metal ions, thiosulfate ions, and iodide ions, has also been investigated.[1] The initiating reaction can be represented as

$$R + S_2O_8^{--} \rightarrow -SO_4^{-} + SO_4^{--} + R^+$$

where R represents the reducing agent and $-SO_4^-$ is the sulfate radical-ion. This radical-ion may react further with water to give hydroxyl radicals

$$-SO_4^- + H_2O \rightarrow HSO_4^- + OH$$

Initial activation of the monomer may be brought about by either the radical-ion or the hydroxyl radical; evidence that such reactions occur is provided by the formation of polymers containing hydroxyl and sulfate residues.

The degree of catalysis brought about by these persulfate systems is very marked. The over-all activation energy for the benzoyl peroxide–catalyzed polymerization of styrene is about 23 to 28 kcal, and the process proceeds only slowly at room temperatures. The value with the persulfate-thiosulfate catalyst is 15.5 kcal, while for the persulfate-silver system it is 12.5 kcal; the reactions occur rapidly at ordinary temperatures.

Chain Transfer, Branching, and Cross-linking. So far the mechanism of polymerization has been discussed in a simplified manner, the arguments being applicable mainly to the formation of straight-chain polymers. Various reaction mechanisms which lead to branched polymer chains may now be discussed briefly.

It was pointed out by Flory[2] that a polymer free radical may, instead of forming an addition compound with an olefin, undergo reaction with a monomer or the solvent, abstracting a hydrogen atom, and hence transferring free-radical activity to the reacting molecule; this type of process may be represented as

$$R_n- + CH_2{=}CHR' \rightarrow R_n{-}H + -CH{=}CHR'$$

and

$$R_n- + H{-}S \rightarrow R_n{-}H + -S$$

[1] Bacon, *loc. cit.;* Morgan, *loc. cit.*

[2] P. J. Flory, *J. Am. Chem. Soc.*, **59**, 241 (1937).

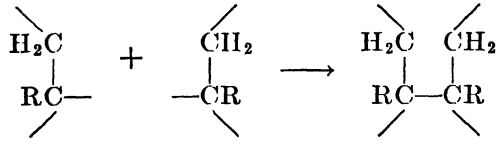
in which R_n— represents a free-radical polymer and H—*S* the solvent. In the former case the monomer radical would continue the chain with the production of a polymer of the normal type, but in the second case the solvent radical, if active, will give rise to polymers which contain residues of the solvent molecules. Examples of the second case have been observed; thus the polymer formed from styrene in carbon tetrachloride solution is found to contain chlorine atoms, which presumably arise from this type of chain transfer.

The converse of this process would be the transfer of activity from a monomer molecule to a polymer molecule, a mechanism that has been suggested by Taylor and Tobolsky;[1] it may be represented as

$$R_1— + R_nH \rightarrow R_1H + R_n—$$

Since this can occur at various positions along the polymer chain and not at the ends only, it can clearly give rise to branching of the polymer chain. In agreement with this, it is almost invariably found that a certain number of branched chains are formed in any process of polymerization.

Another type of linkage that may arise in addition polymerization is due to the combination of two radicals; if these have been formed by a transfer of activity from a monomer to a chain, the following type of reaction may occur:



the product being said to exhibit cross-linking. However this process will be very rare, since radical recombinations are infrequent, particularly on account of the steric hindrance when such complex species are involved.

Ionic mechanisms

A number of polymerizations are found to occur by ionic, rather than free-radical, mechanisms. The evidence for this is that they are catalyzed not by free radicals but by electron-accepting substances like aluminum chloride and boron trifluoride, which are acids in the G. N. Lewis sense (see p. 287). These reactions differ markedly from the free-radical processes, in that oxygen has no influence on them and their rates vary with the dielectric constant of the solvent in the manner expected of ionic processes.[2]

Most of the work on polymerization of this type has been done with

[1] H. S. Taylor and A. V. Tobolsky, *ibid.*, **67**, 2063 (1945).
[2] D. C. Pepper, *Nature*, **158**, 789 (1946).

styrene[1] and isobutene.[2] The latter substance is remarkable in that its polymerization cannot be effected by free radicals, but with aluminum chloride, titanium chloride, and boron trifluoride, the reaction occurs rapidly at temperatures as low as −120°C, the products being of very high molecular weight. The rate of polymerization is only slightly affected by the temperature, which, however, affects the mean molecular weight of the product formed. The effectiveness of the catalyst was found to decrease in the order BF_3, $AlBr_3$, $TiCl_4$, $TiBr_4$, BBr_3, and $SnCl_4$; hydrogen fluoride and chloride were found to be inhibitors.

The behavior of styrene was somewhat similar; catalysis by BF_3, BCl_3, $SnCl_4$, and $SbCl_5$ has been observed, and poisoning by hydrogen chloride and styrene dimer has been found. The rate of disappearance of the monomer in styrene solution was found to be proportional to the third power of the monomer concentration and the first power of the catalyst concentration. The activation energy of the stannic chloride–catalyzed polymerization is less than 3 kcal.[3]

In order to explain this kinetic behavior, the following reaction scheme was proposed by Price,[4] ACl representing the acidic catalyst:

$$(1) \qquad ACl + CH_2{=}CHR \rightleftharpoons ClA^-{-}CH_2{-}C^+HR$$

$$(2) \qquad ClA^-{-}CH_2{-}C^+HR + CH_2{=}CHR \rightarrow ClA^-{-}CH_2{-}CHR{-}CH_2C^+HR$$

. . . . . .

$$(3) \qquad ClA^-{-}(CH_2{-}CHR)_n{-}CH_2C^+HR + CH_2{=}CHR \rightarrow ClA^-{-}(CH_2{-}CHR)_{n+1}{-}CH_2C^+HR$$

$$(4) \qquad ClA^-{-}(CH_2{-}CHR)_{n+1}{-}CH_2C^+HR \rightarrow A{-}(CH_2{-}CHR)_{n+1}{-}CH{=}CHR + HCl$$

Reactions (1) and (2) constitute chain initiation; they are split up in this way to avoid the postulation of a third-order initial step. The equilibrium (1) being assumed to be rapid, the two processes are equivalent to a third-order initiation since the rate of initiation is given by

$$v_i = k_2[ClA^-{-}CH_2{-}C^+HR][CH_2{=}CHR] \qquad (39)$$

$$= K_1k_2[ACl][CH_2{=}CHR]^2 \qquad (40)$$

where K_1 is the equilibrium constant for reaction (1) and k_2 the rate constant for reaction (2). The steady-state expression for $[ClA^-{-}CH_2{-}CHR{-}CH_2{-}C^+HR]$ is

[1] G. Williams, *J. Chem. Soc.*, 775 (1940); J. K. Moore, R. E. Burk, and H. P. Lankelima, *J. Am. Chem. Soc.*, **63**, 2954 (1941); C. Walling, *ibid.*, **66**, 1602 (1944).

[2] A. G. Evans and M. Polanyi, *J. Chem. Soc.*, 252 (1947); H. Plesch, M. Polanyi, and H. A. Skinner, *ibid.*, 257.

