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THE KINETICS OF
CHEMICAL CHANGE
IN
GASEOUS SYSTEMS

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THE KINETICS OF CHEMICAL CHANGE IN GASEOUS SYSTEMS

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FROM THE

PREFACE TO THE FIRST EDITION

In writing this book I have sought to give a continuous account of those phenomena of chemical change which offer some prospect of interpretation in terms of the kinetic theory. These seem to be confined to gaseous systems, to which the scope of the book is therefore restricted.

Continuity has demanded that certain aspects of the subject should be treated but briefly, especially in the later pages. Detail appeared to be less important than the presentation in true perspective of the whole field of inquiry. But I have tried not to suggest, by the omission of relevant facts, a uniformity and simplicity which the subject does not at the moment possess.

PREFACE TO THE SECOND EDITION

In the three years which have elapsed since the publication of the first edition of this book the subject may justly be said to have advanced another whole stage. As a result, Chapters III and V have been completely rewritten, a new chapter on Chain Reactions has been added, and the other chapters have all been added to or revised.

C. N. H.

Oxford,
March 1929.

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I

INTRODUCTION

An attempt to elucidate the actual mechanism by which chemical changes occur is the natural sequel to the development of structural chemistry. The kind of inquiry which it becomes desirable to make can be illustrated by very simple examples. It is known that hydrogen and oxygen in the free state consist of diatomic molecules, and that water is a compound formed as a result of atomic rearrangements which can be expressed by the equation $2\,H_2 + O_2 = 2\,H_2O$. It is observed, moreover, that at ordinary temperatures hydrogen and oxygen may be kept in contact for an indefinite length of time without interacting perceptibly, whilst at high temperatures they react with great rapidity. At intermediate temperatures there is slow combination, the duration of which may be measured by minutes, days, or years. The problem at once presents itself whether, in this process of slow combination, interaction takes place whenever two hydrogen molecules come into contact with an oxygen molecule. Comparison, however, with the analogous reaction $2\,NO + O_2 = 2\,NO_2$, the speed of which is extremely great at temperatures where the union of hydrogen and oxygen is immeasurably slow, shows that the occurrence of the necessary molecular encounters is by no means the only condition which must be fulfilled. The encounters must evidently be between molecules in an exceptional state of some kind.

The question arises in an even more fundamental form when we consider such changes as the slow decomposition of nitrogen pentoxide, and we have to seek the reason why the molecules do not decompose all at once or not at all. Chemical transformations taking place in finite time thus

show that the molecules cannot be all in the same state, for, if they were, certain kinds of chemical reaction would take place with infinite rapidity if able to take place at all.

Although slowly progressing chemical changes attracted the attention of the earliest and most superficial observers, no definite ideas about the intimate nature of chemical action could be formed until quantitative investigations on the rate of progress of reactions were made. Such investigations were first made by Harcourt and Esson and by Wilhelmy. Their work, and that of van't Hoff on chemical dynamics, laid the foundations of the whole subject.

Our attention is to be confined to the rate of chemical change in gases. The gaseous state seems to present special advantages for studies which seek to elucidate the mechanism of chemical change, because the kinetic theory affords a considerable amount of detailed information about the internal state of gases. Knowledge of the liquid state is scanty and not very satisfactory. The question of the degree to which liquids are polymerized, if at all, can only be answered in a more or less qualitative fashion ; there is very little precise information about the mean free path of molecules in liquids, and this prevents the number of collisions between molecules from being calculated. The extent, moreover, to which molecules of a solute are solvated, or even the exact sense in which the word solvation is to be understood, are still matters for discussion. The influence of the solvent on the rate of chemical changes taking place between molecules in solution has been shown by Menschutkin to be enormous. It is evident, therefore, that there is profound interaction of some kind between the solvent and the solute, but its nature remains obscure, all attempts to correlate it with physical properties of the solvent such as dielectric constant having been fruitless. Ionization phenomena fre-

quently play a part in reactions in solution, but all these effects are of considerable complexity, compared with those encountered in gases.

THE KINETIC THEORY OF GASES

In gases, the kinetic theory gives precise information about the following matters:

1. The mean speed of the molecules.
2. The distribution of the speeds about the most probable value. We know, for example, what proportion of the molecules have speeds more than double the mean speed, less than half the mean speed, and so on.
3. The types of motion executed by molecules of different kinds.
4. The mean free path of the molecules, from which, when the velocity is known, the number of collisions taking place in unit time may be calculated.

It will be useful first to deal with these matters in order.

1. *The root mean square velocity.*

This is obtained from the well-known expression for the pressure of a gas $pv = 1/3\, mn\bar{u}^2$ where p = pressure, v = volume, m = mass of a molecule, n = number of molecules in the volume v, and $\bar{u}$ = root mean square velocity.

If v is the molecular volume, n = Avogadro's number, n_1 and $pv = RT$; therefore $1/3\, mn_1\bar{u}^2 = RT$.

Since $$\frac{mn}{v} = \rho, \quad \bar{u} = \sqrt{\frac{3p}{\rho}}.$$

One of the most useful applications of this formula is in the calculation of the number of molecules striking unit area of a surface in a given time. This calculation is of importance in connexion with the interaction of a gas with a solid substance, or in problems relating to contact catalysis, where we may require to know how many molecules strike the solid catalyst in each second. Suppose

we have a solid surface of unit area exposed to the bombardment of gas molecules. Approximately one-sixth of the total number of molecules may be regarded as moving in the direction of the surface with the average velocity. In one second all those within distance $\bar{u}$ could reach and strike the surface, unless turned back by a collision with another molecule, but for every one so turned back, another, originally leaving the surface, is sent back to it. Thus the number of molecules striking the surface in a second is equal to one-sixth of the number contained in a prism of unit base and height $\bar{u}$. This number is $1/6\,\bar{u}n'$, n' being the number of molecules in 1 c.c. Thus the mass of gas impinging on the surface per second is

$$1/6\,\bar{u}n'm = 1/6\,\bar{u}\rho.$$

A more precise investigation allowing for the unequal speeds of different molecules shows that the factor $1/6$ should really be $3/13$. We therefore arrive at the result

Mass of gas striking an area, A, in one second $= 3/13\,\bar{u}\rho A$.

As an example of the use of this result we may consider Strutt's work on the reaction between silver oxide and ozone. The paper in which this is described * is one of the first in which the importance of considering chemical reactions from the point of view of molecular statistics is emphasized.

Silver oxide reacts with and destroys ozone, and the question may be asked, what fraction of the total number of ozone molecules which hit the silver oxide is destroyed? Or otherwise, how many times, on the average, must an ozone molecule hit the solid before it is decomposed? The answer to this question was found in the following manner. If a current of air at low pressure is drawn through a tube where an electric discharge is taking place the issuing gas shows a yellowish glow, the cause of which can be traced to the interaction of nitric oxide and ozone. The glow is

* *Proc. Roy. Soc.*, 1912, A, **87**, 302.

extinguished when the gas is passed through oxidized silver gauze, and the disappearance of the glow must be due to the destruction of the ozone, since if more ozone is introduced into the stream after the silver gauze is passed the glow reappears. Strutt caused a rapid stream of air at low pressure to pass first through a discharge tube and then through a piece of oxidized silver gauze, the total area of which was known. The rate of flow was adjusted until the glow was just destroyed by the passage of the gas over the gauze. If v is the actual volume of ozone streaming by in a second, then a mass ρv passes the gauze, and if A is the total area of the gauze, the mass hitting it is $3/13\ \bar{u}\rho A$. Thus the ratio of the number of molecules of ozone striking the gauze to the number passing is

$$\frac{3/13\ \rho\bar{u}A}{\rho v} = \frac{3\ \bar{u}A}{13\ v}.$$

Since the experiment is so arranged that all the ozone is just destroyed in passing, this gives the number of times each molecule strikes the silver oxide before it is decomposed. The glow was found just to be extinguished when the rate of streaming was 200 c.c. per second at a pressure of 3 mm., the total area of the oxidized silver gauze being 0·037 square centimetres.

$\bar{u} = 3{\cdot}75 \times 10^4$.

Therefore $$\frac{3\ \bar{u}\ A}{13\ v} = \frac{3 \times 3{\cdot}75 \times 10^4 \times 0{\cdot}037}{13 \times 200} = 1{\cdot}6.$$

Thus there are on the average only 1·6 molecular impacts on the solid for every molecule of ozone decomposed. This shows that practically every molecule of ozone which strikes the silver oxide is destroyed.

This calculation illustrates the fundamental importance of quantitative investigation of the behaviour of individual molecules in chemical changes. The application of analogous calculations to problems connected with the passage

of gas streams over solid catalysts in technical processes is obvious.

Langmuir has made a number of studies of the interaction of various gases at low pressures with heated metal filaments;* these illustrate in a very interesting manner similar principles. The action of oxygen at pressures below 0·02 millimetre on a heated tungsten wire was among the examples investigated. The rate at which the oxygen came in contact with the filament was calculated. This gives the maximum possible rate of reaction. The ratio of the observed rate of reaction to this maximum possible rate was found to range from 0·0011 at 1,270° abs. to 0·15 at 2,770° abs. In this case, therefore, only exceptional molecules of oxygen are able to react with the wire.

2. *The distribution of speeds among the molecules.*

As a result of collisions in a gas the speeds of the individual molecules are continually changing. A given molecule may be brought momentarily almost to rest, or, on the other hand, after several successive collisions of a suitable kind it may acquire a velocity much above the average. Theories of chemical change are often concerned with molecules of exceptionally high energy. The chance that a molecule emerges from the hazards of several successive encounters with kinetic energy much above the mean is small, and, as the excess of kinetic energy over the average which it has to acquire increases, so the chance diminishes very rapidly. The number of molecules out of a total number N, the speeds of which lie between c and $c + dc$, is given by Maxwell's law

$$dN = N.\frac{4}{\alpha^3\sqrt{\pi}}.c^2.e^{-c^2/\alpha^2}.dc,$$

where α is the most probable velocity, a quantity not very different from the mean velocity.

The following is an epitome of the derivation of Max-

* *J. Amer. Chem. Soc.*, 1913, **35**, 105, 931 ; 1919, **41**, 167.

well's law. The steps in its proof are given in full in order that the nature of certain approximations occasionally used may be seen, and that the degree of inaccuracy thereby introduced may be exactly estimated.

Let u, v, w be the rectangular components of a velocity c. Then

$$u^2+v^2+w^2 = c^2 \quad . \quad . \quad . \quad . \quad (1)$$

Let the chances that a molecule possesses components of velocity between u and $u+du$, v and $v+dv$, and w and $w+dw$ respectively be $f(u)\,du$, $f(v)\,dv$, and $f(w)\,dw$. Then the probability that it possesses simultaneously three components between these limits is the product of the three independent probabilities, namely

$$f(u) \,.\, f(v) \,.\, f(w)\, du\, dv\, dw \quad . \quad . \quad . \quad (2)$$

If we consider the various ways in which a given value of c can be made up from the resolved parts in three directions, and vary u, v, and w subject to the condition that c must remain constant, we have by differentiating (1)

$$u\, du+v\, dv+w\, dw = 0 \quad . \quad . \quad . \quad . \quad (3)$$

Since, moreover, all directions of motion are equally probable, there must be a definite constant value of $f(u)f(v)f(w)$ for a given value of c, however that c is made up. Therefore by differentiating (2) we obtain

$$f'(u)f(v)f(w)\, du+f'(v)f(u)f(w)\, dv + f'(w)f(u)f(v)\, dw = 0 \quad . \quad (4)$$

Dividing (4) by $f(u)f(v)f(w)$,

$$\frac{f'(u)}{f(u)}du+\frac{f'(v)}{f(v)}dv+\frac{f'(w)}{f(w)}dw = 0 \quad . \quad . \quad (5)$$

Since (3) and (5) both hold simultaneously, they can be combined into one equation. For generality (3) is multiplied by an arbitrary constant λ and added to (5) giving

$$\left[\frac{f'(u)}{f(u)}+\lambda u\right]du+\left[\frac{f'(v)}{f(v)}+\lambda v\right]dv+\left[\frac{f'(w)}{f(w)}+\lambda w\right]dw = 0.$$

(The multiplication by λ takes place, since not only is $0+0=0$, but also $n\,.\,0+m\,.\,0=0$.)

Since du, dv, and dw are arbitrarily chosen infinitesimals, each of the factors in brackets must independently be zero. Thus

$$\frac{f'(u)}{f(u)}+\lambda u = 0,$$

therefore $$\log f(u) = -\frac{\lambda u^2}{2} + \text{constant},$$

$$f(u) = Ae^{-\frac{\lambda u^2}{2}},$$

$\lambda/2$ is usually written $1/\alpha^2$.

Thus $f(u) = Ae^{-u^2/\alpha^2}$, and similarly $f(v) = Ae^{-v^2/\alpha^2}$, $f(w) = Ae^{-w^2/\alpha^2}$.

The evaluation of A depends upon the fact that all molecules must have components of velocity between $-\infty$ and $+\infty$, so that the probability of a value of u between these limits is unity.

Therefore $$A\int_{-\infty}^{+\infty} e^{-u^2/\alpha^2}\,du = 1.$$

This is the well-known probability integral. Its value is

$$A\alpha\sqrt{\pi}, \quad \text{whence} \quad A = \frac{1}{\alpha\sqrt{\pi}}\cdot$$

Therefore $f(u) = \frac{1}{\alpha\sqrt{\pi}}\,.\,e^{-u^2/\alpha^2}$; $f(v) = \frac{1}{\alpha\sqrt{\pi}}\,.\,e^{-v^2/\alpha^2}$;

$$f(w) = \frac{1}{\alpha\sqrt{\pi}}\,.\,e^{-w^2/\alpha^2}.$$

The chance that a molecule possesses simultaneously components of velocity between u and $u+du$, v and $v+dv$, and w and $w+dw$ is

$$f(u)\,f(v)\,f(w)\,du\,dv\,dw = \frac{1}{\alpha^3\pi^{3/2}}\,.\,e^{-\frac{u^2+v^2+w^2}{\alpha^2}}\,du\,dv\,dw.$$

This defines not only the magnitude of c but also its direction. We require to know the probability of a speed between c and $c+dc$ without any restriction of direction.

We transform from rectangular to polar coordinates and define the velocity in terms of the radius vector c and the angles θ and ϕ (Todhunter, *Integral Calculus*, 1886, p. 183).

$c^2 = u^2 + v^2 + w^2$, and the volume element $du\,dv\,dw$ is replaced by the polar volume element $c^2 . \sin\theta\, dc\, d\theta\, d\phi$.

The probability of a speed between c and $c + dc$ without restriction of direction is found by integrating the expression

$$. \frac{1}{a^3 \pi^{3/2}} . e^{-c^2/a^2} . c^2 . \sin\theta . dc . d\theta\, d\phi$$

with respect to θ and π between the limits 0 and π for θ and 0 and 2π for ϕ. The result is

$$\frac{4}{a^3\sqrt{\pi}} . c^2 . e^{-c^2/a^2} . dc. \quad \text{This equals } \frac{dN}{N}.$$

It is convenient to express a in terms of the root mean square velocity $\bar{u}$. If dN is the number of molecules out of a total number N having speeds between c and $c + dc$, the average value of c^2 is given by

$$\bar{u}^2 = \frac{\int_0^\infty c^2 dN}{N},$$

but since

$$\frac{dN}{N} = \frac{4}{\sqrt{\pi} a^3} . c^2 . e^{-c^2/a^2} . dc,$$

$$\bar{u}^2 = \frac{4}{\sqrt{\pi} a^3} \int_0^\infty c^4 . e^{-c^2/a^2} . dc.$$

The method of integration of this kind of expression is given in Jeans, *Dynamical Theory of Gases*, Appendix A. The result is

$$\bar{u}^2 = \frac{3\,a^2}{2},$$

thus $a^2 = 2/3\,\bar{u}^2$, and since $pv = 1/3\, n_1 m \bar{u}^2 = RT$,

$$a^2 = \frac{2\,RT}{m n_1} = \frac{2\,kT}{m}, \text{ where } k = \frac{R}{n_1}.$$

Thus the distribution law becomes

$$\frac{dN}{N} = \frac{4}{\sqrt{\pi}\left(\frac{2kT}{m}\right)^{3/2}} \cdot c^2 \cdot e^{-\frac{mc^2}{2kT}} \cdot dc.$$

The number of molecules, the speeds of which exceed a value c_0, is given by

$$N_1 = \frac{4N}{\sqrt{\pi}\left(\frac{2kT}{m}\right)^{3/2}} \int_{c_0}^{\infty} c^2 \cdot e^{-\frac{mc^2}{2kT}} \cdot dc.$$

If we write

$$\frac{mc^2}{2kT} = x^2 \quad \text{and} \quad \frac{mc_0^2}{2kT} = x_0^2,$$

then

$$N_1 = \frac{4N}{\sqrt{\pi}} \int_{x_0}^{\infty} x^2 \cdot e^{-x^2} \cdot dx.$$

Integrating by parts this becomes

$$\begin{aligned} N_1 &= \frac{2N}{\sqrt{\pi}}\left[\int_{x_0}^{\infty} e^{-x^2} dx + x_0 e^{-x_0^2}\right] \\ &= \frac{2N}{\sqrt{\pi}}\left[\int_{0}^{\infty} e^{-x^2} dx - \int_{0}^{x_0} e^{-x^2} dx + x_0 e^{-x_0^2}\right] \\ &= \frac{2N}{\sqrt{\pi}}\left[\frac{\sqrt{\pi}}{2} + \int_{0}^{x_0} e^{-x^2} dx + x_0 e^{-x_0^2}\right], \end{aligned}$$

therefore

$$\frac{N_1}{N} = \left[1 + \frac{2}{\sqrt{\pi}} \int_{0}^{x_0} e^{-x^2} dx + x_0 e^{-x_0^2}\right].$$

This allows the number of molecules with speeds above an assigned value to be calculated. The value of the integral

$$\frac{2}{\sqrt{\pi}} \int_{0}^{x_0} e^{-x^2} dx$$

for different values of x_0 is to be found in tables such as those given in Jeans (loc. cit.), Appendix B.