[3] Williams, *loc. cit.*

[4] C. C. Price, *Ann. N. Y. Acad. Sci.*, **44**, 351 (1943).

$$k_i[ACl][CH_2{=}CHR]^2 - k_p[ClA^-{-}CH_2{-}C^+HR][CH_2{=}CHR] = 0 \quad (41)$$

where k_i has been written for K_1k_2 and k_p is the rate constant for the chain-propagating reactions. For the intermediate ions of the type ClA^-—$(CH_2$—$CHR)_{n+1}$—CH_2—C^+HR there is a series of equations of the general form

$$k_p[ClA^-{-}(CH_2{-}CHR)_n{-}CH_2C^+HR][CH_2{=}CHR] - k_p[ClA^-{-}(CH_2{-}CHR)_{n+1}{-}CH_2{-}C^+HR][CH_2{=}CHR] - k_t[ClA^-{-}(CH_2{-}CHR)_{n+1}{-}CH_2C^+HR] = 0 \quad (42)$$

The sum of all such equations is seen to be equal to

$$k_i[ACl][CH_2{=}CHR]^2 - k_t \sum_{n=1}^{\infty} [ClA^-{-}(CH_2{-}CHR)_n{-}CH_2C^+HR] = 0 \quad (43)$$

whence

$$\sum_{n=0}^{\infty} [ClA^-{-}(CH_2{-}CHR)_n{-}CH_2C^+HR] = \frac{k_i}{k_t}[ACl][CH_2{=}CHR]^2 \quad (44)$$

The rate of disappearance of monomer is thus

$$-\frac{d[CH_2{=}CHR]}{dt} = k_p \sum_{n=1}^{\infty} [ClA^-{-}(CH_2{-}CHR)_n{-}CH_2C^+HR][CH_2{=}CHR] = \frac{k_ik_p}{k_t}[ACl][CH_2{=}CHR]^3 \quad (45)$$

in agreement with the experimental dependence of the rate. This scheme of reactions is seen to differ from that discussed on page 352 for free-radical polymerization in the initiating step, which is here third order, and in the terminating step, which is first instead of second order.

Such a mechanism, however, does not appear to be applicable to all types of polymerization. In the case of the isobutene reaction, catalyzed by titanic chloride, it was found that traces of water were required and that hydrogen fluoride and hydrogen chloride were inhibitors. The following mechanism has been proposed to explain this behavior:

(1) $TiCl_4 + H_2O \rightarrow TiCl_4 \cdot H_2O$

(2) $TiCl_4 \cdot H_2O + M_n \rightarrow M_nH^+ + TiCl_4 \cdot OH^-$

(3) $M_nH^+ + M \rightarrow M_{n+1}H^+$

(4) $M_nH^+ + TiCl_4 \cdot OH^- \rightarrow M_n + TiCl_4 \cdot H_2O$

According to this scheme the effectiveness of catalysts would depend on the acid strengths of their hydrates, and this would appear to be the case. Inhibition by hydrogen fluoride and chloride is attributed to their suppression of the various proton-transfer reactions.

CHAPTER 13

POTENTIAL-ENERGY SURFACES

In the present chapter will be discussed some of the conclusions that have been reached, on the basis of theoretical and experimental work, concerning the nature of the activated complex and the detailed mechanisms of chemical and certain physical processes.

The activated complex

Although, according to the theory of absolute reaction rates, the mechanism by which the activated complex is formed is unimportant, the actual nature of the activated complex is of the greatest importance. Empirically, a good deal can be learned about its nature from the kinetics; thus the activation energy, determined from the temperature variation of the rate, gives the energy level of the complex with respect to the reacting molecules. Furthermore the entropy of activation, calculated from the frequency factor of the reaction, is the entropy of the complex relative to the free reactant molecules. The problem of calculating the properties of an activated complex without reference to experimentally determined rates of reaction is clearly one of molecular structure and is treated by the methods of quantum mechanics. A detailed treatment of this matter has been given elsewhere;[1] the present section will be devoted to a simplified and descriptive discussion.

A great many reactions can be considered schematically to be of the type

$$X + YZ = XY + Z$$

the process involving the breaking of a chemical bond between Y and Z and the formation of a bond between X and Y. The species X, Y, and Z need not necessarily be atoms; thus in the hydrolysis of a bromide, X might be OH^-, while YZ represents the C-Br bond, the reaction being, *e.g.*,

$$OH^- + CH_3CH_2—Br = CH_3CH_2OH + Br^-$$

[1] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," Chaps. II and III, McGraw-Hill Book Company, Inc., New York, 1941.

However, for simplicity in the present discussion, X, Y, and Z will be referred to as atoms. Since YZ is a stable molecule, the approach of X will give rise to an increase in the potential energy of the system; in other words, a close approach of X to YZ will occur only if the relative translational energy is sufficiently high. If this condition is realized, X will approach YZ sufficiently to bring about electronic interaction, the result being the weakening of the bond between Y and Z and the incipient formation of a bond between X and Y. The atom Z will therefore move away from Y, and if the amount of energy available is adequate, the point may be reached at which Z begins to be repelled. The variation in potential energy as this process occurs may be represented by the curve shown in Fig. 34, the progress of the reaction being represented by motion from left to right. Reaction can proceed only if X and YZ initially have the energy E required to surmount the barrier; this energy is clearly the energy of activation for the reaction, and the molecular configuration at the top of the barrier corresponds to the activated complex. For the reverse reaction, the formation of $X + YZ$ from $XY + Z$, the activated complex is the same, and the energy of activation is greater by the energy ΔE of the reaction.

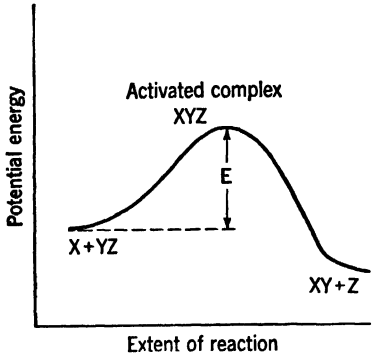


FIG 34. Potential energy of the system $X + YZ \rightarrow XY + Z$ as a function of the extent of reaction.

The first treatment of chemical reactions from this standpoint of molecular structure was carried out by London,[1] who suggested that the properties of an activated complex can be calculated by the same quantum-mechanical methods that are used for calculating those of stable molecules. In the very simplest case, in which the electrons associated with the atoms X, Y, and Z are in s-states, the rearrangement of the atoms during reaction may be regarded as a rearrangement of the three s-electrons. In order to explain how quantum mechanics treats this problem, some discussion will be devoted to the simpler problem of how a simple molecule such as YZ, involving only two electrons, is treated.

The permissible energy levels in which such a molecule can exist are obtained by solving the appropriate Schrödinger wave equation; this is a differential equation involving a function of the various coordinates of the

[1] F. London, "Probleme der Modernen Physik (Sommerfeld Festschrift)," p. 104, S. Hirzel, Leipzig, 1928; *Z. Elektrochem.*, **35**, 552 (1929); *cf.* R. M. Langer, *Phys. Rev.*, **34**, 92 (1929); D. S. Villars, *J. Am. Chem. Soc.*, **52**, 1733 (1930); J. Franck and E. Rabinowitsch, *Z. Elektrochem.*, **36**, 794 (1930).

electrons in the molecule, and its form depends upon the general expressions for the potential energies of the electrons with respect to their coordinates. The wave equation has a solution only for certain discrete values of the total energy of the system, and the function ψ corresponding to these values is known as an eigenfunction. The significance of the eigenfunction is that it is related to the electron density as a function of the coordinates.

The most important result that comes out of the treatment is that the allowed energy levels are the sum or difference of two integrals, which have the dimensions of an energy, *i.e.*, the energy may be expressed approximately as

$$E = A \pm \alpha \tag{1}$$

where A and α are energies. The integral A is known as a "coulombic" energy and is roughly equivalent to the energy which, on the classical theory, arises from the coulombic interaction between the charged particles. The energy α, known as the "exchange" energy, has no counterpart in classical theory but arises in quantum mechanics as a result of the fact that the electrons cannot be regarded as localized with respect to any particular nucleus. The energies A and α are usually both negative in numerical value, and the energy E of the molecule is the energy relative to the separated atoms; the lowest energy, corresponding to the most stable state, is therefore given when the positive sign is taken.

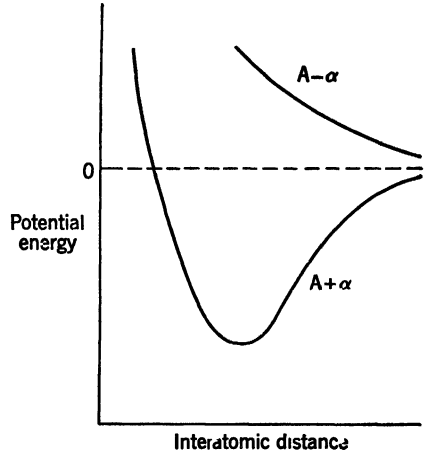


FIG. 35. The energies $A + \alpha$ and $A - \alpha$ as functions of the interatomic distance.

The integrals A and α are both functions of the internuclear distance in the molecule and approach zero as the nuclei are separated from one another. They also approach zero if the nuclei are moved close to one another, and finally attain positive values, corresponding to very strong repulsion. Values of $A + \alpha$ and $A - \alpha$ are plotted in Fig. 35 as functions of the interatomic separation. The function $A + \alpha$ is seen to have a minimum value at a particular separation, which therefore corresponds to the most stable configuration of the molecule; as the molecule vibrates, it does so about this value. The function $A - \alpha$ always corresponds to the repulsion between atoms, and the molecule is therefore not stable. In spectroscopic notation,

the state corresponding to $A + \alpha$ is designated $^1\Sigma_g^+$, while the repulsive curve is $^3\Sigma_u^+$, the three in the latter indicating that the state is a triplet, *i.e.*, corresponds to three different but equivalent wave functions.

Systems of Three Atoms. A similar, but somewhat more complicated, result arises when three atoms are considered. Suppose that the three atoms X, Y, and Z which are involved in the reaction $X + YZ = XY + Z$ are arranged in space in the general way indicated in Fig. 36; here r_1, r_2, and r_3 are the distances X-Y, Y-Z, and X-Z, respectively. If r_1 and r_3 are made infinite, *i.e.*, if X is removed to infinity, the potential energy reduces to that of the molecule YZ, which is $A + \alpha$, the positive sign being taken because only the more stable configuration will now be considered. Similarly, if Z is removed to infinity, the total potential energy is that of the molecule XY, which may be represented as $B + \beta$, where B is the coulombic contribution for this molecule and β is the exchange energy. Finally, for removal of Z the energy is $C + \gamma$. The detailed quantum-mechanical calculation for the triatomic molecule XYZ expresses the energy in terms of three coulombic and three exchange terms, the result being[1]

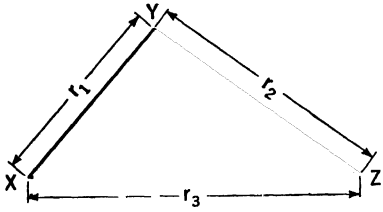


FIG. 36. Nonlinear activated complex $X-Y-Z$.

$$E = A + B + C \pm \{\tfrac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]\}^{\frac{1}{2}} \quad (2)$$

If the square root in this expression is always taken to be of positive sign, it is clear that the most stable state, *i.e.*, the one having the lowest energy, is the one corresponding to the negative sign,

$$E = A + B + C - \{\tfrac{1}{2}[(\alpha - \beta)^2 + (\beta - \gamma)^2 + (\gamma - \alpha)^2]\}^{\frac{1}{2}} \quad (3)$$

If, therefore, the energies A, B, C, α, β, and γ can be calculated for the three molecules YZ, XZ, and XY, as a function of the internuclear separations, it is a relatively simple matter to calculate E for any given configuration.

A considerable simplification of the treatment arises from the fact that, at least in this case of three *s*-electrons, the most stable configuration of the three atoms is the linear one, which, therefore, to a good approximation, is the only one that need be considered in kinetic problems. Expression (3) for the energy may be written as

$$E = A + B + C - (\alpha^2 + \beta^2 + \gamma^2 - \alpha\beta - \beta\gamma - \gamma\alpha)^{\frac{1}{2}} \quad (4)$$

and for given values of α and γ it is seen that this quantity will be smaller, *i.e.*, the molecule will be more stable, the smaller the value of β. This is

[1] London, *loc. cit.*

true when the distance between the atoms X and Z is as great as is possible for a given XY and YZ separation, a situation which corresponds to the linear configuration $X—Y—Z$, which is thus the most stable configuration.

Semiempirical Method. The first application of the London equation to an actual chemical reaction was carried out by Eyring and Polanyi,[1] who evaluated the relevant coulombic and exchange terms using a semiempirical procedure. The reaction they studied was

$$H + H_2 = H_2 + H$$

which is the simplest of all reactions involving three atoms (*cf.* p. 46). For the evaluation of E for such a reaction, it is first necessary to know how the energies of the diatomic molecules XY, YZ, and ZX are separated into their coulombic and exchange parts. The method adopted, after some trials of other possibilities, consisted in assuming that the coulombic energy is a constant fraction of the total energy for all internuclear distances. This is, of course, an approximation, as it is known that a variation with internuclear separation takes place, although not a very great one. The method, which is known as the semiempirical method, introduces a very considerable simplification into the calculations and has proved to be of the greatest value in making rough theoretical estimates of the energy of activation.

The most usual method of obtaining the total energy E as a function of the internuclear distances involves using spectroscopic measurements together with the expression due to Morse[2] relating the energy E to the distance in terms of the heat of dissociation, the equilibrium separation r_0, and other parameters: the equation is

$$E = D'[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] \tag{5}$$

Here D', the heat of dissociation, includes the zero-point energy, and a is given by $0.1227\omega_0(\mu/D)^{1/2}$, where D is a constant, ω_0 is the equilibrium vibration frequency, and μ is the reduced mass of the molecule. The quantities a and r_0, are obtained from spectroscopic measurements. Essentially what the Morse equation does is to reconstruct the entire energy curve from the dissociation energy and the character of the curve in the neighborhood of its minimum. If the requisite spectroscopic data for the diatomic molecules XY, YZ, and ZX are available, or can be derived from other data, the values of $A + \alpha$, $B + \beta$, and $C + \gamma$ can be obtained for any values of the separations r_1, r_2, and r_3. If the assumption is now made that the coulombic parts A, B, and C are certain constant fractions

[1] H. Eyring and M. Polanyi, *Z. physik. Chem.*, **B, 12,** 279 (1931); *cf.* also H. Eyring, *J. Am. Chem. Soc.*, **53,** 2537 (1931); **54,** 3191 (1932); *Chem. Revs.*, **10,** 103 (1932).

[2] P. M. Morse, *Phys. Rev.*, **34,** 57 (1929).

of $A + \alpha$, $B + \beta$, and $C + \gamma$, respectively, the values of A, B, C, α, β, and γ can be determined corresponding to any separation between the nuclei.

Potential-energy Surfaces. The most convenient way to express the value of E as a function of the relative positions of the atoms is by means of a three-dimensional diagram in which one axis is the energy and the other two are interatomic separations. Since, as has been seen, the linear configuration of atoms is the most stable, this alone will be considered. Any linear configuration can be completely represented in terms

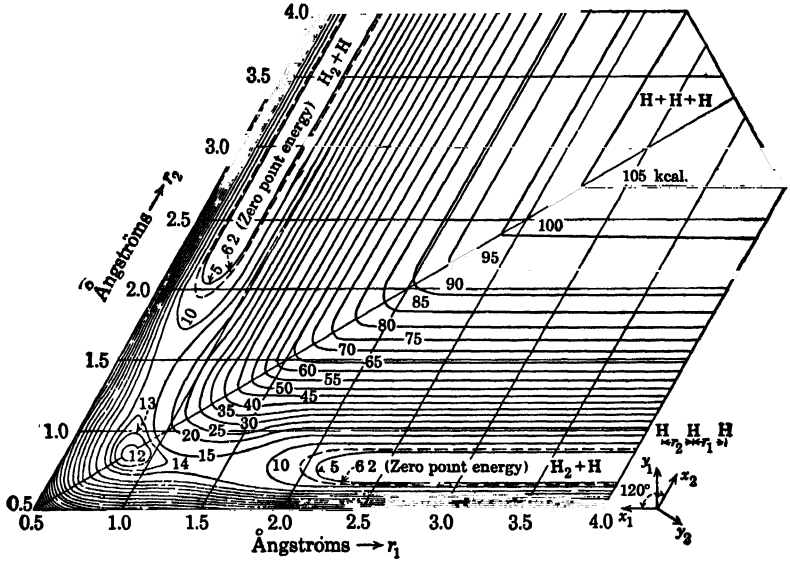


FIG. 37. Potential-energy surfaces for the system of three hydrogen atoms.

of two distances, such as r_1, the distance between X and Y, and r_2, the distance between Y and Z:

$$\overset{\leftarrow r_1 \rightarrow \leftarrow r_2 \rightarrow}{X \text{———} Y \text{———} Z}$$

Calculations of Eyring and Polanyi for the triatomic complex H—H—H gave rise to the diagram shown in Fig. 37. In this figure the two axes shown correspond to the two distances r_1 and r_2, while the third axis, perpendicular to the plane of the paper, represents the potential energy of the system. The values of the potential energy as a function of r_1 and r_2 are shown in the form of contour lines. Another way of expressing the relationship is by means of a three-dimensional model. In making the calculations for the case of three hydrogen atoms, the fraction of coulombic energy was taken to be 14 per cent.