It will be remembered that

$$x_0^2 = \frac{1/2\, mc_0^2}{kT} = \frac{1/2\, mn_1 c_0^2}{n_1 kT},$$

where n_1 is the number of molecules in a gram molecule. Then $n_1 k = R$, and $1/2\, m n_1 c_0^2 = E$, where E is the kinetic energy per gram molecule which the N_1 molecules possess.

Thus $$x_0^2 = \frac{E}{RT}.$$

The usual tables of the integral

$$\int_0^{x_0} e^{-x^2} dx$$

only go up to values of $x_0 = 3$. In chemical calculations it is frequently necessary to calculate the proportion of a total number of molecules for which the value of E/RT is greater than about 30 ; that is to say x_0 is between 5 and 6. For these large values of x_0 the following expansion gives the integral to a quite sufficient degree of approximation :

$$\frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} dx = 1 - \frac{e^{-x_0^2}}{\sqrt{\pi}} \left\{ \frac{1}{x_0} - \frac{1}{2x_0^3} + \frac{3}{4x_0^5} \cdots \right\}.$$

For large values of E/RT we may therefore write

$$\frac{N_1}{N} = \frac{2}{\sqrt{\pi}} e^{-x_0^2} \left\{ x_0 + \frac{1}{2x_0} - \frac{1}{4x_0^3} + \frac{3}{8x_0^5} \cdots \right\}.$$

A much simpler expression is obtained by considering the distribution of velocities in two dimensions instead of three. The distribution law so obtained cannot give numerical results very different from those yielded by the three-dimensional law, and, as it reduces to a very simple algebraic form, it is sometimes an extremely convenient approximation to use in certain cases instead of the true distribution law. It is derived as follows.

The fractional number of molecules which have velocity components between u and $u+du$, and v and $v+dv$ is given by

$$f(u) f(v)\, du\, dv = \frac{1}{\pi a^2} . e^{-\frac{u^2+v^2}{a^2}} du\, dv.$$

Transforming to polar coordinates as before, $u^2 + v^2 = c^2$,

and the element $du\,dv$ has to be replaced by the polar element of area $c\,dc\,d\theta$.

Therefore the number becomes

$$\frac{1}{\pi a^2} \cdot e^{-c^2/a^2} c \cdot dc \cdot d\theta.$$

The total number, dN, of molecules with speeds between c and $c+dc$, irrespective of direction, is obtained by integrating with respect to θ from 0 to 2π. The result is

$$\frac{dN}{N} = \frac{2}{a^2} \cdot e^{-c^2/a^2} \cdot c \cdot dc\,;$$

but $a^2 = \dfrac{2kT}{m}$ and $1/2\, mc^2 = E/n_1$. Also $R = kn_1$,

therefore $$\frac{dN}{N} = \frac{1}{RT} \cdot e^{-E/RT}.$$

Here E is the energy calculated per *gram* molecule.

The proportion of the molecules for which the kinetic energy exceeds E is given by

$$\frac{N_1}{N} = \frac{1}{RT} \int_E^\infty e^{-E/RT} = e^{-E/RT}.$$

For many chemical purposes this simple form of the distribution law, as will be shown later, is actually the correct one to employ.

We will now consider one very important qualitative deduction from it, which relates to the effect of temperature changes on the number of molecules possessing kinetic energy in excess of some specified value. It is convenient to make calculations in terms of gram molecules, the statement that a certain proportion of the molecules have energies greater than, for example, 30,000 calories per gram molecule meaning simply that the individuals among them have energies greater than 30,000 divided by Avogadro's number. At an absolute temperature T the average kinetic energy of translation is $3/2\,RT$. The proportion of molecules which possess kinetic energies greater than

E is $e^{-E/RT}$. This is a very small fraction when E is several times greater than RT. For some fixed value of E the fraction increases very quickly with increase in T. Let us consider as an example what proportion of the molecules of a gas at 1,000° absolute possess, according to this formula, kinetic energies of translation corresponding to 20,000 calories per gram molecule. The fraction is

$$e^{-\frac{20000}{2\times1000}} = 0{\cdot}000045, \text{ or } 0{\cdot}0045\ \%.$$

At an absolute temperature of 2,000°, where the average energy of the molecules is just doubled, the fraction with energies exceeding 20,000 calories becomes

$$e^{-\frac{20000}{2\times2000}} = 0{\cdot}0067, \text{ or } 0{\cdot}67\ \%.$$

It appears, therefore, that an increase of temperature just sufficient to double the average energy causes the proportion of molecules with energies greater than 20,000 calories to increase considerably more than a hundred times.

The result that the proportion of molecules with energies of exceptionally large value increases with temperature at a very much more rapid rate than corresponds to the simple linear increase of the mean energy is of great importance in connexion with the influence of temperature on the rate of chemical reactions.

3. *The Types of Motion executed by the Molecules of a Gas.*

Detailed information about the motion of gas molecules is obtained from the study of specific heats, and to some extent from the study of absorption spectra.

The total translational energy of an ideal monatomic gas is $1/2\, M\bar{u}^2$ per gram molecule, where M is the molecular weight, and, since $pv = RT = 1/3\, M\bar{u}^2$, the kinetic energy is $3/2\, RT$. The increase of kinetic energy of translation per degree is therefore $3/2\, R$, or 2·97 calories. Since this agrees exactly with the observed atomic heat it may be concluded that monatomic gases possess no energy other

than kinetic energy of translation. The atoms therefore are not in rotation.

The principle of the equipartition of energy states that each mechanical degree of freedom possesses the same amount of kinetic energy when statistical equilibrium is established among a large number of bodies, such as gas molecules, which are capable of exchanging energy. The energy associated with the three degrees of freedom of a monatomic gas is $3/2\,RT$ calories per gram molecule, that is to say $1/2\,RT$ for each degree of freedom. From the equipartition principle, therefore, it follows that each degree of freedom of a gas molecule should contribute $1/2\,RT$ calories to the total energy of the gas, and therefore $1/2\,RT$ or 1 calorie, to the molecular heat at constant volume.

Diatomic gases such as oxygen, hydrogen, and nitrogen have a molecular heat of 5 calories over a range of several hundred degrees, whence it is concluded that, in addition to the translational degrees of freedom, they possess two degrees of freedom with respect to rotation. They are capable, therefore, of rotating about two of the three possible axes of rotation. The third axis is evidently, from analogy with monatomic gases, that joining the centres of gravity of the two atoms constituting the molecule.

At higher temperatures the molecular heats of diatomic gases rise above 5 calories, and since this rise takes place at lower temperatures with gases like iodine, in which the atoms are loosely bound together, than with gases like oxygen, in which the binding of the atoms is very strong, it is inferred that intramolecular vibrations come into play.

Eucken discovered that the molecular heat of hydrogen falls at low temperatures from 5 to 3. This and other variations in specific heats with temperature can only be interpreted in terms of quantum dynamics, and the subjection of mechanical processes taking place among gas molecules to quantum principles must be taken into consideration in theories of chemical reaction mechanisms.

A detailed discussion of the quantum theory cannot be given here, but it will be well briefly to illustrate the general nature of its application in the kinetic theory of gases.

This may be done by considering the falling off in the specific heat of hydrogen at low temperatures.

When two molecules collide the rotational energy as well as the translational energy is in general changed by the impact. Molecules of the hydrogen type should be set in rotation by collision with other molecules. If we conceive a large number of hydrogen molecules to exist at $T°$, momentarily devoid of rotations, and to be in a position to draw heat from a reservoir also at $T°$, then, momentarily, the kinetic energy of the gas is $3/2\ RT$ per gram molecule. By collisions the kinetic energy is shared between the degrees of freedom, and the temperature would drop unless the molecules restored their translational energy to its original value by impacts upon the walls of the heat reservoir. The total energy of the gas should therefore reach $5/2\ RT$, and the specific heat should be $5/2\ R$. But, since the specific heat at low temperatures is much less than $5/2\ R$, the total energy evidently does not reach $5/2\ RT$. This is a result of the quantum principle, which states that when a collision takes place between two molecules the angular momenta of the molecules can only change by integral multiples of a definite quantum of angular momentum. The transfer of energy which, according to ordinary dynamical calculations, should occur does not therefore take place at all unless it corresponds to the transfer of at least one quantum of angular momentum. When this condition is fulfilled energy corresponding to this quantum is transferred, and any balance is retained. A molecule without rotational energy is not therefore set in gentle rotation by a gentle impact of a suitable kind. It is incapable of being set in rotation until it receives an impact of such violence, and so directed, that the transfer

of angular momentum calculated according to the ordinary dynamical laws reaches a certain critical value. Thus the contribution it would normally make towards the $5/2\ RT$ is absent.

The law of distribution of rotational energy among the molecules of a diatomic gas receives, therefore, an important modification. Without the quantum laws the distribution of rotational kinetic energy among diatomic molecules with two rotational degrees of freedom would be accurately given by the two-dimensional distribution law derived in the last section. For, rotational velocity being a vector quantity, the derivation of Maxwell's law holds good for rotational velocities. Moreover, only two axes of rotation are effective with diatomic molecules, so that the two-dimensional formula becomes rigidly true. The number N_1 out of a total number N of molecules of which the energy of rotation exceeds E would be given by

$$N_1 = Ne^{-E/RT}.$$

This law does not lose its validity when the quantum restrictions are introduced, but its applicability becomes restricted to the extent that it is no longer possible to assign any desired value to E. The distribution is no longer continuous but discontinuous, and, instead of molecules with every possible angular momentum, there are groups with no angular momentum, one quantum of angular momentum, two quanta, and so on. If the corresponding kinetic energies are $0, E_1, E_2 \ldots$, then $Ne^{-E_1/RT}$ gives exactly the number which have at least one quantum, $Ne^{-E_2/RT}$ gives exactly the number which have at least two quanta. But substitution of values of E between E_1 and E_2 give results which have no physical significance. There will be no objection to the use of this distribution law in calculations relating to chemical critical energies, since these will, from the nature of the case, be quantum values themselves.

Analogous considerations apply to the vibrational energy of molecules. At high temperatures the specific heat of diatomic gases rises above 5 and approaches a value 7, indicating that the vibration of the two atoms within the molecule comes into play, and a new degree of freedom is operative. The kinetic energy of the vibrational degree of freedom is associated with an equal amount of potential energy, since, for small amplitudes, the vibration is nearly simple harmonic. The absence of vibrations at ordinary temperatures, and their gradual appearance at higher temperatures among larger and larger proportions of the molecules of the gas, shows once more the intrusion of the quantum principle.

The quantum law assumes different forms for different kinds of motion. Applied to rotational motions it had the form

$$\text{Angular momentum} = \frac{nh}{2\pi},$$

where n is an integer and h is a universal constant.

Applied to simple harmonic vibrations it becomes

$$\text{Energy} = nh\nu,$$

where n is an integer as before and ν is the frequency of the simple harmonic vibration. h is the same constant as before. These are both comprehended under the general law that for each degree of freedom of any periodic motion

$$\int pdq = nh,$$

where p is a momentum coordinate and q the corresponding space or position coordinate, and the integral is taken over a complete period of the motion.

These special cases are also deducible from Heisenberg's more general quantum mechanics, but with slight changes of form.

The vibrations of diatomic molecules being approximately simple harmonic, the quantum law takes the second

form, namely that the molecule must gain or lose vibrational energy in integral multiples of $h\nu$, where ν is the natural frequency of the vibration. Since the frequency of a simple harmonic vibration is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\text{restoring force per unit displacement}}{\text{mass}}},$$

it follows that the greater the restoring force, that is, the more tightly bound the atoms, the greater the frequency, the greater therefore the quantum, and thus the smaller the proportion of the molecules which, at a given temperature, can acquire it. Thus stable molecules like hydrogen are not set in vibration until high temperatures are reached, whilst unstable molecules like iodine have a small quantum and begin to possess vibrational energy at much lower temperatures. Thus iodine, the instability of which is shown by the very considerable thermal dissociation at 1,000°, has already at ordinary temperatures a specific heat well above 5.

The importance of all this in connexion with the theory of chemical change lies in the fact that molecules are not set in vibration by collision unless the impact is of a certain critical degree of violence: then a quantum of energy is taken up. The law of distribution of vibrational energies is discontinuous in the same manner as that of the distribution of rotational energies. Its form depends on the number of degrees of freedom with which the molecules vibrate. For one internal degree of freedom the law takes the form that the number with energy greater than E is proportional to $e^{-E/RT}$.

The more complex rotations and vibrations of polyatomic molecules are subject to the same principles, and distribution laws of the same kind apply, as will be shown in the following section.

The study of the absorption and emission spectra of gases confirms, and in some respects extends, the information about molecular motions provided by the considera-

tion of specific heats. The whole subject is discussed by Sommerfeld, *Atombau und Spektrallinien*, fourth edition. We will confine ourselves to a statement of the results having a direct bearing on those aspects of molecular mechanics which may be important in the consideration of chemical change.

The kind of spectrum known as a band spectrum is that which is emitted by a molecule and not by an isolated atom or ion. The bands are not continuous, but consist of a large number of fine lines, which are more closely packed together towards the ' head ' of the band.

Three kinds of phenomenon play their part in the production of these band spectra, electronic changes within the molecule, vibration of the atoms in the molecule, and rotation of the molecule as a whole. The electronic processes give rise to emission or absorption in the visible and ultra-violet regions, the intra-atomic vibrations to bands in the short infra-red region at wave-lengths of the order of several μ, and the molecular rotations to bands in the far infra-red at wave-lengths of the order 100 μ.

According to the quantum theory of spectra the emission of each frequency depends upon a passage of the molecule from a condition of greater energy to one of smaller energy, or from what is called a higher energy level to a lower energy level. The energy so set free is converted by whatever mechanism it is which transmits radiation through space into waves, the frequency of which is determined by the relation $h\nu$ = energy set free by the passage of the emitting system (in this case the molecule) from the higher to the lower energy level.

Knowing the value of h ($6{\cdot}55 \times 10^{-27}$ erg-seconds), and the value of Avogadro's number, it is possible to calculate the energy changes per gram molecule associated with the various emission or absorption processes occurring within the molecule. Those producing the rotation bands in the far infra-red correspond to a few hundred calories per gram

molecule, those producing the short infra-red vibration bands to something of the order of some thousands of calories, and the visible bands to some tens of thousands of calories, increasing to over a hundred thousand in the ultra violet.

The rotation bands correspond to changes in the number of quanta of angular momentum possessed by the molecule ; these represent the smallest energy change.

The vibration bands correspond to much larger energy changes. Since changes in the number of quanta of vibrational energy may be accompanied by simultaneous changes in rotational quanta, a single change in the vibrational state of the molecule may give rise to a number of bands corresponding to various rotational changes. As the energy changes involved in the rotational jumps are small compared with those involved in the vibrational jumps, there are produced a number of nearly equidistant lines, the spacing of which is small compared with the frequency of the central one. The frequency difference between the different rotational components of a vibration band gives the energy corresponding to a quantum of angular momentum. From this the moment of inertia of the molecule may be found. In the same way the superposition of vibrational and rotational changes on the electronic orbital changes produces a fine structure of the bands in the visible region, from which both the moment of inertia of the molecule and the frequency of the intramolecular vibrations can, in principle, be calculated.

In this way the study of spectra gives even more detailed information than the consideration of specific heats. It is found that infra-red rotation and vibration spectra are only given by those molecules, such as HCl, which are composed of a negative and a positive portion. Strictly homo-polar molecules do not absorb in the infra-red, although the theory of specific heats, and the analysis of the visible spectrum, leave no doubt about the existence of

molecular rotations and, in such cases as iodine, of vibrations. We may note, therefore, the important conclusion that a molecule of homo-polar type, even though it possesses an appropriate natural frequency, is apparently not stimulated by radiation to execute either rotations or vibrations. Electronic processes within it are, however, influenced by radiation of the appropriate wave-length.