The potential-energy surface for the system of three hydrogen atoms is seen to consist of two valleys, which run approximately parallel to the two axes and which are separated by a pass. The most stable configurations are those corresponding to the lowest points in the valley: consequently the system will tend to assume such configurations. Thus the approach of the atom X toward YZ from a considerable distance is represented by a movement along the valley which runs parallel to the r_1 axis, and for energetic reasons the system will tend to remain at the lowest point in the valley. It will be seen that X approaches fairly closely to YZ before any appreciable increase in the Y-Z separation takes place. By the time the system has reached the top of the pass, a definite increase in the Y-Z distance has taken place, and as the system travels along the second valley, parallel to the r_2 axis, a rapid increase in the distance takes place, together with a small decrease in the X-Y distance.

For the case of three hydrogen atoms, the energy corresponding to the lowest point at the top of the pass is about 14 kcal. This would be the classical energy of activation. According to the quantum theory, there is a zero-point energy corresponding to the activated state, so that the lowest permissible energy would be somewhat higher than 14 kcal. In the same way there is a zero-point energy for the hydrogen molecule, and the effect of this will be to reduce the energy of activation again; consequently the activation energy at the abolute zero, according to the modern treatment, would not be far from that of the classical theory. The activation energy at other temperatures will, as has been seen on page 60, depend upon the nature of the temperature dependence of the frequency factor.

When the reaction is not a symmetrical one, but rather involves three atoms that are not all the same, the results are similar, but the potential-energy surfaces are now no longer symmetrical with respect to the two axes.

It is of interest at this point to compare the reaction by this mechanism with the reaction which occurs by an initial decomposition of the hydrogen molecule into three atoms followed by a recombination of the atoms. The activation energy corresponding to this process would be the heat of dissociation of the hydrogen atom, *i.e.*, 103.2 kcal. On the potential-energy surface this would correspond to the movement of the system to the top of the plateau represented in Fig. 37, followed by a descent into the other valley. It is clear that by moving along the valleys the system can achieve reaction at the expense of very much less energy than would be required for the mechanism involving complete dissociation. The physical explanation of this is that the energy released by the making of the second bond continuously contributes toward the energy requirement for the breaking of the first bond. A number of reactions are known in

which this is the case. On the other hand, reaction sometimes proceeds almost entirely by a mechanism involving an initial dissociation into atoms or free radicals; however, this occurs only when there is the possibility of chain reactions which may compensate for the disadvantage arising from the initial mode of decomposition.

Potential-energy Profiles. Instead of constructing contour diagrams of potential-energy surfaces, it is frequently convenient to represent the course of a chemical reaction by means of sections through a potential-energy surface.[1] If Fig. 38 represents the surface for a reaction $X + YZ =$

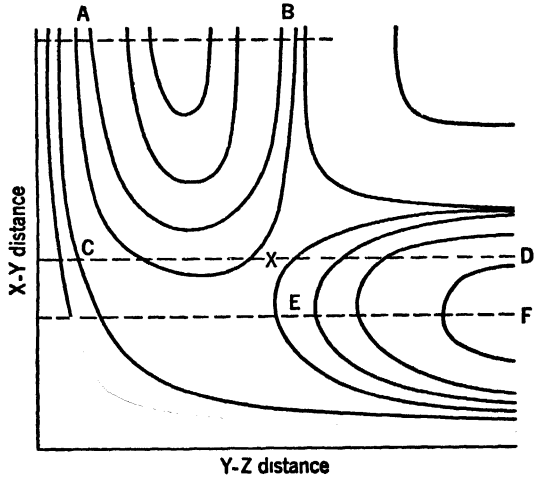


FIG. 38. Potential-energy surfaces for the reaction $X + YZ \rightarrow XY + Z$.

$XY + Z$, the section through AB shows the variation of potential energy of the reacting molecule YZ, when X is far away, as a function of the distance YZ. The lowest point of this curve is shown as AB in Fig. 39, in which the ordinate is the energy and the abscissa the distance Y-Z. As X approaches YZ, the variation in energy with distance Y-Z is represented by a series of sections parallel to AB; at the separation between X and YZ corresponding to the activated state, the section is denoted by CD in Figs. 38 and 39. If there were no reaction, this curve would continue up as indicated by the dotted curve H. The difference in energy between the lowest point of AB and the highest of CD is the energy of activation of the process. The energy difference between the lowest points of AB and CD is due to repulsion energy between X and YZ in passing from the initial to the activated state.

The section through EF, passing through the bottom of the east-west

[1] R. A. Ogg and M. Polanyi, *Trans. Faraday Soc*, **31**, 604, 1375 (1935); M. G. Evans and M. Polanyi, *ibid.*, **34**, 11 (1938).

valley in Fig. 38, is shown in Fig. 39; as Z is brought up to XY, *i.e.*, when the reaction goes in reverse, if the X-Y distance remains constant, the potential energy rises on account of repulsion between XY and Z. The curve DG (partly dotted) therefore corresponds to a somewhat higher separation of X and Y; the difference between the lowest portions of D and F is thus the energy required to stretch the X- -Y bond from its equilibrium distance to that in the activated state.

It is clear that apart from the resonance energy the activation energy is determined by the point of crossing of the curves CH and DG. Consideration of the resonance energy results in a rounding off of the curves at their crossing point and therefore reduces the activation energy. Curves obtained by taking sections through surfaces have been called "potential-energy profiles."

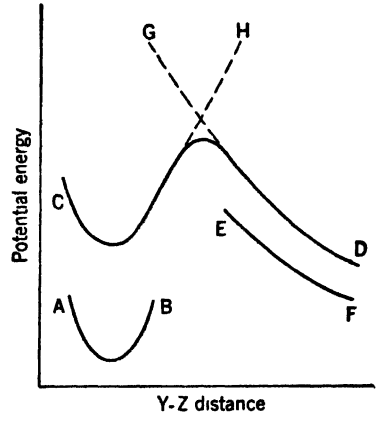


FIG. 39. Potential-energy profiles for the reaction $X + YZ \rightarrow XY + Z$.

It can be seen from an examination of Fig. 39 that the activation energy is determined by four factors:[1]

1. The strength of the bond Y Z which is broken
2. The repulsion energy between X and YZ
3. The repulsion energy between XY and Z
4. The strength of the bond $X—Y$ which is formed

These factors may now be discussed in relation to the activation energy:

1. The stronger the bond $Y—Z$, the greater is the energy of dissociation of the molecule YZ and hence the higher is the energy level to which curve CH becomes asymptotic. The curve CH will thus be steeper, and hence the activation energy is higher, since the point of intersection of curves CH and DG will be higher.

2. The greater the repulsion energy between X and YZ, the higher is curve CH with respect to AB; therefore the greater is the activation energy.

3. The greater the repulsion energy between XY and Z, the more steeply will curve DG rise as the distance Y-Z is diminished; thus the activation energy will be higher.

4. The greater the strength of the bond X- Y, the lower is the potential energy of XY; hence the curve F is lower, and therefore the curve D is lower. The point of crossing with CH will therefore be the *lower*, and so will the energy of activation.

[1] M. G. Evans and M. Polanyi, *loc. cit.*; *cf.* C. N. Hinshelwood, K. J. Laidler, and E. W. Timm, *J. Chem. Soc.*, 848 (1938).