4. *The Distribution of Energy among Complex Molecules.*

In section 2 the distribution of speeds among the molecules of a gas was discussed. According to Maxwell's law the fractional number of molecules possessing energies corresponding to velocity components between u and $u+du$ is given by the expression

$$\frac{dN}{N} = \frac{1}{\alpha\sqrt{\pi}} \cdot e^{-u^2/\alpha^2} \cdot du.$$

Since $\alpha^2 = 2/3\,\bar{u}^2$ and $1/3\,n_1 m\bar{u}^2 = RT$, this becomes

$$\frac{dN}{N} = \frac{1}{\sqrt{\pi}\sqrt{\frac{2RT}{n_1 m}}} \cdot e^{-\frac{1/2\,n_1 mu^2}{RT}} \cdot du;$$

but
$$1/2\,n_1 mu^2 = E,$$
$$n_1 mu\,du = dE,$$
$$du = \frac{dE}{\sqrt{n_1 m}\sqrt{2E}},$$

thus
$$\frac{dN}{N} = \frac{E^{-1/2}}{2\sqrt{\pi RT}} \cdot e^{-E/RT} \cdot dE.$$

This applies to velocities between u and $u+du$. Velocities between $-u$ and $-(u+du)$ also correspond to kinetic energies between E and $E+dE$. Thus the fractional numbers of molecules with kinetic energies between E and $E+dE$ in *one degree of freedom* is given by twice the above expression, namely by

$$\frac{dN}{N} = \frac{E^{-1/2}}{(\pi RT)^{1/2}} \cdot e^{-E/RT} \cdot dE.$$

If the proof in section 2 is studied carefully, it will be seen that there is nothing in the derivation of this law which could not be applied *mutatis mutandis* to any kind of energy representable in the form mx^2. For, apart from general considerations of probability, the only condition assumed in the proof was that the total kinetic energy could be expressed as a sum of three quadratic terms—equation 1 of section 2 multiplied by $1/2m$ expresses this condition.

Thus the expression just recorded for $\frac{dN}{N}$ need not be restricted to kinetic energy of translation but may be applied to any form, since rotational energy and vibrational kinetic energy may be expressed in a quadratic form, as may also the potential energy associated with simple harmonic motion.

Now let us consider a molecule of complex structure; the total energy may be made up in many different ways. Let each kind of energy, potential and kinetic, in each degree of freedom be representable by a 'square term' and let there be n such terms. The chance of an energy between Q and $Q+dQ$ in one particular term, e.g. one particular component of translational motion, or a particular vibration, is given by

$$\frac{Q^{-1/2}}{(\pi RT)^{1/2}} . e^{-Q/RT} . dQ.$$

The chance that simultaneously the energy in one term is between Q_1+dQ_1 and in another term between Q_2+dQ_2 is the product of the expressions for Q_1 and Q_2, namely

$$\frac{1}{\pi RT} . Q_1^{-1/2} . e^{-Q_1/RT} dQ_1 \times Q_2^{-1/2} . e^{-Q_2/RT} . dQ_2.$$

Suppose $$Q_1+Q_2 = E.$$

We may now inquire what is the chance of a total energy between E and $E+dE$ in the two terms together without reference to how it is shared between them. This is given

by putting $Q_2 = E - Q_1$ and then integrating with respect to Q_1 from 0 to E. Thus

$$\frac{dN}{N} = \frac{1}{\pi RT}\int_0^E Q_1^{-1/2} \cdot e^{-Q_1/RT} dQ_1 (E - Q_1)^{-1/2} \cdot e^{-(E-Q_1)/RT} \cdot dE.$$

$$= \frac{e^{-E/RT} \cdot dE}{\pi RT}\int_0^E Q_1^{-1/2}\,(E - Q_1)^{-1/2}\, dQ_1.$$

The method of integration will be found in any text-book of the Integral Calculus which deals with Gamma Functions. The value of the expression under the integral sign is π.

Thus
$$\frac{dN}{N} = \frac{e^{-E/RT} \cdot dE}{RT}.$$

If we now wish for the number of molecules with energy greater than E in the two terms jointly we integrate with respect to E from E to ∞ and obtain

$$\frac{1}{RT}\int_E^\infty e^{-E/RT} \cdot dE = e^{-E/RT}.$$

This expression is most important: it is the result already obtained on page 12 for the probability of an energy greater than E in two translational terms. But its importance lies in the fact that it also represents the chance of an energy greater than E in any two terms jointly, and applies to the total rotational energy of a diatomic molecule, or to the total energy, kinetic plus potential, in a single vibration, where the degree of freedom involves two square terms. It will be found of importance in the next chapter.

In a similar way we may represent the fractional number of molecules for which the total energy in n terms is between E and $E + dE$ by the expression

$$\frac{1}{(\pi RT)^{1/2n}}\int_0^E \int_0^E \ldots Q_1^{-1/2} \cdot e^{-Q_1/RT} \cdot dQ_1 \times Q_2^{-1/2} \cdot e^{-Q_2/RT} \cdot dQ_2 \ldots$$

$$\ldots \{E - (Q_1 + Q_2 \ldots)\}^{-1/2} \cdot e^{-\{E-(Q_1+Q_2\ldots)\}/RT} \cdot dE,$$

where
$$Q_1 + Q_2 + \ldots = E.$$

This is because the total energy can be made up with anything from 0 to E in each term, subject to the condition that the total does not exceed E; and in general the chance of Q_1 in one term, Q_2 in the next, and so on, is the product of the separate probabilities.

The integral is equal to

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

The chance that a molecule possesses energy greater than E is

$$\frac{1}{\Gamma(\frac{1}{2}n)\,(RT)^{1/2\,n}} \cdot \int_E^\infty e^{-E/RT} \cdot E^{(1/2\,n-1)} \cdot dE.$$

This integral is equal to

$$e^{-E/RT}\left[\frac{1}{\lfloor\frac{1}{2}n-1}\left(\frac{E}{RT}\right)^{1/2\,n-1} + \frac{1}{\lfloor\frac{1}{2}n-2}\left(\frac{E}{RT}\right)^{1/2\,n-2} + \ldots + 1\right].$$

When E/RT is large, as in most chemical applications, we may take the first term only of the expansion

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

This gives the chance of a total energy in the whole n terms which exceeds E without any restriction as to how the energy is shared among the separate terms.

This expression will be found of importance in dealing with chemical changes of complex molecules with many internal degrees of freedom. Each internal vibration contributes two quadratic terms, one for the kinetic energy and one for the potential energy. It should be realized that when we are dealing with the statistics of a large number of molecules the kinetic energy and the potential energy of a vibration are quite independent quantities. Some molecules at a given instant may have a large kinetic energy and a small potential energy and vice versa.

The following summary of formulae is given for reference.

(i) Out of N molecules the number N_1 possessing translational velocities greater than c_0 is given by the equation

$$\frac{N_1}{N} = 1 + \frac{2}{\sqrt{\pi}} x_0 e^{-x_0^2} - \frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} dx,$$

where

$$x_0^2 = \frac{1/2\, mc_0^2}{kT} = \frac{1/2\, n_1 mc^2}{n_1 kT} = \frac{E}{RT},$$

E being the energy of a gram molecule when each individual molecule has speed c_0. The value of R is 1·98 calories per gram molecule.

$$n_1 = 6{\cdot}06 \times 10^{23}.$$

(ii) The value of the integral

$$\frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} dx$$

is given in tables. For values of x_0 greater than unity it is given by the expansion

$$\frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} dx = 1 - \frac{e^{-x_0^2}}{\sqrt{\pi}} \left\{ \frac{1}{x_0} - \frac{1}{2x_0^3} + \frac{3}{4x_0^5} \cdots \right\},$$

hence for values of E/RT several times greater than unity

$$\frac{N_1}{N} = \frac{2}{\sqrt{\pi}} e^{-x_0^2} \left\{ x_0 + \frac{1}{2x_0} - \frac{1}{4x_0^3} + \frac{3}{8x_0^5} \cdots \right\}.$$

(iii) For a distribution of energy in n ' square terms ' the fractional number of molecules possessing a total energy greater than E is given by

$$\frac{N_1}{N} = \frac{e^{-E/RT} (E/RT)^{1/2\, n - 1}}{\lfloor 1/2\, n - 1}.$$

(iv) The fractional number of molecules with a joint energy greater than E in two terms is given by

$$\frac{N_1}{N} = e^{-E/RT}.$$

5. *The mean free path and the collision number.*

Knowledge of the number of collisions taking place in unit time between the molecules of a gas is obviously of

great importance in the consideration of bimolecular chemical reactions. It is found as follows.

Let the diameter of a molecule be σ. If we regard σ as a value of the effective diameter rather than a quantity with a strict geometrical significance, we may take a simple mechanical view of a molecular collision and regard two molecules as entering into collision whenever their centres approach to within a distance σ of each other.

For the calculation of the number of collisions suffered by a given molecule all the other molecules can be regarded as stationary, and the given molecule imagined to be moving about among them with a definite velocity r. This is equal to the mean relative velocity, a quantity which is easily shown to be $4/3\ \bar{u}$. If the given molecule is further assumed to have a radius, instead of a diameter σ, all the others may be regarded as points. In one second the given molecule sweeps out a cylindrical space of length $4/3\ \bar{u}$ and cross-section $\pi\sigma^2$, the volume of which is $4/3\ \pi\sigma^2\bar{u}$. In this space $4/3\ \pi\sigma^2\bar{u}n$ point molecules will have been encountered, n being the number of molecules in a cubic centimetre. The cylinder will not have been straight but zigzag. $4/3\ \pi\sigma^2\bar{u}n$, therefore, gives the number of collisions suffered per second by any molecule. But each molecule undergoes the same process, so that the total number entering into collision in a second in one cubic centimetre is $4/3\ \pi\sigma^2\bar{u}n^2$. The number of collisions is exactly half the number of molecules entering into collision, since two molecules participate in each impact. The factor 4/3 requires, moreover, slight correction when allowance is made for the distribution of velocities in accordance with Maxwell's law. The corrected value for the number entering into collision is $\sqrt{2}\,\pi\sigma^2\bar{u}n^2$.

The value of σ is obtained from viscosity data and has been determined for a great many gases by Rankine. It is always of the order 10^{-8} cm.

The viscosity is directly connected with the mean free

path l. The number of collisions in unit time is $\bar{u}/l$ for each molecule, neglecting the difference between the mean velocity and the root mean square velocity. Thus $\frac{\bar{u}}{l} = \sqrt{2}\pi\sigma^2\bar{u}n$. The mean free path is connected with the viscosity by the relation

$$\eta = 1/3\,\rho\bar{u}l, \quad \rho \text{ being the density.}$$

Rankine* has made numerous accurate measurements of η and calculated the molecular diameters from them. For calculating the number of molecules entering into collision in a gas it is therefore convenient to use Rankine's tables of σ and the expression $\sqrt{2}\pi\sigma^2\bar{u}n^2$.

It might be objected that this formula is based upon assumptions about the nature of a collision which may not correspond to reality, and that therefore it cannot be an accurate one. This is not a real difficulty. Rankine's values of σ are obtained by use of the formula in question, the number of collisions being found from the mean free path which, in its turn, is derived directly from the viscosity. Thus the ordinary method of calculating the collision number from tables of σ for different molecules is in effect a direct calculation from the viscosity, the introduction of σ being merely a convenience but essentially irrelevant. In the theory of viscosity nothing whatever is assumed about the mechanical nature of a collision, whether, for example, it can be treated as an elastic impact of smooth spheres, or whether it should rather be regarded as analogous to the passage of a comet round the sun.

Some of Rankine's values are given below.

Gas	*Molecular radius*	*Gas*	*Molecular radius*
Chlorine	$1{\cdot}60 \times 10^{-8}$ cm.	Argon	$1{\cdot}28 \times 10^{-8}$ cm.
Bromine	$1{\cdot}71 \times 10^{-8}$	Krypton	$1{\cdot}38 \times 10^{-8}$
Iodine	$1{\cdot}88 \times 10^{-8}$	Xenon	$1{\cdot}53 \times 10^{-8}$

* *Proc. Roy. Soc.*, 1910, A, **83**, 516; 1910, **84**, 181; 1912, **86**, 162; 1915, **91**, 201. *Phil. Mag.*, 1915, **29**, 552.

The question of molecular diameters is also dealt with by Sutherland, who gives a table of values.

It is sometimes necessary to calculate the number of collisions suffered by a molecule during the time that it has undergone a linear displacement x from its original position, x being measured in a straight line, and taking no account of the zigzag path actually traversed.

Einstein, in a paper dealing with the Brownian movement,† shows that the mean displacement is proportional not to the time, but to the square root of the time, being given by

$$\bar{x}^2 = 2Dt,$$

where t is the time and D the coefficient of diffusion.

The coefficient of diffusion of gas molecules can be calculated from the kinetic theory: the simplest formula, which, however, is not quite exact, is due to Meyer.

$$D = \eta/\rho = 1/3\,\bar{u}l,$$

whence

$$\bar{x}^2 = 2/3\,\bar{u}l\,.\,t.$$

Meyer's formula is only approximate, but the error introduced by its use would not affect the order of magnitude of the result.

Smoluchowsky‡ finds the expression

$$\bar{x}^2 = \frac{4}{3\pi}\,.\,\bar{u}l\,.\,t$$

which only differs from the above by a small numerical factor.

Now let Z be the number of collisions suffered during the displacement $\bar{x}$, then Zl is the total length of the zigzag path. Thus $Zl = \bar{u}t$.

Therefore

$$Z = \frac{\bar{u}t}{l}$$

$$= \frac{\bar{u}\,.\,\bar{x}^2}{2lD} \quad \text{(from Einstein's formula)}$$

* *Phil. Mag.*, 1910, **19**, 25. † *Ann. Phys.*, 1905, [IV], **17**, 549.
‡ *Bull. Intern. Acad. Cracovie*, 1906, 202.

$$= \frac{3\bar{x}^2}{2l^2} \text{ (from Meyer's formula for } D)$$

$$\text{or} \quad Z = \frac{3\pi\,\bar{x}^2}{4l^2} \text{ (Smoluchowsky's formula).}$$

These formulae are useful in calculating the number of collisions suffered by a molecule in the gas phase before it reaches the wall of the vessel at a distance $\bar{x}$ from the original position of the molecule. The difference in the numerical factor is unimportant in most applications.

When the diffusing molecule is surrounded by a mixture of gases a more complicated expression for D is required (see Jeans's *Dynamical Theory of Gases*).

GENERAL CONSIDERATIONS ABOUT THE NATURE OF CHEMICAL CHANGE

Rate of chemical change is most profitably regarded from the point of view of molecular statistics. In chemical changes which proceed with finite speed a certain fraction only of the molecules become reactive in each second, and it is evident that these must be in some state which differs from the average condition. The nature of this exceptional state remains to be discovered. It is not possible to follow the history of individual molecules, but the kinetic theory affords information of a statistical kind about such matters as the number of molecules entering into collision in unit time, and the number of molecules which at any moment are endowed with abnormally great or abnormally small speeds, or with a number of quanta of angular momentum, or vibrational energy, above the average. Correlation of these numbers with the number of molecules actually observed to undergo transformation seems to offer the best prospect of illumination about the conditions governing the occurrence of chemical changes.

Since chemical transformation depends upon the entry of molecules individually into an exceptional condition it

is useless to seek any direct connexion between reaction velocity and purely thermodynamic quantities such as the affinity. At one time the equation

$$\text{Reaction velocity} = \frac{\text{Chemical affinity}}{\text{Chemical resistance}}$$

was used in a qualitative and descriptive way, but it is really rather misleading, because there is no correlation whatever between chemical affinity, as measured by the maximum work, and speed of reaction. A cursory survey of some of the most familiar systems, such as hydrogen and oxygen on the one hand, and hydrogen and iodine on the other, seems indeed almost to reveal an inverse relationship between affinity and speed. But no relationship of any kind is to be expected. Affinity depends solely upon initial and final states. Velocity of reaction, on the other hand, depends upon the nature of some specific intermediate reactive state in which the molecules become capable of rearrangement. This bears no more relation to the initial and final states than the height of a pass bears to the relative levels of the valleys which it separates.

It is relevant at this point to consider two matters, first the nature of chemical union, and secondly what kinds of exceptional condition molecules are capable of assuming under the influence of various agencies.

In terms of the electronic theory two kinds of chemical union have to be distinguished, namely polar union and non-polar union. To understand the nature of these, certain facts about the disposition of electrons within the atom have to be known. Each neutral atom contains a number of electrons equal to its atomic number. Certain arrangements of these, recurring periodically and recognized in the atoms of the inert gases, form stable 'closed' systems. The constitution of each completed stable electronic system is governed by a principle called the Pauli principle.

Each electron in an atom possesses potential and kinetic energy : if it changes its state, the energy of the atom as a whole changes, and radiation may be emitted or absorbed. According to the Planck-Bohr principle the frequency of the corresponding spectral line is given by the difference in energy divided by Planck's constant h, a law which at once interprets the well-known Ritz combination principle of the additive nature of spectral frequencies. Thus the study of spectra reveals the existence of various 'energy levels' in the atom. To explain all the various energy levels indicated by the fine structure of spectral lines each electron in an atom has to be assigned four quantum numbers. The Pauli principle states that no two electrons in an atom can have all four quantum numbers the same. Taking the simple Bohr picture of the atom, the four quantum numbers would determine the major axis of the elliptical orbit, the eccentricity, the orientation of the orbit, and the spin of the electron. For a given major axis, i.e. principal quantum number, the Pauli principle fixes the total number of electrons possible, and thus determines the structure of the periodic system.

Polar combination comes about as a result of the tendency of atoms with a few electrons more than a completed 'inert gas' group to lose them, and of those with a few less to gain electrons. Lithium possesses the two electrons of helium plus a third which forms the beginning of a new system, and which it readily loses, forming a lithium ion. Fluorine, on the other hand, requires an electron to complete a 'neon' structure. If fluorine and lithium are brought together an electron passes from one to the other and both assume the form of ions with stable electronic configurations. This is the real chemical change. The purely electrostatic attraction between the oppositely charged ions is all that constitutes the polar linkage.

Non-polar linkages are formed by the sharing of a pair of electrons by two atoms. Fluorine, lacking in the atomic

form one electron to complete the stable neon-like structure, combines with another fluorine atom to form the molecule F_2, in which two electrons are held in common by the two atoms.

It is clear that there is a quite fundamental difference between these two kinds of union, which is of great importance for chemical kinetics.

The polar linkage can hardly be called a linkage at all, and where a simple rearrangement of polar linkages occurs, as in a reaction of the type $AgNO_3 + NaCl = AgCl + NaNO_3$, the rate of chemical change is determined simply by the rate at which the silver ions and chlorine ions can reach and attach themselves to the lattice of the solid silver chloride. For this reason all purely ionic reactions are practically instantaneous unless the concentrations of the ions are very small indeed.

Reactions in the gaseous state, and naturally also many reactions in solution, nearly always involve rearrangement of non-polar linkages, and this is a much profounder change. It should also be borne in mind that a reaction such as that taking place between hydrochloric acid and sodium thiosulphate is not truly ionic, although all the substances initially involved are ionized, because there is formation of free sulphur and this process necessitates the rearrangement of non-polar linkages within the thiosulphate ion itself.

Since the non-polar linkage involves the fusion of two atoms into one structure to a much greater extent than the polar linkage, it appears probable that a rearrangement of non-polar linkages will usually only take place if a certain amount of energy is first communicated to the molecule. This communication of energy is called activation, and in subsequent chapters will be seen to be one of the most important factors is determining chemical transformation.

The dynamics of a chemical bond can only be worked

out when some picture has been formed of what constitutes the sharing of an electron by two atoms. The picture of the atom presented by the simple Bohr theory was that of electrons describing orbits round the atomic nucleus, and the obvious interpretation of the sharing process was that the electron held in common encircled both nuclei. The idea of the binuclear orbit has not, however, been a very fruitful one.

In the meantime the development of wave mechanics and its application by Schrödinger to atomic theory has given a picture of the atom which is better adapted for quantitative calculations. In the Schrödinger atom the electron no longer appears as a point charge but as a continuous 'cloud' of electricity, and its motions are represented by an equation having formal similarity to the equations which describe wave motion in classical physics. The possible quantum states appear as various solutions of this equation. To avoid the physical difficulty of the non-discrete character apparently attributed to the electron, a statistical interpretation can be given to the picture, Schrödinger's electric density at any point being taken to represent the probability that the electron in any given atom shall be at that point.

The great advantage of this method of describing the state of affairs is that the mutual action of two atoms, which in the earlier forms of the quantum theory was very indeterminate, can be calculated by combining their wave equations, in a manner more or less analogous to that which would be used to calculate the resonance of two oscillating electric circuits.

The result of such calculations is to show that two neutral hydrogen atoms,* for example, can react upon one another in two ways. One of the solutions gives repulsion at all distances, but the other makes the mutual potential

* Heitler and London, *Z. Physik*, 1927, **44**, 455 ; ' Quantentheorie und Chemie,' *Leipziger Vorträge*, 1928, p. 59.

energy a minimum for a certain distance between the two atoms. There is thus a position of equilibrium at this point, and the two atoms can combine to form a molecule. (Incidentally it may be noted that of the two solutions possible, the 'symmetrical' and 'anti-symmetrical', the first is the one which allows attraction. It would be inconsistent with the Pauli principle if the two electrons which are 'symmetrically' coupled had not opposite 'spins'. Since only two values of the spin are possible, it can be shown that combination of H_2 with a third atom of hydrogen is 'forbidden' by the Pauli principle, which also accounts for the fact that helium forms no molecule.)

This interpretation of the non-polar chemical bond is formally consistent with the older idea of the atoms bound by a 'quasi-elastic' force. When displaced from their position of equilibrium the two atoms will vibrate. This vibration is the one which, as has been mentioned, reveals its existence in the specific heat and in the band spectrum of a molecule.

If now the interaction of a molecule AB with an atom C is considered, it may happen that the combination AC is more strongly linked than AB. If A, B, and C were put together AC would be formed. But if AB is first formed and then C allowed to approach, the fact that A and B in AB are already in a position of minimum potential energy may render the rearrangement to give AC and B impossible without the previous separation of A and B to some extent. This is called activation, and obviously demands the addition to the molecule AB of a certain number of quanta of vibrational energy. In the study of band spectra it appears clearly that the number of vibrational quanta possessed by a molecule may increase steadily up to the point where the molecule dissociates into atoms. Some intermediate number, not sufficient to bring about dissociation, is enough to loosen AB and render it open to attack by C.

It appears obvious from this that the vibrational quanta are the significant ones in the process of chemical activation.

Other forms of energy may, however, be communicated to molecules, as the theory of spectra shows. Electronic activation is produced by visible light; and rotational quantum changes of the molecule occur simultaneously with the vibrational changes.

The rotational quanta are too small to be of much importance in chemical processes. The quanta involved in electronic activation are, however, much greater than the vibrational quanta. Nevertheless they do not directly affect the linking of the atoms in the molecule, and indeed molecules may be activated by electronic quanta considerably greater than the chemical heat of dissociation without falling apart into their constituent atoms.

The fact that chemical change can be induced by visible light shows that the energy of electronic activation can under appropriate circumstances find its way to the critical position in the molecule, but from what has been said it should be clear that no direct connexion exists between the magnitude of light quanta and their possible chemical effects. This statement is borne out by all the facts of photochemistry.

A mechanism by which electronic energy is sometimes made available for chemical purposes is that which occurs in the so-called 'Stoss zweiter Art', or 'collision of the second kind'. Cario and Franck* found that on exposure of a mixture of mercury vapour and hydrogen to the mercury line 2536·7 Å, the absorbed light stimulated the mercury atoms electronically, and that the excited mercury atoms were able on collision with hydrogen molecules to resolve them into atoms. The atomic hydrogen so produced was detected by its great chemical activity. A number of other examples of this phenomenon were found

* *Z. Physik*, 1922, **21**, 161.

by H. S. Taylor and Marshall,* who made the hydrogen activated by mercury react with ethylene, carbon monoxide, and nitrous oxide at room temperature. If mercury hydride is formed in these experiments, the fact does not alter the principle of the 'Stoss zweiter Art'.

* *J. Physical Chem.*, 1925, **29**, 1140.

II

BIMOLECULAR REACTIONS

GENERAL REMARKS

BIMOLECULAR reactions constitute in some ways the most important class of changes taking place in the gaseous phase, and the study of them leads to simple and illuminating results. Before we proceed to the discussion of special instances certain matters of a general nature must be dealt with.

Homogeneous and heterogeneous reactions.

Many reactions which at first sight might be thought to be reactions in the gaseous phase are found on closer investigation to take place entirely on the walls of the containing vessel. This is so general a phenomenon that true gaseous reactions are the exception rather than the rule. A true gas reaction is called a homogeneous reaction; a reaction taking place at the surface of a solid, and in particular on the walls of the containing vessel, is called a heterogeneous reaction. A reaction may be partly homogeneous and partly heterogeneous. In very many instances, however, the velocity of the heterogeneous reaction is relatively so great that the homogeneous reaction remains an insignificant fraction of the total change throughout the whole range of temperature where measurement of reaction velocity is practically possible. This circumstance renders the detection and measurement of the homogeneous part difficult or impossible. Examples of the very large number of predominantly heterogeneous changes are the union of carbon monoxide and oxygen in vessels of glass and of quartz, the thermal decomposition of the hydrides of arsenic and antimony, the thermal decomposition of ammonia, of phosphine, and the interaction of nitric oxide with carbon monoxide. In all these

reactions, the progress of which has been observed in vessels of either glass, quartz, fused silica, or porcelain, the wall reaction predominates overwhelmingly at all temperatures where the speed is not too great to be measured.

The first necessity, therefore, in an experimental investigation is to determine whether the reaction dealt with is homogeneous or heterogeneous. The criterion of a homogeneous reaction is that the velocity is independent of the area of the surface of the vessel in which the reacting gases are contained; that of a heterogeneous reaction that the velocity is, for vessels of the same material and volume, directly proportional to the internal area.

If the volume, as well as the surface area, is varied the velocity of reaction should be proportional to the ratio surface/volume. The usual way of varying this ratio is to have vessels of different shapes and volumes, a spiral-shaped tube having, for example, a considerably greater ratio of surface to volume than a spherical bulb. Owing to the fact, however, that even with vessels of the most varied shapes the surface/volume ratio can only be varied two or three times, this method is not a very sensitive one for detecting a heterogeneous reaction occurring to a small extent concurrently with a homogeneous reaction. It is frequently desirable to obtain information as to whether a heterogeneous reaction accounts for any fraction of a change which is known to be at least predominantly homogeneous, and the method is to introduce into the reaction vessel, in the form of powder, a considerable quantity of the material of which the vessel is made. In this way a very large increase of surface is produced, and a heterogeneous reaction taking place to the extent of a few per cent. only of the total change can be detected.

If the homogeneous and heterogeneous reactions proceed at rates of the same order it is found that the curve obtained by plotting velocity of reaction against the ratio surface/volume does not pass through the origin. The

velocity corresponding to zero value of this ratio is that of the homogeneous part of the reaction.

Determination of the order of gaseous reactions.

Of the different standard methods for determining the order of chemical reactions the one on which most reliance can be placed, in dealing with gaseous changes, is that depending upon variation of the initial pressure.

For a unimolecular reaction, if a is the initial concentration and $(a-x)$ that after time t,

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

whence

$$kt = \log\frac{a}{a-x},$$

and for a bimolecular reaction with equivalent quantities initially present

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

whence

$$kt = \frac{x}{a\,(a-x)}.$$

Taking the time of half change, that is the time required for the concentration to fall to half its initial value, as τ, then for the unimolecular reaction $\tau = 1/k \,.\, \log 2$, and for the bimolecular reaction $\tau = 1/ka$. Thus the ' half-life ' in the unimolecular reaction is independent of the initial concentration, while in the bimolecular reaction it is inversely proportional to it. In general it is easily shown that in a reaction of the nth order, following the equation $-dc/dt = kc^n$, the time of half change, or half-life, is inversely proportional to the $(n-1)^{\text{th}}$ power of the initial concentration. In dealing with gases concentration is proportional to the partial pressure if the volume of the system remains constant.

The certainty of this criterion is illustrated by the two examples given below. The thermal decomposition of

nitrous oxide is kinetically bimolecular; that of phosphine, although really a heterogeneous reaction, follows the unimolecular law.

Thermal decomposition of nitrous oxide

Initial pressure (millimetres)	Half-life in seconds
296	255
139	470
52·5	860

Thermal decomposition of phosphine

Initial pressure	Half-life
707	84
79	84
37·5	83

Attempts to judge from the constancy or otherwise of k would often give much less unequivocal results, since k sometimes shows a drift in value, caused by the catalytic action of the products, or the imperfection of the experimental arrangements almost inevitable in work at high temperatures, or other factors.

The Arrhenius Equation for the Variation of Reaction Velocity with Temperature.

In a balanced reaction, where the velocity constant of the direct reaction is k_1 and that of the reverse reaction is k_2, the variation with temperature of the equilibrium constant K, which equals k_1/k_2, is given by the van't Hoff equation

$$\frac{d \log K}{dT} = \frac{Q}{RT^2},$$

where Q is the heat of reaction.

Since $$\log K = \log k_1 - \log k_2$$

$$\frac{d \log k_1}{dT} - \frac{d \log k_2}{dT} = \frac{Q}{RT^2},$$

and therefore $$\frac{d \log k_1}{dT} = \frac{A_1}{RT^2} + B$$

and $$\frac{d \log k_2}{dT} = \frac{A_2}{RT^2} + B,$$

where $$A_1 - A_2 = Q.$$

It does not follow from this that B is independent of temperature, but Arrhenius found empirically that the variation of the velocity constant, k, with temperature can be expressed satisfactorily by the simplified equation

$$\frac{d \log k}{dT} = \frac{A}{RT^2} \quad \text{or} \quad \log k = C - A/RT.$$

The method of testing this equation is to plot the logarithm of the velocity constant against the reciprocal of the absolute temperature. A straight line is obtained if the equation is satisfied. The slope of the line gives the value of A. The quantity A has the dimensions of energy, and if R is taken as 1·98 calories, then A is measured in calories per gram molecule.

Arrhenius* interpreted the equation by suggesting that there exists an equilibrium between normal molecules and what he called 'active' molecules, and that only the active molecules undergo chemical change. The active molecules were supposed to be formed endothermically from the normal molecules. The rapid increase in the rate of chemical change with rising temperature is therefore caused by the shift in the equilibrium between the two kinds of molecules, and, since k is proportional to the number of active molecules, the equation $d \log k/dT = A/RT^2$ represents this shift in the ordinary thermodynamic way. A is the heat absorbed in the formation of an active molecule from a normal one and is therefore called the heat of activation.

This view, though indefinite, is accepted as essentially correct. It is, however, no longer believed that anything of the nature of a tautomeric change is involved in the conversion of an ordinary molecule into an active one ; it

* *Z. physikal. Chem.*, 1889, **4**, 226.

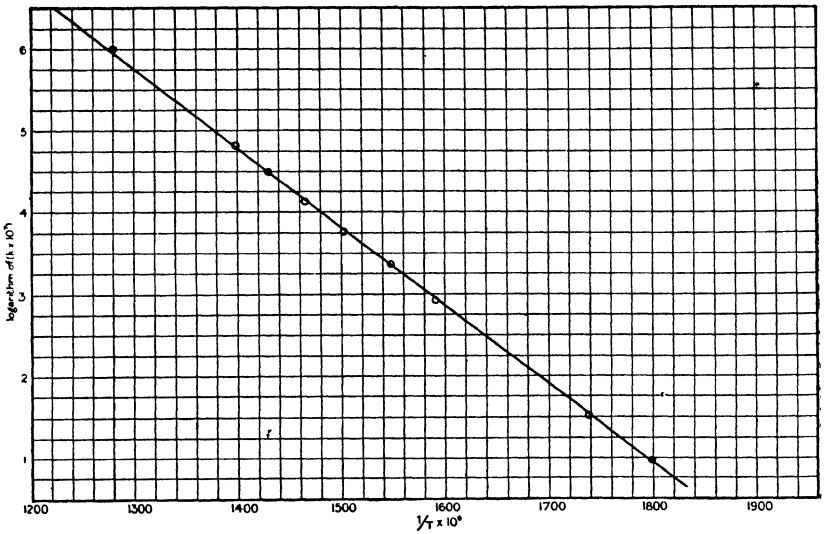


FIG. 1 a.—Influence of temperature on the rate of decomposition of hydrogen iodide.

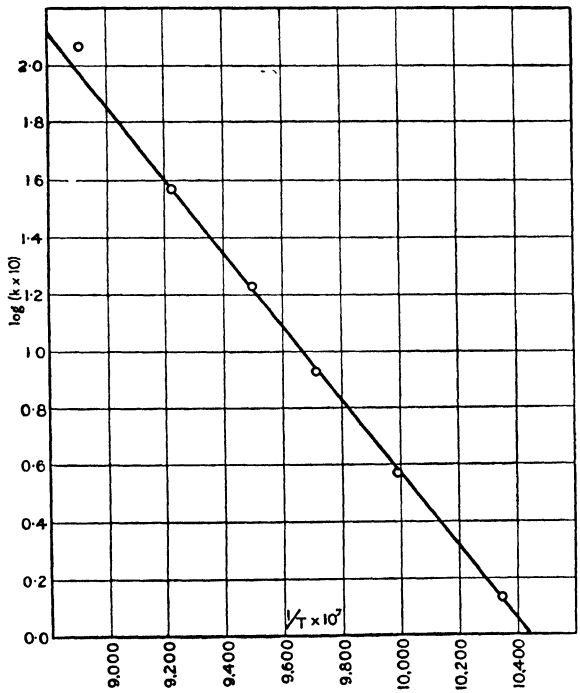


FIG. 1 b.—Influence of temperature on the rate of decomposition of nitrous oxide.