It has thus been seen that increases in the factors 1, 2, and 3 will increase the activation energy, whereas an increase in 4 will decrease it. As a result of this, the first three factors have been described as the "inertia" of the reaction and the last as its "driving force." A number of chemical reactions have been discussed from the standpoint of potential-energy profiles, and particularly using the ideas of inertia and driving force.[1] Some reactions are known for which the repulsion energy between the reactants is very small,[2] and as a result of this, the calculation of activation energy is much simplified. Potential-energy profiles have also been used for explaining the fact that in homologous reactions there is frequently a relationship between the energy of activation and the heat of reaction.[3]

Transfer of energy on collision[4]

Hitherto the discussion has been confined to purely chemical reactions, involving the formation of new chemical species by the making and breaking of bonds. Of great importance in the study of chemical kinetics are certain processes in which there is no rearrangement of atoms but which involve a transfer of energy from one atom or molecule to another during a collision, or which involve a change from one type of energy to another.

Such processes are not strictly chemical processes, which by definition involve a change of chemical species. Their importance in connection with chemical kinetics lies in the fact that they are often found associated with chemical reactions, either as side processes or as links in a chain of processes. It has already been seen, for example, that in unimolecular reactions the initial process of activation is quite distinct from the subsequent rearrangement of the molecule and may be separated from it by an appreciable period of time. The process of activation must therefore be studied, and it has already been seen that there is a considerable variation in the effectiveness with which various molecules transfer energy in this way. Transfer of energy is also of importance in connection with atomic recombination reactions (for which a third body is needed) and with the quenching of fluorescence.

Processes involving simply a transfer of energy are more difficult to treat theoretically than are chemical processes. The most direct treatment of both types is by the method of potential-energy surfaces, and purely chemical reactions involve, as has been seen, a transition from one valley to another. In each valley, representing the reactants and products, a large number of energy levels are possible, but transitions between these

[1] Ogg and Polanyi, *loc. cit.*; Evans and Polanyi, *loc. cit.*; M. G. Evans and E. Warhurst, *Trans. Faraday Soc.*, **34**, 614 (1938); **35**, 593 (1939)

[2] Ogg and Polanyi, *loc. cit.*; Evans and Warhurst, *loc. cit.*

[3] S. Horiuti and M. Polanyi, *Acta Physicochim. U.R.S.S.*, **2**, 505 (1935); Ogg and Polanyi, *loc. cit.*; Evans and Polanyi, *loc. cit.*

[4] *Cf.* O. Oldenburg and A. A. Frost, *Chem. Revs.*, **20**, 99 (1937).

are largely overshadowed by the major transition between the valleys; the treatment considers a statistical average of the various energy levels in the valleys and does not treat explicitly the individual energy levels or transitions between them. In purely physical processes, on the other hand, the problem is the transition between the levels within one or two valleys. The number of possible initial and final states may be very large, and even between two given states the number of likely reaction paths may be very great. In view of this complexity, it is necessary to rely less on fundamental theory and to pay greater attention to the experimental evidence.

The number of possible types of transition between the four types of energy, *viz.*, electronic, translation, rotational, and vibrational, is very large, and no attempt at a complete discussion will be made. Instead a few special types of transfer, which have a practical application to kinetic problems, will be considered. These are the following:

1. The transfer of translational energy from one atom or molecule to another on collision; this is important in connection with the question of whether molecules produced with abnormally high amounts of translational energy can influence the rate of chemical reactions.

2. The change in rotational and vibrational energy on collision; this has an important application in connection with the excitation of molecules in unimolecular decompositions.

3. The transfer of electronic energy on collision, the energy usually being converted into vibrational and rotational energy. Such transfer takes place in the quenching of fluorescence, which is always associated with photosensitized reactions in which the electronic energy is used to bring about chemical change. The reverse processes, in which electronically excited molecules are formed in a reaction, are of great importance in connection with oxidation reactions resulting in flames.

Transfer of Translational Energy on Collision. Not much is known on the experimental side about the transfer of translational energy from one molecule to another, since the translational energy of a molecule cannot be determined directly. However, the problem can easily be treated on the basis of classical theory, which should be sufficiently accurate since the masses concerned are generally sufficiently large for quantum deviations to be absent. On the basis of classical theory, it can be shown that a molecule tends to undergo a change of translational energy on every collision and that a molecule having more than an average amount of translational energy is more likely to lose energy than to gain it on colliding with another molecule; in other words there is a tendency toward thermal equilibrium within any system.

A molecule may acquire more than an average amount of translational energy as a result of a favorable collision, or a favorable series of collisions,

or in more specific ways. For example, after electronic excitation a molecule may vibrate strongly and subsequently dissociate, the resulting atoms or radicals having abnormally high amounts of translational energy. Alternatively, atoms and radicals set free in ordinary thermal dissociations may have much translational energy. However, the production of such atoms or radicals within a reaction system will not affect appreciably the rate of reaction unless they can react without suffering many intervening collisions which will reduce their energy. In certain chain reactions it has been postulated that abnormal translational energy plays a part, but it would seem that this is rather unusual.

In some instances the effectiveness of abnormally high translational energy in bringing about chemical reactions is restricted in another and more special way. If a heavy atom or molecule with high translational energy strikes a lighter molecule, the center of gravity of the resulting collision complex will tend to move in the original direction of the excited species; consequently all the energy of the latter is not available for inducing chemical reaction.

Transfers of Vibrational and Rotational Energy. The application of classical theory to vibrational and rotational energy also leads to the conclusion that abnormally high amounts of either will tend to be dissipated rapidly on collision. A detailed quantum-mechanical treatment has not, however, been worked out, so that conclusions must be reached on the basis of considerations of the experimental results.

The subject is particularly amenable to experimental investigation, since excited vibrational and rotational states are easily produced by the absorption of radiation and can be detected spectroscopically. A study of this kind has been carried out by Roessler,[1] using iodine vapor, which was raised to an excited electronic state in which there were 26 vibrational and 34 rotational quanta. This amount of rotational energy is in this case well within the range of energies set up by collision, but the vibrational energy represents a high degree of excitation, which is far outside the thermal range. On introducing foreign gases to the excited iodine, a large number of new rotational and vibrational states appear; these can be identified spectroscopically and their intensities measured. This has been done for a range of pressures of the added gas, and the results analyzed. It was found that when an excited iodine molecule collides with a foreign molecule, a transfer of vibrational and rotational energy occurs in almost every case. The rotational energy, which is initially within the thermal range, may be increased or decreased on such a collision; on the other hand, the vibrational energy, which initially is abnormally high, is nearly always reduced on collision, usually by one quantum at a time. The results have been analyzed in terms of the collision diameters which,

[1] F Roessler, *Z. Physik*, **96**, 251 (1935).

on the basis of collision theory and the assumption of a zero energy of activation, have to be assumed in order to explain the kinetic values. The collision diameters obtained in this way are found to be somewhat higher than the ordinary kinetic-theory diameters obtained from viscosity data and in other ways. The probability of reaction varies with the atomic weight of the colliding gas, but not in any simple manner. A further conclusion that has been drawn is that the larger the quantum to be transferred, the less is the probability of its transference on collision. Somewhat similar results have been obtained by Rieke,[1] working with excited HgH radicals and with nitrogen as the foreign gas.

Influence of Gases on the Dispersion of Sound. It was found by Pierce,[2] working with sound of frequencies far above the audible range, that the velocity of sound is a function of the frequency. Over a range of lower frequencies, the velocity remains constant and is "normal" in the sense that it can be predicted from the known specific heats. At a certain higher frequency, the velocity begins to fall and continues to do so until, at a higher frequency, it becomes constant. The constant velocity in this higher frequency range corresponds to the specific heat the molecule would have if the vibrational degrees of freedom played no part.