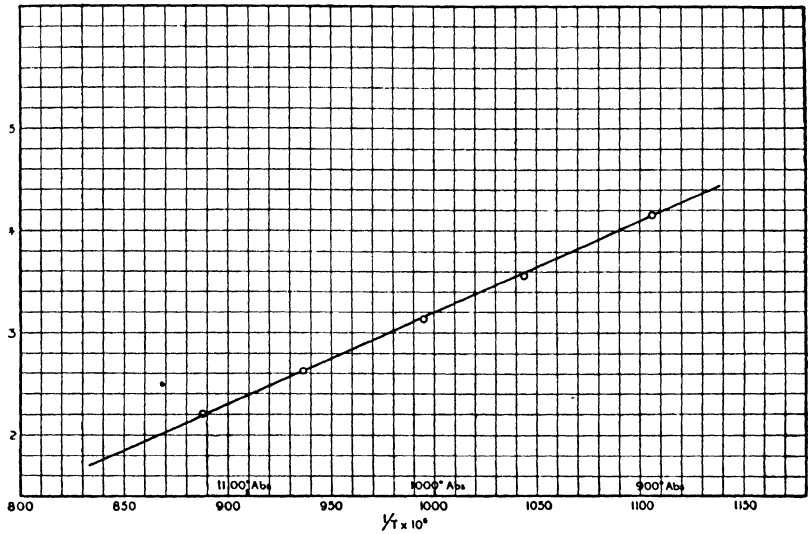


FIG. 1 c.—Influence of temperature on the rate of thermal decomposition of ammonia on a tungsten filament.

Instead of log k the values plotted in these two diagrams (figs. 1 c, 1 d) are those of log t, where t is the *time* required for a definite fraction of the reaction to accomplish itself at a given pressure. Since $t \propto \frac{1}{k}$, log k is equal to constant − log t. This means that the slope of the curve is unchanged, but the curve runs up instead of down with increasing values of $1/T$.

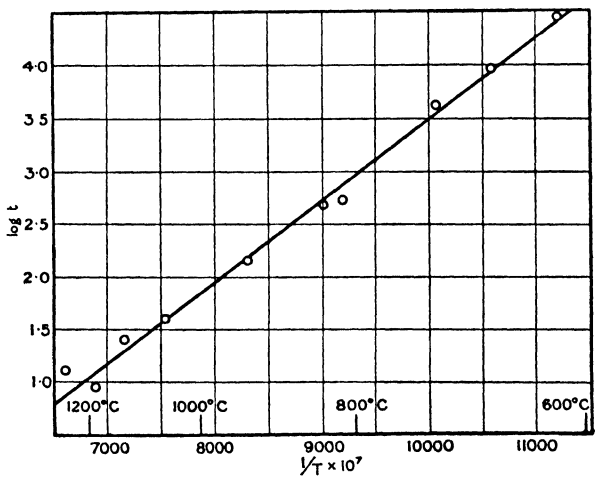


FIG. 1 d.—Influence of temperature on the heterogeneous decomposition of nitrous oxide on a platinum wire.

is, indeed, difficult to imagine what change simple molecules like hydrogen and iodine could suffer as a preliminary to chemical transformation. The active molecules are regarded simply as those endowed with exceptionally large amounts of energy. In this sense they are formed endothermically from the normal ones. The more precise physical significance of A will be discussed presently, but it may be pointed out that the idea of activation is in accordance with the general principles relating to the nature of chemical change which were outlined in the last chapter.

The Arrhenius equation applies equally well to homogeneous and heterogeneous reactions. The figure shows Bodenstein's results* for the homogeneous decomposition of hydrogen iodide. Other examples are shown also.

Heterogeneous and catalytic reactions also give straight lines over as wide ranges of temperature as can be investigated. For example, in the catalytic decomposition of ammonia on the surface of a tungsten wire the value of A remains constant over the range 904° to 1,129° abs. in a manner which confirms the equation completely.

The idea of activation applies to these catalytic reactions also, but A is naturally a function of the catalyst as well as of the reacting substances.

If when $\log k$ is plotted against $1/T$ a straight line is not obtained, this is an almost certain indication that the observed reaction is a composite one made up of two or more concurrent reactions differently influenced by temperature. At low temperatures, one of the reactions may preponderate so that the slope of the curve corresponds to the value of A proper to this reaction. If the second reaction has a larger temperature coefficient, its velocity will increase relatively to that of the first as the temperature rises, and ultimately it will constitute the major portion of the total change. The slope of the $\log k \Big/ \frac{1}{T}$

* *Z. physikal. Chem.*, 1899, **29**, 295.

curve now corresponds to the greater value of A characteristic of the second reaction. The influence of temperature on the composite reaction is represented by a curve similar to that shown in the figure.

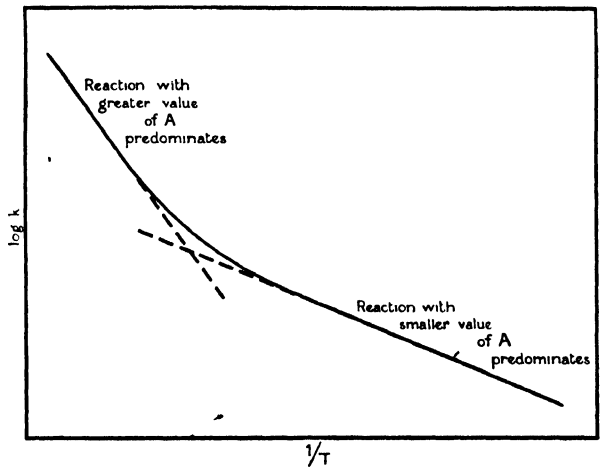


FIG. 2.—Influence of temperature on the speed of a composite reaction.

An example is found in the work of Norrish and Rideal* on the union of hydrogen and sulphur; the combination takes place by two concurrent reactions, a homogeneous reaction between hydrogen and sulphur vapour and a heterogeneous reaction between hydrogen and liquid sulphur at the interface of the liquid and gas phases. The two reactions have widely different temperature coefficients, that of the homogeneous change being roughly double that of the surface change. The result is an apparent pronounced divergence from the behaviour which would be expected if the Arrhenius equation held good. The individual reactions, however, when disentangled, are found separately to be normal in this respect.

* *J. Chem. Soc.*, 1923, **123**, 696.

EXPERIMENTAL DATA RELATING TO BIMOLECULAR HOMOGENEOUS REACTIONS

The number of reactions which proceed in a direct and simple manner is very limited. Those which have been investigated will be taken in order.

The thermal decomposition of hydrogen iodide.

Bodenstein* made a comprehensive study of the equilibrium between hydrogen, iodine, and hydrogen iodide, and a complete series of measurements of the velocity of formation and decomposition of hydrogen iodide at various temperatures. We are concerned now with the kinetic measurements only. He used the method of sealing up the reacting gases in bulbs and analysing the products after keeping for a known time in a thermostat, usually a vapour bath. The bulbs used in the decomposition experiments were filled with hydrogen iodide at 0° and 760 mm., and contained initially, therefore, one gram molecule in 22·4 litres. If x is the fraction of the hydrogen iodide decomposed after time t, then since the reaction is a reversible one,

$$\frac{dx}{dt} = k(1-x)^2 - k'(x/2)^2.$$

If ξ is the fraction decomposed at equilibrium,

$$k(1-\xi)^2 = k'(\xi/2)^2,$$

whence

$$k = \frac{\log_{10}\left[\dfrac{\dfrac{\xi}{2\xi-1} - x}{\xi - x} \cdot (2\xi - 1)\right]}{0{\cdot}8686 \cdot \dfrac{1-\xi}{\xi} \cdot t}.$$

Thus k can be calculated from the amount decomposed in time t and the amount decomposed at equilibrium. The

* *Z. physikal. Chem.*, 1899, **29**, 295.

values of k calculated in terms of x and ξ in this way are not independent of the initial concentration, which, in the experiments, was actually one gram molecule in 22·4 litres. In the second column of the table below, Bodenstein's values of k are given, the time unit being the minute, and in the third column are given the values of k recalculated, with the time expressed in seconds, and the concentrations in gram molecules per litre instead of per 22·4 litres.

Decomposition of hydrogen iodide

T (abs.)	k Time in minutes. Conc. in gram molecules per 22·4 litres	k Time in seconds. Conc. in gram molecules per litre
781	0·1059	0·0395
716	0·00670	0·00250
700	0·00310	0·00116
683	0·00137	0·000512
666	0·000588	0·000220
647	0·000230	0·0000859
629	0·0000809	0·0000302
575	0·00000326	0·00000122
556	0·000000942	0·000000352

Figure 1 a (page 42) shows that when $\log k$ is plotted against the reciprocal of the absolute temperature an excellent straight line is obtained.

Before any analysis of these results is attempted it is necessary to deal with some work on the same subject by H. A. Taylor,* who questions the utility of Bodenstein's results on the ground that the reaction is not completely homogeneous. But the experiments of Taylor, in which the reaction proved to be partly heterogeneous, were not made under the same conditions as those of Bodenstein, and a comparison of the two investigations leaves little or no doubt that the reaction measured by Bodenstein was almost completely a true gas reaction.

Taylor studied the decomposition of hydrogen iodide by a streaming method, using a tube of Pyrex glass of 600

* *J. Physical Chem.*, 1924, **28**, 984.

square centimetres surface. The fractional amounts of hydrogen iodide decomposed in streaming through the tube were very small, and determined by absorption of the iodine in potassium iodide and titration. From the total volume of hydrogen iodide passing in a given time, and the volume of the tube, the actual time during which the gas was heated could be calculated, and the velocity constants found. The introduction of Pyrex glass powder into the tube brought about a considerable increase of velocity, showing that the reaction was partly heterogeneous. Moreover, when $\log k$ was plotted against $1/T$ a curve was obtained which was not a straight line, but which indicated a more rapid increase of k with temperature than corresponds to the Arrhenius equation. Under the conditions of these experiments, therefore, the reaction appears to be composite, consisting partly of wall reaction and partly of homogeneous reaction, the latter predominating as the temperature increases.

This, however, leaves the utility of Bodenstein's results unaffected for the following reasons: first, the values of $\log k$ and $1/T$ given by Bodenstein lie on an excellent straight line, showing that the reaction, as it took place in the bulbs used by him, was simple and not composite; secondly, the actual values of k given by Taylor appear to be many times greater than the values found by Bodenstein at equal temperatures. Thus at 400° and 500° the values read off from a curve of Bodenstein's results compare with Taylor's as follows:

	Bodenstein	Taylor
400°	$3{\cdot}4 \times 10^{-4}$	$1{\cdot}23 \times 10^{-2}$
500°	$3{\cdot}1 \times 10^{-2}$	$9{\cdot}8 \times 10^{-2}$

From these it appears that the catalytic part of Taylor's reaction may well have been very great in comparison with that of Bodenstein's reaction.

B. Lewis and Rideal* also cast some doubt on the simple bimolecular character of the reaction, and stated

* *J. Amer. Chem. Soc.*, 1926, **48**, 2553.

that when hydrogen iodide decomposed in presence of phosphorus pentoxide it gave, not the equilibrium mixture, but hydrogen and iodine corresponding to complete decomposition. They suggested that drying inhibited the union of the elements but not the dissociation of the compound. Bodenstein and Jost,* however, traced the observed effects to a chemical reaction between phosphorus pentoxide and the hydrogen iodide: thus there is still no reason to doubt the simple character of the decomposition.

Kistiakowsky† has recently investigated the reaction over a much wider range of concentration, from 0·02 to 7 gram molecules per litre, i.e. up to several hundred atmospheres. He finds the reaction to be homogeneous, and strictly bimolecular over the whole range of concentration. At the higher pressures there is an apparent increase in the velocity constant, but this is traced to the fact that at high concentrations the collision number is no longer proportional strictly to the square of the pressure, and a correction, depending upon the volume actually filled by the molecules, must be introduced. The correction factor is $\frac{1}{1-Nb}$, where N is the number of molecules per unit volume and b is four times the actual volume of the molecule, assumed spherical. The value of b required to give the observed change of k with pressure is in good agreement with the known size of the hydrogen iodide molecule.

The observed values of k at lower concentrations are in very good agreement with Bodenstein's values.

Kistiakowsky finds that intensive drying makes no difference to the results.

Molecular Statistics of the Bimolecular Hydrogen Iodide Decomposition. The theory of activation by collision.

The calculations which follow are due to W. C. McC. Lewis,‡ but are put in a form which does not involve the

* *J. Amer. Chem. Soc.*, 1927, **49**, 1416. † Ibid., 1928, **50**, 2315.

‡ *J. Chem. Soc.*, 1918, **113**, 471.

assumptions of the radiation theory. He made them originally in a paper dealing with this theory, but they are quite independent of it, and can be interpreted equally well in terms of the simple kinetic theory of gases.

The number of collisions between molecules of hydrogen iodide at a given temperature and pressure can be calculated from the kinetic theory in the manner already described.

This number comes out to be many millions of times greater than the number of molecules reacting, as determined by experiment. It must be concluded therefore that only exceptional molecules react. This is consistent with anticipations based upon the theory of molecular structure and upon the Arrhenius idea of active molecules.

Moreover, the rate of reaction varies with temperature very rapidly, which means that the exceptional state corresponding to 'activation' is very much favoured by increase of temperature, since the number of collisions is increased but slightly. In so simple a reaction as the bimolecular decomposition of hydrogen iodide it is difficult to imagine what can vary with temperature in this way except the number of molecules which possess energy of some kind in excess of a specified amount. The obvious hypothesis to test is that a collision of a certain critical degree of violence is necessary for reaction to occur, or, at all events, a collision between two molecules possessing supplies of energy of some kind in excess of a critical amount.

Let us first consider kinetic energy of translation for the sake of simplicity. At the moment of collision most of this kinetic energy may be transferred to the interior of the molecules, and the result may be a sufficient loosening of the two molecules of HI to permit their rearrangement to $H_2 + I_2$. Activated reaction products are thus produced, which in due season lose their excess energy by collision or otherwise.

We have specified kinetic energy as the kind of energy which might be involved, but there is no reason why other forms of molecular energy should not play their part, since at the moment of collision the energy is all thrown into the pool for redistribution.

Apart from the original idea of Arrhenius about active molecules, views of this sort have been put forward by Marcelin,* Rice,† Trautz,‡ Krüger,§ and others.

We now come to the specific application of these general ideas to the bimolecular reaction. The method of calculation used by Lewis will be followed, although, as will appear later, the equation he derives may be obtained rather more satisfactorily from the kinetic theory by slightly different assumptions.

Suppose Z molecules enter into collision in one second.

Adopting the simplest possible form of distribution law derived in the last chapter, we have for the fraction of these which possess energy greater than E_1 the expression $e^{-E_1/RT}$, and for the fraction possessing energy greater than E_2 the expression $e^{-E_2/RT}$.

The chance, therefore, that two molecules in a collision will be such that the energy of one exceeds E_1 and the energy of the other exceeds E_2 is $e^{-E_1R/T} \times e^{-E_2/RT}$. This is equal to $e^{-(E_1+E_2)/RT}$. We may write $E_1 + E_2 = E$. We are not now concerned with the separate values E_1 and E_2 but with their sum E, which is the energy of activation in the bimolecular reaction.

Thus the total number of molecules which collide with a joint energy exceeding E is $Ze^{-E/RT}$.

But $$Z = \sqrt{2}\pi\sigma^2 \bar{u} n^2,$$

where σ is the molecular diameter, $\bar{u}$ the root mean square

* *Ann. de Phys.*, 1915 [ix], **3**, 120.

† *Brit. Assoc. Rep.*, 1915, p. 397.

‡ Compare inter alia *Z. Elektrochem.*, 1909, **15**, 692.

§ See Jellinek, *Physikalische Chemie der Gasreaktionen*, Leipzig, 1913, p. 725.

velocity, and n the number of molecules per cubic centimetre.

Thus the total number of collisions between activated molecules is $\sqrt{2}\pi\sigma^2\bar{u}n^2 . e^{-E/RT}$.

If each of these collisions is assumed to result in the disruption of the two molecules involved, then the number of molecules reacting in one second per cubic centimetre should be $\sqrt{2}\pi\sigma^2\bar{u}n^2 e^{-E/RT}$.

Expressed otherwise, the assumption that each collision in which the joint energy exceeds E is effective in bringing about chemical change gives the relation

$$\frac{\text{number of effective collisions}}{\text{total number of collisions}} = e^{-E/RT}.$$

Thus from the observed number of molecules reacting and the total number of collisions the value of E may be calculated.

There is also an entirely independent method of finding E, which does not involve any knowledge of the collision number.

This independent method is based upon measurement of the temperature coefficient of the reaction velocity. Since $\bar{u}$ varies with temperature only slightly in comparison with $e^{-E/RT}$, we may write for the velocity constant of the reaction $k = Ce^{-E/RT}$, where C is a constant. Taking logarithms and differentiating we find

$$\frac{d \log k}{dT} = \frac{E}{RT^2}.$$

Thus E is seen to be the constant of the Arrhenius equation. A small correction is required for the variation of $\bar{u}$ with temperature, the method of applying which is given later, but it may in anticipation be stated that it amounts to one or two per cent. only.

The hypothesis that reaction results from collision between activated molecules may now be tested by comparing the values of E obtained by these two independent methods.

Another way of applying the same test is to find E from the Arrhenius equation and then using this value to calculate k and compare it with the experimentally determined value. Lewis adopts this latter course.

From the temperature coefficient of the rate of decomposition of hydrogen iodide E is found to be 44,000 calories.

At 556° abs. $\bar{u}$ is found by the method of the last chapter to be $3{\cdot}3 \times 10^4$ cm. per second.

Lewis takes σ as 2×10^{-8} cm., but a more correct value is $3{\cdot}5 \times 10^{-8}$ cm., which we will adopt here.

If the concentration of the hydrogen iodide is one gram molecule per litre and Avogadro's number is $6{\cdot}1 \times 10^{23}$, then $n = 6{\cdot}1 \times 10^{20}$.

The value of $\sqrt{2}\pi\sigma^2\bar{u}n^2e^{-E/RT}$ is thus found to be $3{\cdot}25 \times 10^{14}$. This is the number of collisions per second between the activated molecules in one c.c.

Thus the number of molecules which should react in each second is $3{\cdot}25 \times 10^{14}$ per c.c. or $3{\cdot}25 \times 10^{17}$ per litre.

Expressing this as a fraction of a gram molecule by division with Avogadro's number the value

$$\frac{3{\cdot}25 \times 10^{17}}{6{\cdot}1 \times 10^{23}} = 5{\cdot}3 \times 10^{-7}$$

is obtained.*

This gives the fraction of one gram molecule reacting in one second when the concentration is one gram molecule per litre. It is therefore the velocity constant k expressed in gram molecules per litre per second.

It agrees well with the experimentally obtained velocity constant $3{\cdot}5 \times 10^{-7}$.

This is a very striking calculation of the absolute velocity of a reaction, but we must examine carefully the exact significance of the degree of numerical agreement between the two values of k.

* An arithmetical error in Lewis's calculation of the collision number has been corrected here, which appeared also in the first edition of this book in several places.

The value taken for σ is inevitably not very accurate, and, since k is proportional to the square of σ, a somewhat different value for the molecular diameter would completely destroy any exact numerical agreement. Even more serious would be a change in the value of E, since small changes in E make a great difference in the exponential term $e^{-E/RT}$. The numerical concordance of the two values of k must therefore be considered as good as could possibly be expected.

The point of real significance is that an absolute value of k can be calculated which is of the right order of magnitude. The theory allows a calculation of the velocity constant from an experimentally determined value of E. E is subject to certain experimental errors which, from the nature of the relation between E and k, appear as proportional errors not in k itself but in the logarithm of k. The accuracy, therefore, with which the logarithm of k can be calculated is a just test of the theory; the accuracy with which k itself can be calculated an excessively severe test, having regard to the inevitable errors involved in the determination of E.

The calculation in no way depends upon interpolation, but is absolute, there being nothing in the form of the equations which constrains $\log k$ to lie between fixed values. It might have almost any value, and an essentially wrong theory could lead to results tens of millions of times too large or too small. Hence an even less exact agreement than that obtained here would have been satisfactory from the point of view of ascertaining the general correctness of the assumptions made.

The best method of calculation is one which gives the experimental errors a proportional effect on the results. In this instance such a method is to compare the value of E calculated from the Arrhenius equation with that found from the relation

$$\frac{\text{number of effective collisions}}{\text{total number of collisions}} = e^{-E/RT}.$$

When the comparison of the two values of E is made for the hydrogen iodide decomposition, practically identical values, namely 44,400 and 44,000 calories, are obtained.

Further discussion and development of this subject is reserved till later, in particular a more satisfactory derivation of the equation given a few lines above.

It may be mentioned in anticipation, however, that we shall decide to adopt a correction for $\bar{u}$, since the active molecules are moving more rapidly than the average. The result will be to multiply the number of collisions which lead to reaction by about 2·5 times. If the two values of E given above are compared after this correction has been made, the values appear as 45,400 and 44,000. The second naturally is unaffected.

The union of Hydrogen and Iodine.

The velocity of combination of hydrogen and iodine was also measured by Bodenstein. Known amounts of hydrogen and iodine were sealed in bulbs and heated for given times, after which the fraction of iodine transformed into hydrogen iodide was determined.

It was impossible to work with equimolecular amounts, and the velocity equation therefore assumes the form

$$\frac{dx}{dt} = k'\left(a - \frac{x}{2}\right)\left(b - \frac{x}{2}\right) - kx^2,$$

where a is the initial concentration of hydrogen, and b that of iodine. x is the amount of hydrogen iodide formed at time t.

In Bodenstein's experiments a, b, and x are all expressed as fractions of 'normal concentration', that is, the concentration at which the substances would each exert a pressure of 760 mm. at 0° C.

Integration by means of partial fractions gives

$$k' = \frac{2}{mt}\left[ln \frac{\frac{a+b-m}{1-4K} - x}{\frac{a+b+m}{1-4K} - x} + ln \frac{a+b-m}{a+b+m} \right],$$

where

$$m = \sqrt{(a+b)^2 - 4ab\,(1-4K)}$$

and $K = k/k'$, k being known from the previous experiments on the hydrogen iodide decomposition.

The following is a typical series of experiments carried out at 393° C.

t (minutes)	a	b	x	k'
120	0·4681	0·2797	0·3239	0·0394
120	0·4681	0·3703	0·4061	0·0392
60	0·4681	0·5492	0·3561	0·0358
30	0·4681	0·9865	0·3534	0·0378
30	0·4681	1·2230	0·4019	0·0336
122	0·9086	0·2101	0·3599	0·0416
45	0·9086	0·4608	0·4405	0·0370
30	0·9086	0·6039	0·4448	0·0390
15	0·9086	1·3890	0·5190	0·0358
15	0·9086	2·2410	0·8076	0·0393

The considerable range of variation of a and b is to be noted, the constancy of k' under these circumstances being a quite conclusive proof that the bimolecular law is followed.

The measurements showing the influence of temperature are given in the following table. The units are the original ones of Bodenstein, namely time in minutes, and concentrations in gram molecules per 22·4 litres.

T (abs.)	k'
781	3·58
716	0·375
700	0·172
683	0·0659
666	0·0379
647	0·0140
629	0·00676
599	0·00146
575	0·000353
556	0·000119

From these, using the equation $d \log k'/dT = E/RT^2$, Lewis has calculated a value of E of 40,000 calories for the gram molecule of hydrogen plus the gram molecule of iodine, and investigated, in the manner explained in the

last section, whether it is possible to calculate the absolute rate of reaction by assuming that all collisions between activated molecules lead to combination.

The number of collisions between two unlike molecules is given by the expression

$$\pi\sigma^2 n_1 n_2 \sqrt{\bar{u}_1^2 + \bar{u}_2^2},$$

where σ is the sum of the effective radii and n_1 and n_2 are the numbers of molecules of each kind per unit volume, $\bar{u}_1$ and $\bar{u}_2$ are the respective root mean square velocities.

Thus at 700° abs. $\sqrt{\bar{u}_1^2 + \bar{u}_2^2} = 29{\cdot}7 \times 10^{-4}$.

σ is taken as 2×10^{-8} cm.

$e^{-\frac{40{,}000}{RT}}$ has the value $3{\cdot}16 \times 10^{-13}$.

Hence the calculated value of k' is 14×10^{-2}.

The experimental value with the time measured in minutes and the concentration in gram molecules per 22·4 litres is 0·172. When the units are changed to seconds and gram molecules per litre the value becomes $6{\cdot}4 \times 10^{-2}$, which must be admitted to be in very good agreement with the calculated value when it is once more borne in mind that the calculation is absolute.

The Thermal Decomposition of Ozone.

The evidence about the nature of this reaction appears at first sight to be somewhat conflicting.

Chapman and Clarke* demonstrated that at 100° C. the reaction is predominantly homogeneous. They used five vessels among which the ratio area/volume varied very considerably. The rate of reaction was found to be independent of the vessel, and to be a function of the ozone concentration only.

Chapman and Jones† measured the rate of decomposition at 100° C. by observing the rate of increase of pressure on a sulphuric acid manometer, and concluded that ' if the

* *J. Chem. Soc.*, 1908, **93**, 1638.

† Ibid., 1910, **97**, 2463.

order of the change can be represented by an integral ordinal number that number is the second'. Warburg * had also concluded that the reaction was bimolecular.

Jahn,† and Perman and Greaves,‡ came to the conclusion that the rate of decomposition varied inversely as the pressure of the oxygen present, and Jahn suggested that the course of the change was not the simple one

$$2\,O_3 = 3\,O_2,$$

but consisted of the stages

$$O_3 = O_2 + O$$
$$O_3 + O = 2\,O_2.$$

The first stage was assumed to be rapid and reversible and the observed rate to be determined by the second reaction.

This, however, seems to be erroneous. In the experiments of Perman and Greaves, which were made at temperatures between 40° and 120° C., the effect of the walls of the soda glass vessels was very pronounced. For example, when the area of the glass surface was increased six times by packing the reaction vessel with pieces of glass tube the rate of decomposition at 119·9° C. was found to be 4·27 times as fast as in the unpacked vessel. They attribute the inverse proportionality of rate to oxygen pressure to the poisoning action of the oxygen on the catalytic activity of the surface. In the experiments of Chapman and Jones (loc. cit.), in which the absence of any appreciable heterogeneous reaction was demonstrated, oxygen was found to be without any marked influence on the rate of change of the ozone.

It is remarkable that the bulbs used by different investigators should differ so greatly in catalytic activity, but the fact seems to be well established.

* *Sitzungsber. K. Akad. Wiss.*, Berlin, 1901, **48**, 1126.
† *Z. Anorg. Chem.*, 1906, **48**, 260.
‡ *Proc. Roy. Soc.*, 1908, A, **80**, 353.

A later investigation of the matter by Griffith and McKeown* led to results not entirely in agreement with those of Chapman and Jones. The reaction was still found to be bimolecular, and, in the tubes employed, partly homogeneous and partly heterogeneous. In view of the disagreement between different investigators it is unfortunate that an attempt to determine the proportion of each kind of reaction was not made, since it was found that the total reaction was retarded by oxygen and apparently accelerated slightly by inert gases such as argon, nitrogen, and helium. Griffith and McKeown conclude from the fact that the velocity constants drift less in the presence of the inert gas than in its absence that the homogeneous change is the one accelerated. They suggest that the activated ozone molecules unite to form a 'complex', which may then revert to normal ozone molecules—a process facilitated by collision with oxygen—or decompose—a process facilitated by collision with the molecules of the inert gas.

The effect of temperature on the rate of reaction was not determined by Chapman and Jones, and the measurements of Perman and Greaves do not relate to the homogeneous reaction. Clement,† however, measured the rate of decomposition of ozone at temperatures up to 200° C. He streamed ozonized oxygen through a decomposition vessel heated in a bath, and determined iodimetrically the percentage of ozone in the entering and leaving gas. Clement did not test the homogeneous nature of the reaction other than by using two reacting vessels the volumes of which were 30·4 c.c. and 3·32 c.c. respectively, but expressed the belief that at the high temperatures employed the effect of external factors would be a minimum. It is a little difficult to judge how completely this expectation was fulfilled, but it seems probable that he was dealing with a predominantly homogeneous change.

* *J. Chem. Soc.*, 1925, **127**, 2086.

† *Ann. Physik* [IV], 1904, **14**, 341.

The following table gives some of the individual constants:

Temperature	k (large vessel)	k (small vessel)
150° C.	27·5	33·4
	26·8	31·0
175°	125·0	179
	114·0	183
200°	766	760
	642	772

Clement's constants for the different temperatures conform in a satisfactory manner to the Arrhenius equation, the value of E being approximately 26,000 calories.

More recently the reaction has been carefully studied by Wulf and Tolman,* by Riesenfeld and Bohnholtzer,† and by Riesenfeld and Schumacher.‡

Wulf and Tolman used ozonized oxygen in all their experiments: they found the reaction to be homogeneous and strictly bimolecular with respect to ozone. The velocity constants, however, appeared to be inversely proportional to the total pressure, an effect which is attributed by the investigators to retardation of the reaction by oxygen, in contradiction to the findings of Chapman and Jones. Wulf and Tolman state that various oxygen samples are liable to contain traces of a substance which catalyses the decomposition of ozone, and they suggest that where oxygen appears to have no influence on the reaction it is as a result of the accidental balancing of the catalytic and the inhibiting effect. They reject Jahn's mechanism for the reaction, since calculation shows that the number of collisions between ozone molecules and oxygen atoms which could occur is far too small to account for the observed rate of reaction. Wulf and Tolman's value for the heat of activation is 29,600 calories, and, taking into account the retarding influence of oxygen,

* *J. Amer. Chem. Soc.*, 1927, **49**, 1183, 1202, 1650.

† *Z. physikal. Chem.*, 1927, **130**, 241.

‡ Ibid., 1928, A, **138**, 268.

they give the following equation for the rate of reaction of the ozone

$$-\frac{dC}{dt} = \left(5{\cdot}89 \times 10^{13}/C_{O_2}\right) T^{1/2} \,.\, e^{-29{,}600/RT} \,.\, C^2$$

the units being gram molecules per c.c. and seconds.

Riesenfeld and Bohnholtzer and Riesenfeld and Schumacher used ozone concentrated by liquefaction and distillation. From their kinetic measurements they conclude that a reaction of the second order and one of the first order take place simultaneously; at quite low pressures, 6–60 mm. *Hg* the first order reaction predominates. The velocity constants of the second order reaction are not influenced by the total pressure, while those of the first order reaction appear to be inversely proportional to the total pressure. The figures given show that the first order reaction at the lower pressures is considerably influenced by the surface, and is quite probably a heterogeneous reaction, though the authors themselves do not consider this to be definitely shown. The decomposition appears to be rather sensitive to catalysts such as dust particles.

Taking all the facts into account, it seems to be definitely established that the predominant reaction in ozone at ordinary pressures is a homogeneous bimolecular reaction. The influence of the surface of the vessel, however, easily obtrudes itself and gives rise to a first order reaction, which is retarded by oxygen. This reaction becomes prominent at low pressures. There seems to be doubt about the influence of oxygen and other gases on the bimolecular reaction, and the difficulty in deciding whether or not the influence exists seems to depend partly upon the sensitiveness of the reaction to certain catalytic impurities, and partly to the fact that the wall reaction is liable to contribute to the total change in a way not quite easy to allow for. It is possible, moreover, that since the decomposition of ozone is exothermic chain processes may play some part

(Chapter VI) and account for the rather puzzling and apparently erratic influence of catalysts and inhibitors.

It should be mentioned, however, that the absolute rates of reaction found by the various investigators are, on the whole, in quite good agreement.

If the values of E found by Wulf and Tolman or the other recent value, 27,800, found by Belton, Griffith, and McKeown* are substituted in the equation *number of molecules reacting = number entering into collision* $\times e^{-E/RT}$, it appears that the rate of activation is not great enough to account for the rate of reaction. The reason for this departure from the simple theory is discussed on page 102.

The Thermal Decomposition of Nitrous Oxide

$$2\,N_2O = 2\,N_2 + O_2.$$

This reaction was first investigated by Hunter,† who used a streaming method. He found that bimolecular constants were obtained, but the decomposition was only followed over small ranges. The experiments were all made at atmospheric pressure. The homogeneous or heterogeneous nature of the reaction was not ascertained. Small quantities of other oxides of nitrogen were found to be formed as by-products in addition to oxygen and nitrogen.

Hinshelwood and Burk‡ measured the rate of reaction in a silica bulb by observing the pressure increase accompanying the change; over the range of temperature 565° to 852° C. the reaction is homogeneous, since even with the silica reaction vessel filled to the extent of two-thirds with coarse silica powder no measurable increase in reaction velocity is observable. Variation of the initial pressure of the nitrous oxide shows the reaction to be bimolecular. Platinum and rhodium have no appreciable catalytic effect. Although the bimolecular velocity 'constants' are

* *J.C.S.*, 1926, 3153. † *Z. physikal. Chem.*, 1905, **53**, 441.
‡ *Proc. Roy. Soc.*, 1924, A, **106**, 284.

constant over the ranges of decomposition in Hunter's experiments, a pronounced drift appears when they are calculated over the whole course of the reaction. This is probably due to catalysis by traces of the by-products.