This behavior has been explained by Herzfeld and Rice[3] on the basis that vibrations are slow at picking up the energy that corresponds to equilibrium, so that at sufficiently high frequencies, the molecules will not be fully excited vibrationally. According to this view, foreign gases should have a varied influence in preventing "dispersion," *i.e.*, in preventing the fall of velocity at higher frequencies, and their influence should depend upon their effectiveness in transferring vibrational energy. This aspect of the problem has been investigated by Eucken and his coworkers, some of whose values[4] are given in Table 49, the figures representing the effectiveness of the added gas in transferring energy, relative to the gas itself.

In discussing these results, Eucken and Becker[5] have noted that the probability of transference of energy on collision is larger, the greater the chemical reactivity of the two colliding molecules, even though no chemical change takes place. For example, nitrogen, which does not react with chlorine, is less effective than carbon dioxide, which does. This rule is not universally followed, as is shown by the high values for helium. The dispersion-of-sound experiments are carried out at ordinary temperatures, and under these conditions many thousands of collisions are required to

[1] F. F. Rieke, *J Chem. Phys.*, **4**, 513 (1936); **5**, 831 (1937).
[2] G. W Pierce, *Proc Am. Acad. Arts Sci* , **60**, 271 (1925).
[3] K. F. Herzfeld and F. O. Rice, *Phys Rev* , **31**, 691 (1928).
[4] A. Eucken, *Oesterr. Chem -Ztg.*, **38**, 162 (1935).
[5] A. Eucken and R. Becker, *Z. physik. Chem.*, **B, 27**, 235 (1934).

effect a change of one quantum of vibrational energy. This high persistence of vibrational energy is to be contrasted with the low persistence found in the spectroscopic investigations, in which the molecules are more strongly excited.

The parallelism which is found to exist between the effectiveness in transferring vibrational energy and chemical reactivity makes it clear that a purely mechanical explanation of the process is not adequate,[1] and Eyring, Gershinowitz, and Sun[2] have discussed the problem in terms of potential-energy surfaces. The surfaces which are used in this connection are constructed with skewed axes, of which an example is shown in Fig. 40, which

TABLE 49 RELATIVE EFFECTIVENESS OF VARIOUS GASES IN TRANSFERRING VIBRATIONAL ENERGY
As determined by dispersion-of-sound experiments

Added gas	Relative effectiveness of added gas when introduced into		
	Chlorine	Nitrous oxide	Carbon dioxide
N_2	0.88		
A	1.1		1.0
He	33 3	3 3	33.3
D_2	. .	12 5	. .
H_2	50	9 1	125
CO	107	1.6	.
CH_4 ..	200	6 7	25
HCl .	200		500
NH_3	.	12 5	
H_2O	.		2,000

refers to a hypothetical system XYZ; this is relevant to the system consisting of a molecule YZ, the vibration of which is under consideration, and a colliding molecule X. If the potential-energy surface is constructed with an appropriate angle between the axes, the transformations of the system are represented exactly by the motion of a frictionless particle moving on the surface.[3] The contour lines on the figure may be drawn in such a manner as to represent vibrational energy levels. It may be supposed that initially the molecule YZ is in such a vibrational level that its motion on the surface is initially represented by the motion of the mass point between A and B.

Whether or not a change to another vibrational level takes place on collision with X, when the system moves along the valley, depends upon

[1] *Cf.* J. Franck and A. Eucken, *ibid.*, **B, 20,** 460 (1933).
[2] H. Eyring, H. Gershinowitz, and C. E. Sun, *J. Chem. Phys.*, **3,** 786 (1935).
[3] J. O. Hirschfelder, Thesis, Princeton University, 1935.

the shape of the valley. If there is no chemical interaction between X and YZ, the valley will be a completely symmetrical one. This is the case shown in Fig. 40, and in this instance there will be no transfer to another

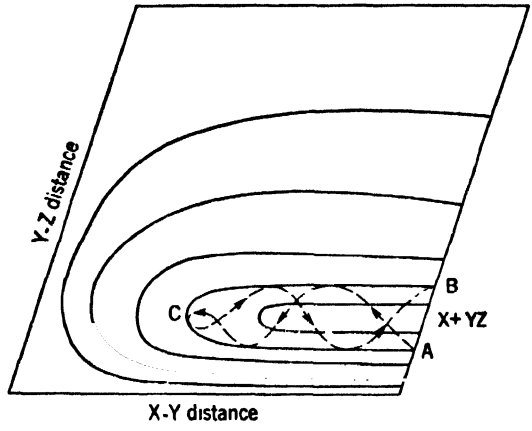


FIG. 40. Potential-energy surfaces for the system $X + YZ$. There is no chemical interaction between the colliding molecules and consequently no interconversion of energy.

vibrational level on collision, *i.e.*, the system will remain on the contour line ACB.

If on the other hand chemical reaction of the type $X + YZ = XY + Z$

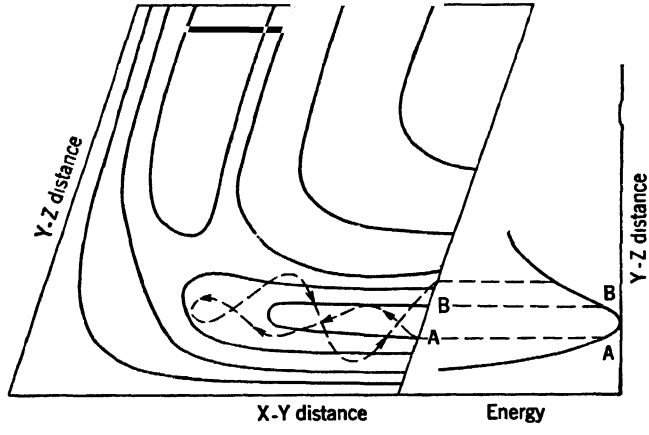


FIG. 41 Potential-energy surface for the system $X + YZ$, illustrating the interconversion of translational into vibrational energy.

is possible, the surfaces will be of the form shown in Fig. 41. In this case there are two valleys, of which the one corresponding to $X + YZ$ (*i.e.*, the one at the lower right of the diagram) no longer has a plane of sym-

metry, but is distorted, particularly at positions corresponding to a close approach of X to YZ. If the system enters this distorted region, the probability of a transfer to another vibrational level becomes appreciable and may be high. It is therefore to be expected that transference of energy is associated in an approximate manner with chemical reactivity. The correlation is not, however, strong in the dispersion-of-sound experiments, since, owing to the low temperatures, the vibrational levels are far down the potential-energy valleys, in which region the distortion is very small; the connection with reactivity is therefore slight, and the number of collisions required to effect a change of level is very large. In the spectroscopic work, on the other hand, and also in unimolecular reactions, the vibrational levels are higher; the number of collisions required is therefore less and the correlation with chemical reactivity much more pronounced.

The theoretical discussion of the triatomic system can readily be extended in principle to more complicated molecules to which multidimensional potential-energy surfaces apply. The relationship with reactivity is again to be expected. One important difference is that in this instance a transfer of energy can now take place not only between translational and vibrational energy, but between vibrational and vibrational if the colliding species contains more than one atom.

Atom-combination Reactions. Another type of chemical reaction to which considerations regarding the transfer of energy are directly applicable comprises combinations of atoms, which have been seen to combine only by a three-body collision. The processes may be represented as

$$A + A + Z \rightarrow A_2 + Z$$

where Z is the foreign molecule. This process is clearly the reverse of the unimolecular dissociation of A_2 into $A + A$, and since Z can have no effect on the equilibrium, it must influence both forward and reverse reactions to an equal degree.

The relative efficiencies of certain gases in facilitating the combination of halogen atoms are given in Table 50.[1] Some parallelism with the results in Table 49 is to be noted and is sufficient to be significant; an exact parallelism is, of course, not to be expected since different reactions are under consideration.