The effect of temperature is shown by the following table:

Absolute temperature	$\log_{10}(k \times 10^3)$ Time in seconds, conc. in gram molecules per litre
1125°	4·064
1085°	3·575
1053°	3·223
1030°	2·940
1001°	2·580
967°	2·133
838°	0·040

The value of the heat of activation is 58,500 calories for the two gram molecules of nitrous oxide. At these high temperatures a small correction to the Arrhenius equation becomes necessary, which is explained in the next chapter.

The application of the previously developed theory of bimolecular reactions gives satisfactory results.

Taking k at 1,000° abs. to be 0·39, we find that the actual number of molecules reacting per c.c. per second at 760 mm. is $3{\cdot}58 \times 10^{16}$.

The diameter of the nitrous oxide molecule* may be taken as $3{\cdot}32 \times 10^{-8}$ cm.

The number of collisions at 1,000° abs. and 760 mm. pressure is thus found to be $2{\cdot}09 \times 10^{28}$. This we multiply by the factor 2·5 to allow for the fact that the active molecules collide more often than those with speed $\bar{u}$ (see page 100).

Thus
$$\frac{3{\cdot}58 \times 10^{16}}{2{\cdot}5 \times 2{\cdot}09 \times 10^{28}} = e^{-E/RT},$$

whence $E = 55{,}500$ calories.

The agreement with the experimental value is as good as

* Rankine, *Proc. Roy. Soc.*, 1921, A, **98**, 369.

can be expected. Two factors, beside experimental error, contribute to the discrepancy.

First, the reaction seems to be slightly catalysed by traces of by-products. Thus k as measured is larger than the true bimolecular constant, and E, calculated from the observed number of molecules reacting, is too small.

Secondly, at high temperatures the molecules of nitrous oxide have more rotational quanta than at low temperatures. Thus the 'collision area' is greater than that calculated from Rankine's viscosity data, which are obtained at ordinary temperatures.

Both factors involve comparatively small correction terms, but each correction would diminish the difference between the two values of E.

At very low pressures, Hibben finds the reaction to be of the first order. The explanation of this is that the speed of the bimolecular change has become negligible and that the wall reaction, which at higher pressures was a very small fraction of the whole, now predominates.

The Thermal Decomposition of Chlorine Monoxide.

Although contact with organic matter, or local overheating, readily initiates explosion waves in chlorine monoxide, the slow decomposition can conveniently be observed between about 60° and 140° C., and has been studied by Hinshelwood and Prichard* and Hinshelwood and Hughes.†

The change is homogeneous, uninfluenced by the glass walls of the containing vessel or by glass wool.

If the change took place in the one simple stage $2\,Cl_2O = 2\,Cl_2 + O_2$ the increase in pressure at any time would be a direct measure of the extent to which the reaction had progressed. When the pressure increase is plotted against time the curve shows that the reaction apparently accelerates as it proceeds, as though the chlorine or the oxygen

* *J. Chem. Soc.*, 1923, **123**, 2730. † Ibid., 1924, **125**, 1841.

which are produced had an autocatalytic effect. Experiments in which excess of chlorine or of oxygen is present initially show, however, that these gases exert no influence whatever on the course of the reaction. The acceleration is not, therefore, due to autocatalysis, but is attributable to the occurrence of the change in consecutive stages of which the first is not accompanied by so marked a pressure change as the subsequent ones. There is chemical as well as kinetic evidence for the existence of these consecutive reactions, which possibly involve the formation of an unknown oxide of chlorine.*

The rate of reaction is influenced by pressure in such a way as to indicate that each stage in the complex process is bimolecular, for the time taken to reach any given stage of the reaction is inversely as the initial pressure of chlorine monoxide, and the curves obtained at different initial pressures become superposable over their whole course if the time scales are altered so as to make them coincide at one point.

The complications arising from the existence of these consecutive reactions seems to hinder the testing of the theory of bimolecular changes which we have applied to the other examples, since at least two values of k must be involved. These cannot be separately determined by mathematical means, since the differential equations for bimolecular consecutive reactions are not soluble in simple form, and calculation even by differential methods is not possible in ignorance of what part of the pressure change is due to each reaction.

The difficulty is, however, not insurmountable. This is

* Booth and Bowen (*J. Chem. Soc.*, 1925, **127**, 510) give good reasons for assuming that an unknown oxide of chlorine intervenes in the photochemical decomposition of chlorine peroxide. When gaseous chlorine peroxide is exposed to light oily drops of a liquid which was at first thought to be Cl_2O_7 are formed. According to Bodenstein, Harteck, and Padelt (*Z. Anorg. Chem.*, 1925, **147**, 233) analysis shows this liquid to consist of Cl_2O_6.

due to the exponential relation between k and E. Since the various stages of the reaction are not sharply defined, the separate values of k are obviously of the same order of magnitude. Moreover, since each k is principally determined by the corresponding value of $e^{-E/RT}$, values of k which lie fairly close together should correspond to values of E which are practically identical. It might therefore be expected that E would show little or no variation at different stages of the reaction, and experiment confirms this expectation. The influence of temperatures is found to be uniform, and thus E to be nearly constant, throughout the reaction.

Plotting against the reciprocal of the absolute temperature the logarithm of the velocity of reaction for the ranges 20 % to 40 %, 40 % to 60 %, and 60 % to 80 %, parallel straight lines are obtained, giving for E a uniform value of 21,000 calories.

From the nature of the relation between k and E, it is now permissible to take an average of k for the whole reaction and to investigate the relation between this and the constant value of E. Substitution of such an average value of k in the equation for bimolecular reaction rates leads to a value of E equal to 22,000 calories. This agrees well with the value 21,000 found from the temperature coefficient. In this calculation the molecular diameter of the chlorine monoxide molecule is taken $4{\cdot}8 \times 10^{-8}$ cm. Rankine does not give values for this gas, but the value is inferred from the size of the molecules of gases of similar structure.

The ease with which explosion waves are set up in chlorine monoxide can be explained. The heat of activation is 21,000 calories. The heat of reaction is 32,000 calories. Simplifying the calculation by supposing the reaction to consist of the one stage $2\,Cl_2O = 2\,Cl_2 + O_2$, in which the 32,000 calories are liberated, it may be inferred that the products have an excess energy of 32,000 + 21,000

calories. If this 53,000 calories appears as kinetic energy and is more or less equally shared between the three molecules formed, each of these has an excess energy corresponding to nearly 18,000 calories. This, if transferred by collision to any average chlorine monoxide molecule, would be almost enough to enable it to enter into reaction, without further activation, with the next chlorine monoxide molecule it encountered. Hence it is clear how, with a little extra stimulation, the slow change may pass into an explosion.

The applicability of the collision theory to this reaction is therefore specially interesting. If explosion waves are easily propagated in the gas it seems not impossible that, even in the slow decomposition, quite long 'reaction chains' might be set up, the activation of a single pair of molecules being sufficient to cause the decomposition of some hundreds or thousands. But if this happened the calculated and observed values of E could not have been even approximately concordant.

The Union of Hydrogen and Sulphur Vapour.

The results of earlier workers on this subject were vitiated by experimental errors. These arose from the circumstance that union takes place quite rapidly at temperatures below the boiling-point of sulphur, and is not conveniently measurable at higher temperatures. Consequently experiments were always made in presence of liquid sulphur, which possesses the property of dissolving hydrogen sulphide, so that the products of reaction are removed to a greater or less extent depending on the amount of sulphur in the reaction bulb.

Pélabon's results* appeared to show that the reaction came to a standstill before a true equilibrium state was reached, and served as the basis for an erroneous theory about 'false equilibria'. Neither the results of Pélabon

* *Compt. rend.*, 1897, **124**, 686.

nor those of Bodenstein * yielded definite information about the actual gaseous reaction between sulphur vapour and hydrogen.

Norrish and Rideal † have studied the reaction by a streaming method, passing hydrogen over molten sulphur at temperatures below the boiling-point of sulphur, and determining the amount of hydrogen sulphide in the issuing gas by a colorimetric method. Replacing the static methods of the earlier experimenters by this dynamic one, and allowing the hydrogen to stream for some time before any analysis of the issuing gas was made, they hoped to eliminate errors due to the solution of hydrogen sulphide, since the liquid sulphur would at all times be saturated.

The reaction occurring under these conditions was found to be a composite one, consisting of a gaseous reaction between hydrogen and the vapour of the sulphur, and of a heterogeneous change at the surface of the liquid sulphur. This was demonstrated directly by using as reaction vessels flasks of different internal surface.

The variation of the reaction rate with temperature also provides evidence of the superposition of two reactions, one with a considerably higher temperature coefficient than the other.

The velocity of the gaseous reaction is proportional to the pressure of the hydrogen ; that of the surface reaction independent of it. Subtraction of the total reaction at pressure p_1 of hydrogen from that at pressure p_2 gives the purely gaseous reaction corresponding to a pressure $(p_2 - p_1)$.

Plotting, therefore, the difference in rate at two fixed pressures of hydrogen against temperature gives the variation with temperature of the homogeneous part of the reaction. This variation is partly due to the change with temperature in the concentration of the sulphur vapour

* *Z. physikal. Chem.*, 1899, **29**, 315.

† *J. Chem. Soc.*, 1923, **123**, 696, 1689, 3202 ; and 1924, **125**, 2070.

itself. The temperature coefficient of the purely gaseous reaction, corrected for the changing concentration of the saturated sulphur vapour, is 2·19 for ten degrees over the range investigated, that is in the neighbourhood of 300° C. Norrish and Rideal find from this a value of 52,400 calories for the heat of activation.

With regard to the mechanism of the change, Norrish and Rideal consider the gaseous reaction to consist in the direct union of a hydrogen molecule with an atom of sulphur, produced by the dissociation of the more complex molecules in the vapour. Some support is lent to this view by the agreement between the heat of activation, 52,400 calories, and Budde's value for the heat of dissociation of S_2, which is 50,000 calories per gram atom of sulphur.

In view, however, of the complexity of the system

$$S_8 \rightleftharpoons 4\,S_2 \rightleftharpoons 8\,S$$
$$H_2 + S = H_2S$$

and the lack of knowledge of the equilibrium constants involved, it seems hopeless at the present moment to attempt a more detailed inquiry into the molecular statistics of the reaction. If the suggested mechanism is the true one it would be necessary for the purpose to know the concentration of sulphur atoms at any moment, and to calculate their rate of collision with hydrogen molecules.

The approximate agreement of the heat of activation with the heat of dissociation of S_2 seems at all events to show that the variation of the reaction rate with temperature is determined mainly by the variation in the concentration of the sulphur atoms, so that when these meet hydrogen molecules it does not appear that much further activation is required. Probably most of the collisions are effective. A more detailed analysis of a reaction which depends upon the production of free atoms is given later in connexion with the combination of hydrogen and bromine.

It must be remarked, however, that the reaction might take place as follows:

$H_2 + S_2 + \text{heat of activation} = H_2S + S$ (both activated)

instead of according to the scheme

$$S_2 + \text{heat of dissociation} = 2\,S$$

followed by

$$H_2 + S = H_2S.$$

The approximate agreement between the heat of activation and the heat of dissociation is, however, very suggestive.

The Thermal Decomposition of Nitric Oxide and the Union of Nitrogen and Oxygen to Nitric Oxide.

The formation of nitric oxide from its elements was investigated by Nernst* at 1,538° and 1,737° C., the decomposition by Jellinek† between 650° and 1,750° C. Both investigations were made by the streaming method. Each of the reactions is stated to be bimolecular.

If the logarithms of the velocity constants of the decomposition are plotted against the reciprocal of the absolute temperature in the usual way the line which is obtained is strongly curved, the curvature being in the sense which indicates that the heat of activation increases in a marked manner with rise of temperature. It seems probable that a composite homogeneous and heterogeneous reaction is involved.

The matter is in need of further investigation.

The Thermal Decomposition of Gaseous Acetaldehyde.

The decomposition takes place according to the equation

$$CH_3CHO = CH_4 + CO,$$

but the reaction is kinetically bimolecular except at quite low pressures.‡ The chemical transformation depends therefore upon the collision of two acetaldehyde molecules.

* *Z. Anorg. Chem.*, 1906, **49**, 213. † Ibid., 229.

‡ Hinshelwood and Hutchison, *Proc. Roy. Soc.*, A, 1926, **111**, 380.

At quite low pressures there is some first order reaction which is probably a surface reaction.

The bimolecular velocity constant can be expressed by the equation

$$k = 5{\cdot}5 \times 10^{10}\sqrt{T} \;.\; e^{-45{,}500/RT}$$

the units being gram molecules per litre and seconds.

At 800° abs. and 760 mm. pressure the number of molecules which react per c.c. per second is $7{\cdot}3 \times 10^{16}$. Assuming the molecular diameter of the acetaldehyde molecule to be 5×10^{-8} cm., the number of molecules, calculated from the formula $2{\cdot}5 \times \sqrt{2} \times \pi\sigma^2 \bar{u} n^2 \,.\, e^{-E/RT}$ (page 100), which might be expected to react per second is $5{\cdot}4 \times 10^{16}$. Thus the simple theory of activation is applicable.

Since the participation of two molecules in the reaction is not necessary on purely chemical grounds, as the equation at the beginning of this section shows, it might be expected that collisions between molecules of acetaldehyde and molecules of some other gas would bring about chemical transformation. It is in fact found that in the presence of hydrogen the decomposition takes place according to the equation

$$-\frac{d[CH_3CHO]}{dt} = k_1[CH_3CHO]^2 + k_2[H_2][CH_3CHO]$$

and similarly in presence of nitrogen. But the constant k_2 both for nitrogen and hydrogen is only about one-tenth as great as k_1.*

The Thermal Decomposition of Nitrogen Peroxide.

In the course of a comprehensive study of the formation and decomposition of the higher oxides of nitrogen, Bodenstein and Ramstetter† found that the reaction

$$2\,NO_2 = 2\,NO + O_2$$

is a homogeneous, bimolecular reaction.

* Hinshelwood and Askey, *Proc. Roy. Soc.*, A, 1927, **116**, 163, and unpublished observations.

† *Z. physikal. Chem.*, 1922, **100**, 68.

At 627° abs. the velocity constant is 204 gram molecules per litre per minute, and the temperature coefficient is 1·51 for a 10° change of temperature.

Taking the molecular diameter of NO_2 as $3{\cdot}33 \times 10^{-8}$ cm. Norrish * calculates the value of the heat of activation to be 33,200 calories from the theoretical formula for the rate of a bimolecular reaction, and 32,000 calories from the temperature coefficient and the Arrhenius equation. If the correction for the greater speeds of the active molecules be applied, the first value becomes 33,500 calories.

Some general considerations about Photochemical Changes. The Union of Hydrogen and Chlorine.

Although photochemical changes are really outside the province of this book it will nevertheless be useful to summarize certain general results which have a bearing on the whole problem of chemical reaction velocity.

Only light which is absorbed by one of the reacting substances can be chemically active, but absorption, although a necessary, is not a sufficient condition for reaction. Of frequencies corresponding to absorption bands in different parts of the spectrum some may be effective and some not. The experimental investigation of this matter is still in a very rudimentary state. Examples suitable for experiment are not easy to find.

Light is absorbed by atoms or molecules in quanta of magnitude $h\nu$, where ν is the frequency of the light and h is Planck's constant. The result of absorption is that an electron in one of the atoms of the absorbing molecule is raised to a higher energy level.

This may be called electronic activation of the atom or molecule. When sufficiently activated in this way a molecule may undergo chemical transformation giving rise to products still in possession of extra energy which they lose either by radiation—a form of fluorescence—or by collision.

* *Nature*, 1928, **122**, 923.

It is clear that in a purely photochemical reaction there must be at least one quantum absorbed for each molecule which becomes activated.

For visible light the $h\nu$ is a very large quantity compared with the ordinary thermal energy of a single molecule. There is therefore a certain likelihood that the effectiveness or otherwise of a quantum of light will not, in simple cases, be profoundly influenced by minor variations in the internal state of the molecule due to purely thermal causes. If, therefore, the disturbance produced in a molecule by the absorption of the quantum of light is great enough to cause its transformation in one case it will do so in all.

In simple instances, therefore, we should expect to find one molecule transformed for each quantum of light absorbed, provided that the light is active at all. This is Einstein's law of photochemical equivalence.