The interpretation of atom-recombination reactions in terms of potential-energy surfaces is as follows: The surface relevant to the reaction

$$X + Y + Z = XY + Z$$

is the same as that for the reaction $X + YZ = XY + Z$ (*cf.* Fig. 41) and

[1] E. Rabinowitsch and W. C. Wood, *Trans. Faraday Soc.*, **31**, 689 (1935); **32**, 907 (1936); *J. Chem. Phys.*, **4**, 497 (1936).

is shown in Fig. 42. The initial state is now represented by the plateau at the top right-hand corner, and the final state is the valley in the left-hand upper corner. If the mass point representing the system were simply to slide directly into this valley from the plateau, it would return to the

TABLE 50. RELATIVE EFFICIENCIES OF GASES IN TRANSFERRING ENERGY
As indicated by their catalysis of atom combinations

Foreign gas	Bromine	Iodine
He	1.00	1.00
A	1.68	1.94
H_2	2 85	2.16
N_2	3.25	3.60
O_2	4.10	5.67
CH_4	4.65	6.57
CO_2	7.15	9.85

plateau and there would be no over-all reaction. Reaction can occur only if the system slides into the valleys at an appropriate angle, such as in the manner represented by the dotted line in the figure; in this case the system first enters the $X + YZ$ valley and then passes into the $XY + Z$ valley,

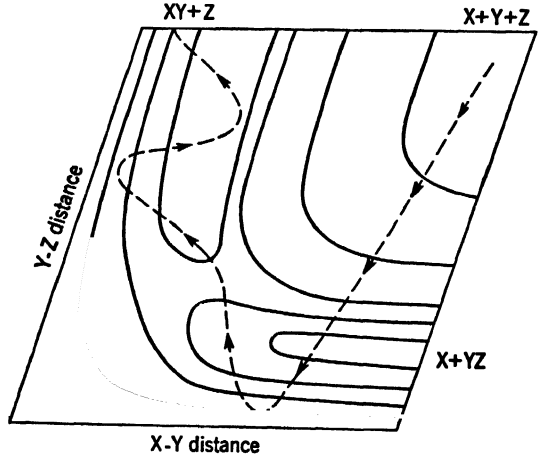


FIG. 42. Potential-energy surface for the system XYZ, showing the course of the reaction $X + Y + Z \rightarrow XY + Z$.

the translational energy being converted into vibrational. The efficiency of Z in facilitating the combination of X and Y depends upon the form of the potential-energy valley. If Y and Z interact to an appreciable degree, the right-hand valley will be deep and the ridge separating the two valleys

will be low, so that passage from one to the other will not be difficult. If, on the other hand, there is little or no attraction between Y and Z, the right-hand valley will be shallow or nonexistent, in which case the probability of a system leaving the plateau and passing out through the left-hand valley will be greatly decreased.

Reactions Involving Transfer of Electronic Energy. There are now known a large number of elementary processes which involve atoms or molecules in excited electronic states. In some of these the electronically excited species are reactants, while in some they are products; in some there is a transfer of electronic energy from one molecule to another, so that both a reactant and a product are excited. The present section is concerned with a discussion of the mechanisms of such processes.

Reactions in which a reactant is electronically excited are of particular importance in photochemistry, while those in which a product is excited are important in connection with flames. In some flames, such as the cool flames studied by Polanyi and others (see p. 227), the emitted radiation is entirely given off by electronically excited atoms or molecules, and the manner of formation of these is of some interest. In hot flames, some of the radiation is of the black-body type, but superimposed on this is usually some radiation emitted by molecules produced in specific reactions involving transfer of energy from one form into another. In the highly luminous carbon monoxide flame, for example, an appreciable fraction of the total radiation has been seen (p. 326) to be emitted by electronically excited oxygen.

The number of reactions that can, in general, occur after a molecule has become excited electronically is considerable. Some of the more important types, with examples, are as follows:

1. Dissociation,

$$AB^* \rightarrow A + B$$

Predissociations are of this type, as are the following dissociations of electronically excited olefins:[1]

$$C_2H_4^* \rightarrow C_2H_2 + H_2$$
$$C_3H_6^* \rightarrow C_3H_5 + H$$

2. Isomerization, which may be represented as

$$AB^* \rightarrow BA$$

Several cis-trans isomerizations can be induced to proceed by initial electronic excitation and are therefore of this type.[2]

[1] D. J. Le Roy and E. W. R. Steacie, *ibid.*, **9**, 829 (1941); **10**, 676 (1942).
[2] H. E. Mahncke and W. A. Noyes, *J. Am. Chem. Soc.*, **58**, 932 (1936).

The above two reactions are unimolecular; in addition there are the following bimolecular processes:

3. Physical quenching, in which the electronic energy is removed from the molecule without the occurrence of any reaction,

$$A^* + B \rightarrow A + B$$

An example is the quenching of electronically excited sodium by hydrogen molecules,[1]

$$\mathrm{Na}(^2P) + \mathrm{H_2} \rightarrow \mathrm{Na}(^2S) + \mathrm{H_2}$$

4. Transfer of electronic energy to the colliding molecule,

$$A^* + B \rightarrow A + B^*$$

This type of process was first discovered by Cario and Franck,[2] who found that excited mercury atoms could excite thallium atoms to various excited states,

$$\mathrm{Hg}(^3P_1) + \mathrm{Tl}(^2P) \rightarrow \mathrm{Hg}(^1S) + \mathrm{Tl}^*$$

5. Quenching accompanied by dissociation of the colliding molecule, the fragments resulting remaining free,

$$A^* + BC \rightarrow A + B + C$$

Such a process occurs in the quenching of mercury radiation by hydrogen,[3]

$$\mathrm{Hg}(^3P_1) + \mathrm{H_2} \rightarrow \mathrm{Hg}(^1S) + 2\mathrm{H}$$

6. Chemical quenching with dissociation, one of the products of the dissociation becoming associated with the quenched molecule,

$$A^* + BC \rightarrow AB + C$$

An example is the quenching of excited cadmium by hydrogen, in which case the cadmium hydride is formed,[4]

$$\mathrm{Cd}(^3P_1) + \mathrm{H_2} \rightarrow \mathrm{CdH} + \mathrm{H}$$

7. Quenching with dissociation of the quenched species,

$$AB^* + C \rightarrow A + B + C$$

[1] R. G. W. Norrish and W. MacF. Smith, *Proc. Roy. Soc.* (*London*), **A, 176,** 295 (1940).

[2] G. Cario and J. Franck, *Z. Physik*, **17,** 202 (1923).

[3] L. O. Olsen, *J. Chem. Phys.*, **6,** 307 (1938); L. B. Thomas and W. D. Gwinn, *J. Am. Chem. Soc.*, **70,** 2643 (1948).

[4] H. C. Lipson and A. C. G. Mitchell, *Phys. Rev.*, **48,** 625 (1935).

The following reaction, an example of this, has been postulated as occurring in the hydrogen-oxygen flame:

$$OH(^2\Sigma) + H_2 \rightarrow O + H + H_2$$

8. Quenching with isomerization of the quenched species,

$$AB^* + C \rightarrow BA + C$$

Such a process has been shown to occur when an electronically excited molecule of 1-butene collides with a normal molecule[1]

$$1\text{-}C_4H_8^* + 1\text{-}C_4H_8 \rightarrow 2\text{-}C_4H_8 + 1\text{-}C_4H_8$$

9. Association between the excited molecule and the colliding molecule,

$$A^* + B \rightarrow AB$$

An example is the reaction between excited oxygen atoms and carbon monoxide, with the formation of carbon dioxide in its normal state,

$$O(^1D) + CO(^1\Sigma) \rightarrow CO_2$$

In addition to the above processes, there are reactions between normal molecules with the formation of electronically excited molecules. Thus two molecules may associate to give an electronically excited molecule,

$$A + B \rightarrow AB^*$$

examples of which are

$$O + CO \rightarrow CO_2^*$$

and

$$O + NO \rightarrow NO_2^*$$

the latter reaction having been mentioned on page 187. Another type of reaction is exemplified by

$$Na + NaCl' \rightarrow Na^* + NaCl$$

which was seen on page 229 to be responsible for the formation of electronically excited sodium in the cool flame of sodium and chlorine.

In view of the large number of reactions that might be expected to occur in any one reaction system, it is clearly of importance to study the factors influencing the rates of reactions of this type. This may be considered with reference to (1) the entropy of activation, (2) the energy of activation,

[1] D. J. Le Roy and E. W. R. Steacie, *J. Chem. Phys.*, **10**, 683 (1942); H. E. Gunning and E. W. R. Steacie, *ibid.*, **14**, 581 (1946).

and (3) the transmission coefficient, and in order to do this, the relevant potential-energy surfaces must be discussed.

In the treatment of a reaction in which no electronic excitation is involved, the potential-energy surface on which reaction occurs is the lowest one for the system, and the reaction is represented by a smooth movement over this surface. When a reactant or a product is excited, on the other hand, it is necessary to take upper surfaces into consideration. There is then a set of surfaces, some of which may be regarded as crossing one another, and in some cases reaction can again be represented as a smooth transition on one of these surfaces; the reaction will then proceed with a transmission coefficient close to unity. In other cases, reaction involves a crossing from one surface to another, and the probability of such crossing,

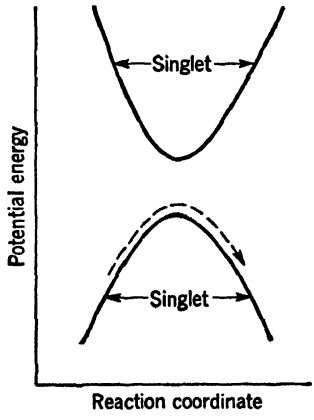


FIG. 43. Potential-energy profiles for surfaces of the same multiplicity.

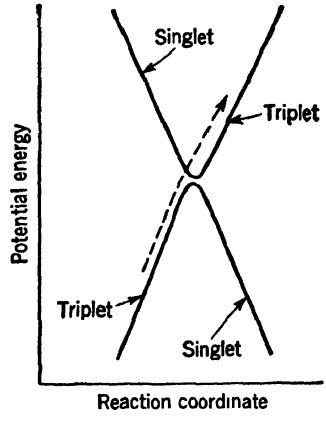


FIG. 44. Potential-energy profiles for surfaces of different multiplicity.

which influences the transmission coefficient and hence the rate of the reaction, depends on certain factors which will now be considered in a qualitative way.

The number and spectroscopic designation of potential-energy surfaces can be obtained in the same manner as for molecules, by making use of the vector model and the Wigner-Witmer correlation rules.[1] This procedure, however, takes no account of the resonance splitting that may occur instead of crossing. When surfaces are of the same multiplicity and have the same symmetry properties, the resonance separation is large, the surfaces corresponding to an upper and a lower state as shown diagram-

[1] See, for example, G. Herzberg, "Molecular Spectra and Molecular Structure, I. Diatomic Molecules," Chap. VI. D. Van Nostrand Company Inc., New York, 1950.

matically in Fig. 43. When this is the case, the probability of a crossing between the two surfaces is very small, so that, for example, a reaction system initially on a lower surface has little probability of passing to the upper one.

When, on the other hand, the surfaces obtained on the basis of the vector model are of different multiplicity, the resonance splitting is extremely slight (Fig. 44); the probability of crossing is now close to unity, while that of staying on the upper or lower surface is close to zero. This is equivalent to saying that the reaction system behaves as if the surfaces really crossed and that systems resist any change in spin angular momentum and hence of multiplicity. This principle, which is often known as the Wigner spin-conservation rule, has been of great value in excluding reaction mechanisms which might otherwise be considered. The value of the transmission coefficient for a reaction involving a change in multiplicity is probably always less than 10^{-4}, and such processes therefore play little part in reaction mechanisms, being overwhelmed by more efficient ones.

In considering the rates of reactions involving excited electronic states, attention must therefore be paid to the multiplicities of the surfaces corresponding to the reactants and the products; if these are the same, there may be no restriction to reaction, while if they are different, the reaction must be slow owing to a small transmission coefficient. The determination of the multiplicities of potential-energy surfaces is done by application of the Wigner-Witmer correlation rules for finding the multiplicity of a molecule from the multiplicities of its constituent atoms. The multiplicities S_1 and S_2 of two reactant molecules are related to the electron spins s_1 and s_2 by

$$S_1 = 2s_1 + 1 \qquad \text{and} \qquad S_2 = 2s_2 + 1$$

and the resultant permitted spins in the potential-energy surfaces are

$$s_1 + s_2, \qquad s_1 + s_2 - 1, \qquad s_1 + s_2 - 2, \cdots, \qquad |s_1 - s_2|$$

In Table 51 are shown some of the more common correlations. From it may be seen, for example, that a molecule in a triplet state combines with one in a singlet state to give a potential-energy surface of triplet multiplicity. If the over-all reaction is an association between the two molecules, the product must then be a triplet. If, on the other hand, the surface gives rise to two molecules as products of reaction, the multiplicities of these must be such as to combine with the triplet surface. Thus the products may be a singlet and a triplet, a triplet and a triplet, etc.

It may easily be verified that the reactions mentioned on pages 383 and

384 are consistent with these rules and can therefore occur with transmission coefficients close to unity. The reaction

$$N_2O(^1\Sigma) \rightarrow N_2(^1\Sigma) + O(^3P)$$

violates the selection rules, however, and will therefore occur with low probability; its rate is probably sufficiently high, in spite of this, for it to play a part in the decomposition of nitrous oxide.[1] The following reactions have frequently been postulated as playing a part in reaction mechanisms

TABLE 51. RESULTANT MULTIPLICITIES OF POTENTIAL-ENERGY SURFACES RELATIVE TO THOSE OF THE CONSTITUENT MOLECULES

Molecule *A*	Molecule *B*	Potential-energy surface
Singlet	Singlet	Singlet
Doublet	Doublet	
Singlet	Doublet	Doublet
Doublet	Triplet	
Quartet	Triplet	
Singlet	Triplet	Triplet
Triplet	Triplet	
Doublet	Quartet	

but probably occur too slowly, owing to a change in multiplicity, to be of importance:

$$N_2O_5(^1A) \rightarrow N_2O_3(^1A) + O_2(^3\Sigma)$$
$$O(^3P) + CO(^1\Sigma) \rightarrow CO_2(^1\Sigma)$$
$$Hg(^3P) + H_2(^1\Sigma) \rightarrow Hg(^1S) + H_2(^1\Sigma)$$

The rates of reactions involving excited electronic states depend also, of course, on the entropies and energies of activation. This will not be considered here, since no new principles are involved in the construction of the potential-energy surfaces. In view of the complexity of the situation, this is best done by empirical methods, and surfaces have been constructed in this way for various quenching[2] and photosensitization[3] processes, and for certain reactions occurring in the carbon monoxide flame.[4]

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PROBLEM

***1.** The potential energy of the hydrogen molecule is related to the internuclear distance by the Morse equation [Eq. (5), p. 369] with $D' = 108.9$ kcal, $a = 1.954$, and $r_0 = 0.74$ A. Calculate the values of the potential energy corresponding to the following internuclear distances

$$r = 0.5,\ 0.75,\ 1.0,\ 1.5,\ 2.0,\ 3.0,\ 4.0,\ \text{A}$$

Draw a graph of E vs. r.

On the assumption that the coulombic energy is 14 per cent of the total potential energy, calculate the coulombic and exchange energies corresponding to each of the above distances. Plot these two curves on the same graph as used above.

Construct a potential-energy surface for the linear H_3 system according to the following procedure: First take $r_1 = 0.5$ A and $r_2 = 0.5$ A and calculate the energy using the London equation (take the negative sign). Repeat this with the series of r_2 values up to $r_2 = 3$, and plot E vs. r_2 corresponding to $r_1 = 0.5$ A. Repeat this procedure with the r_1 values up to $r_1 = 2$, in each case going to $r_1 + r_2 = 4$. Draw the curves on the one sheet.

On a separate sheet of graph paper, prepare rectangular axes corresponding to r_1 and r_2, the values ranging from zero to 3 A. Plot points corresponding to energies of

$$-20,\ -40,\ -60,\ -80,\ -90,\ -95,\ -100\ \text{kcal}$$

and draw in the contour lines.

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