With regard to the photochemical effectiveness of light of different frequencies we should rather expect that there would be a limiting frequency above which the quanta are large enough to activate the molecules and below which they are ineffective. Above this critical frequency the effect of the light would be proportional simply to the number of quanta which it contained, that is for equal intensities would diminish slightly as the frequency increased. Below the critical frequency the light would be ineffective. It is also possible that quanta too small to be effective at low temperatures might become effective in activating molecules already partially activated by an increase of temperature. But reliable experimental data relating to these interesting points are almost entirely lacking.

Coehn and Jung* state that the absorption band of chlorine in the red region is photochemically ineffective. They also state that in the photochemical union of hydrogen and chlorine in presence of moisture the longest waves

* *Z. physikal. Chem.*, 1924, **110**, 705.

which are active are those of length 540 $\mu\mu$ approximately; longer waves do not cause combination. Bowen* has, however, pointed out that these statements are partly based upon an erroneous interpretation of the experimental results, and that there is really no sharp limit at or near 540 $\mu\mu$, but that in this region the photochemical effect is everywhere proportional to the absorbed energy. This does not disprove the existence of photochemical critical frequencies, but illustrates the inadequacy of the existing experimental data. A true photochemical threshold in the blue has quite recently been found by Dickinson and Baxter for the decomposition of nitrogen peroxide.

The Einstein law has been found to hold good in many examples. A summary of its application to reactions of various kinds has been given by Bodenstein,† and more recently by Allmand (*Trans. Faraday Soc.*, 1926, 438); its applicability to the decomposition of ozone under the influence of ultra-violet light has been shown by Warburg,‡ and it was shown to hold with considerable accuracy by Noddack§ in the reaction $Cl_2 + 2\,CCl_3Br = 2\,CCl_4 + Br_2$, which is provoked by violet light.

Bowen|| has shown that it is applicable in the case of the decomposition in carbon tetrachloride solution of chlorine monoxide and peroxide, and that the decomposition of nitrogen trichloride under the same conditions is not far removed from the requirements of the law.

With regard to purely gaseous reactions about four quanta per molecule appeared to be required in the decomposition of ammonia (Bodenstein, loc. cit), but this result is not very accurate. Bowen¶ has found that in the photochemical decomposition of gaseous chlorine monoxide by blue and violet light two molecules are decomposed for

* Discussion on Photochemistry, Oxford, October 1925. *Trans. Faraday Soc.*, 1926, 543.
† *Z. physikal. Chem.*, 1913, **85**, 329.
‡ *Z. Elektrochem.*, 1920, **26**, 54.
§ Ibid., 1921, **27**, 359.
|| *J. Chem. Soc.*, 1923, **123**, 1199.
¶ Ibid., 2328.

each quantum of light absorbed, and suggests one of the following mechanisms,

$$Cl_2O + h\nu = Cl_2 + O$$

followed by the spontaneous reaction

$$Cl_2O + O = Cl_2 + O_2,$$

or $$Cl_2O + h\nu = \text{active } Cl_2O$$

followed by $$\text{active } Cl_2O + Cl_2O = 2\,Cl_2 + O_2.$$

Deviations from Einstein's law can occur in true photochemical reactions owing to the degradation of the absorbed light energy into thermal energy as a result of collisions with other molecules which the activated molecules suffer before they have a chance to react. This makes the number of quanta absorbed greater than the number of molecules transformed.

A similar relation between number of quanta and molecules transformed would be found if two or more quanta were actually needed to activate each molecule for chemical transformation. In this event, however, it is easily shown that the rate of reaction would be nearly proportional to the nth power of the light intensity, where n is the number of quanta required to be simultaneously absorbed.

No instance is known in which the rate of reaction is proportional to a power of the light intensity greater than the first. It is, indeed, very improbable that a molecule would remain in a condition where it possessed so large an excess of energy as a quantum of visible light long enough to acquire a second quantum, since all the time it would be subject to collisions which would rapidly deprive it of its first quantum. Probably all photochemical transformations are one-quantum processes.

We are here chiefly concerned with the relation of photochemical to thermal changes. We have seen that thermal heats of activation range from about 20,000 to about 60,000 calories as a rule. The quanta corresponding to the red lithium line and the violet mercury line amount

in calories to $7{\cdot}01 \times 10^{-20}$ and $1{\cdot}078 \times 10^{-19}$ respectively. Allowing one quantum to a molecule, this would represent activation in a photochemical reaction to the extent of $Nh\nu$ or 42,480 calories and 65,360 calories per gram molecule.

From this we see that the absorption of visible light can lead to a high degree of activation. Ozone, for example, is decomposed by ultra-violet light of wave-length 254 $\mu\mu$, the quantum of which corresponds to 111,000 calories per gram molecule, compared with the value 26,000 for the bimolecular thermal reaction. Activation to this degree could conceivably bring about the transformation $O_3 = O_2 + O$, which, resulting as it does in the production of atomic oxygen, is a more profound change than the bimolecular reaction.*

This, moreover, makes it easy to understand the exclusive prevalence of one-quantum processes in photochemical reactions.

It has been suggested that in photochemical changes 'activation' actually consists in the resolution of a molecule into free atoms.† For example, activation in reactions involving the halogens and their hydrides has been supposed to consist in the production of free atoms of hydrogen, chlorine, bromine, or iodine as the case may be. There is no direct evidence for this suggestion, though on the basis of it plausible mechanisms for many reactions can be devised.

It would be of great interest to know whether the photochemical decomposition of ozone proceeds by the mechanism

$$(1)\quad O_3 + h\nu = O_2 + O,$$

or by the alternative mechanism

$$(2)\quad O_3 + h\nu = O_3 \text{ (activated)}$$
$$O_3 \text{ (activated)} + O_3 = 3\,O_2.$$

* Cf. a discussion by W. C. McC. Lewis. *Trans. Faraday Soc.*, 1922, **17**, 577.

† Cf. Bowen, *J. Chem. Soc.*, 1924, **125**, 1233, where other references are given.

But the answer to this, and to similar questions arising out of analogous instances, is not forthcoming. The reason is partly that thorough investigations of the relation between concentration and velocity of reaction have seldom been made in suitable cases, and partly because, even when they have been made, the interpretation of the results is not easy.

The difficulty arises from the fact that change in concentration has not merely the mass action effect* which would allow mechanism (1) to be distinguished from mechanism (2), but also an effect on the light absorption itself, for which the allowance may be extremely uncertain. If the active light is feebly absorbed, then the number of quanta absorbed will be proportional to the concentration, while, if it is strongly absorbed, this number will be independent of the concentration. Although the extinction coefficient can be determined there remains the question as to which wave-lengths in a given spectral region are really the active ones, and how the extinction coefficient of these compares with the mean extinction coefficient.

As in many other branches of chemistry, the answer to the simple and direct questions which present themselves is often rendered ambiguous by complicating circumstances. Advance depends upon the discovery of special instances where, by some fortunate chance, the complicating factors are inoperative.

Turning now to the combination of hydrogen and chlorine, which must be dealt with partly because of its intrinsic importance and partly because it illustrates a

* The point is that if mechanism (2) were the real one, many of the activated O_3 molecules would probably emit their quanta before they encountered other suitable O_3 molecules. Hence the reaction velocity ought to vary roughly as the square of the ozone concentration. If, of course, the activated ozone molecules retained their energy for so long a time that they were almost certain to meet a suitable molecule with which to react before they became deactivated, then mechanisms (1) and (2) would be indistinguishable in this way.

completely new type of reaction mechanism, we find one of the most complicated cases of all.

The principal facts about it may be summarized as follows:

I. The reaction is provoked by the light absorbed by the chlorine.

II. There may be a long 'indication period' during which no change takes place. This has been traced by Burgess and Chapman* to the presence of nitrogenous impurities which give rise to nitrogen chloride and 'inhibit' the reaction. The inhibitors are gradually destroyed by the light, and the combination starts. In their absence the induction period disappears.

III. The rate of reaction, when the phenomena of the induction period are eliminated, is strictly proportional to the light intensity. Statements to the contrary by Baly and Barker† have been disproved by Mrs. M. C. C. Chapman.‡

IV. The Einstein law is not even approximately obeyed.§ One quantum of light brings about the union of many millions of molecules.

To explain this important fact Nernst|| suggests the following series of changes:

$$(1)\ Cl_2 + h\nu = 2\,Cl.$$
$$(2)\ Cl + H_2 = HCl + H.$$
$$(3)\ H + Cl_2 = HCl + Cl.$$

(1) is the only purely photochemical change; the reactions (2) and (3) proceed without the absorption of fresh quanta of light. The chlorine atom produced in (3) takes part in reaction (2) once more and a 'chain' is set up, which may lead to the union of millions of molecules for

* *J. Chem. Soc.*, 1906, **89**, 1399. † Ibid., 1921, **119**, 653.
‡ Ibid., 1924, **125**, 1521.
§ Cf. Bodenstein, *Z. physikal. Chem.*, 1913, **85**, 329.
|| *Z. Elektrochem.*, 1918, **24**, 335.

the one quantum originally absorbed. The chain is broken by one of the reactions

$$2\,Cl = Cl_2;$$
$$2\,H = H_2;$$
$$H + Cl = HCl.$$

This 'reaction-chain' mechanism is important, and will be further discussed in Chapter VI.

V. The actual kinetics of the reaction are very complicated.

The rate is inversely proportional to the concentration of oxygen,* and appears to increase almost indefinitely as the gases are freed from oxygen. It is therefore necessary, in making measurements of the reaction velocity, always to work in the presence of a small but definite concentration of oxygen.

This remarkable influence is explained by Chapman† in terms of a degradation of the energy of the activated chlorine molecules by collision with oxygen molecules. On the basis of the Nernst chain hypothesis the effect can also be explained by supposing that the oxygen removes the atomic hydrogen by combining with it and thus interrupts the chain of reactions.‡

If the original hypothesis of Chapman and his collaborators is correct, namely that the excited chlorine molecules are deactivated by simple collision with oxygen independently of the water formation, then the fact that oxygen has a specific effect different from other foreign gases is very important. It is, indeed, a problem of very general importance whether such specific transfers of energy are common. The assumption that they are not

* Bodenstein and Dux, *Z. physikal. Chem.*, 1913, **85**, 297. Chapman and Macmahon, *J. Chem. Soc.*, 1909, **95**, 959.

† *J. Chem. Soc.*, 1913, **103**, 496; 1919, **115**, 1264.

‡ Nernst, *Z. Elektrochem.*, 1918, **24**, 335. Cf. also Weigert, *Ann. Physik*, 1907, **24**, 243, and Norrish and Rideal, *J. Chem. Soc.*, 1925, **127**, 787.

unusual is helpful in other connexions, but this is the first example of the kind which we have yet encountered.*

VI. The rate of combination increases at first in direct proportion to the pressure of hydrogen, when the pressure of chlorine and of oxygen is kept constant, then passes through a maximum and slowly declines as the pressure of hydrogen is further increased.†

VII. Bodenstein and Dux ‡ found that, for constant pressures of hydrogen, the rate of reaction was given by the formula

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k \,.\, I \,.\, [\mathrm{Cl_2}]^2}{[\mathrm{O_2}]},$$

where I is the intensity of the light and k a constant, whilst Chapman and Whiston § found it to be more nearly expressed by the formula

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k \,.\, I \,.\, [\mathrm{Cl_2}]}{[\mathrm{O_2}]}.$$

VIII. Mrs. C. C. Chapman || has submitted the matter to a very careful re-investigation, and finds that the rate of combination is proportional to the first power of the concentration of the chlorine when the proportion of hydrogen present is small, and proportional to the square of the concentration of the chlorine when the proportion of hydrogen present is large.

Another important result was that as the pressure of hydrogen becomes smaller the rate of reaction becomes less and less dependent on the oxygen concentration.

The results are summarized in the formula

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k_1[\mathrm{H_2}][\mathrm{Cl_2}]^2}{k_3[\mathrm{H_2}]^{2-x}[\mathrm{O_2}] + [\mathrm{Cl_2}]},$$

where x is a fraction less than 0·5.

* Cf. Chapter VI.

† Chapman and Underhill, *J. Chem. Soc.*, 1913, **103**, 496.

‡ *Z. physikal. Chem.*, 1913, **85**, 297.

§ *J. Chem. Soc.*, 1919, **115**, 1264. || Ibid., 1923, **123**, 3062.

An interpretation of this formula, on the basis of the assumptions that chlorine is activated by light and can be deactivated by the joint action of hydrogen and oxygen, is given by Mrs. M. C. C. Chapman and D. L. Chapman.*

IX. Thon,† in a critical survey of the problem, questions the reality of the slight retardation caused by excess of hydrogen in Chapman's experiments, and suggests the equation

$$\frac{d[HCl]}{dt} = \frac{k[Cl_2]^2[H_2]}{k'[H_2][O_2] + k''[Cl_2]}.$$

The apparently divergent results of different investigators can, on the whole, be regarded as special cases of this general equation. It is clear, for example, that with different relative proportions of chlorine and hydrogen the rate could be nearly proportional either to $[Cl_2]^2$ or to $[Cl_2]$.

Cremer‡ suggests the following mechanism, in which the index a denotes an activated atom or molecule

$$\begin{aligned}
&(1)\ Cl_2 + h\nu = Cl^a + Cl\\
&(2)\ Cl^a + Cl_2 = Cl_3{}^a\\
&(3)\ Cl_3{}^a + H_2 = 2\,HCl + Cl^a\\
&(4)\ Cl^a + O_2 = O_2{}^a + Cl\\
&(5)\ Cl_3{}^a + O_2 = O_2{}^a + Cl_2 + Cl\\
&(6)\ Cl_3{}^a = Cl_2 + Cl\\
&(7)\ Cl^a = Cl
\end{aligned}$$

This leads to the equation

$$\frac{d[HCl]}{dt} = \frac{k[Cl_2]^2[H_2]}{[Cl_2] + k'[H_2][O_2]}.$$

In this mechanism the oxygen does not act as a remover of atomic hydrogen, but degrades the energy of the chlorine as in the original theory of Chapman. Thon indeed

* *J. Chem. Soc.*, 1923, **123**, 3079.

† 'Die Chlorknallgasreaktion,' *Fortschritte der Chemie, Physik und physikalischen Chemie*, Band 18, Heft 11 (Berlin 1926).

‡ *Z. physikal. Chem.*, 1927, **128**, 285.

pointed out that, since the amount of water formed when oxygen inhibits the combination is very small compared with the amount of hydrogen chloride produced, it is quite unlikely the oxygen combines with the atomic hydrogen of a Nernst chain. Reaction (6) of the above scheme is supposed to be markedly catalysed by the walls of the reaction vessel: this would explain some of the discrepancies between the results of different observers.

X. Whatever be the exact mechanism of the chain process set up in mixtures of hydrogen and chlorine by illumination, it is evident that the wall of the containing vessel might play an important part in deactivating or destroying some active molecule or some catalyst upon which the propagation of the chain depends.

Chapman and Grigg* have indeed shown that in light of the same intensity the rate of combination of hydrogen and chlorine is less in capillary tubes than in tubes of wider diameter.

XI. Very complete desiccation prevents the combination of hydrogen and chlorine under the influence of light of the visible region. Coehn and Jung† found that there was no combination in systems where the pressure of water vapour was estimated to be 10^{-7} mm. Hg, but that the reaction took place rapidly when the pressure was 10^{-5} mm. Bodenstein and Dux‡ had found that variation of the pressure of water vapour between 10 mm. and 10^{-3} mm. had no effect on the combination.

In ultra-violet light, on the other hand, Coehn and Jung found that the thoroughly dried mixture combined as well as the moist mixture.

XII. Kistiakowsky has shown that when light is absorbed by intensively dried chlorine no appreciable part of it is re-emitted by fluorescence. Since, moreover, the total absorption is unaffected, it seems impossible that the

* *J.C.S.*, 1928, 3233. † *Z. physikal. Chem.*, 1924, **110**, 705.
‡ Loc. cit., *supra*.

water can play any part in the dissociation of chlorine molecules. Its role in the hydrogen chlorine combination must be at some later stage of the chains.

The remarkable thing about the action of water is that minute traces are effective and larger quantities without further influence. It has been pointed out that the amount necessary to give the maximum effect is such as would be just sufficient to form a unimolecular layer on the surface of the vessel. Similarly the minute traces of nitrogen chloride which can inhibit the decomposition are just sufficient to act as a catalytic poison by forming a layer over the surface. Taken in conjunction with the results of Chapman and Grigg these facts are very significant, but other possibilities for the explanation of the influence of minute traces of foreign substances on the initiation or breaking of reaction chains will be dealt with in Chapter VI.

The Union of Hydrogen and Bromine.

The thermal combination of hydrogen and bromine, and of hydrogen and chlorine, might be expected to be reactions analogous to the combination of hydrogen and iodine.

Only fragmentary information is available about the thermal union of hydrogen and chlorine, nearly all investigators having confined their attention to the photochemical reaction. The matter is in need of further investigation.

The formation of hydrogen bromide from its elements takes place in an unexpectedly complicated manner. Bodenstein and Lind* measured the velocity at 200° to 300° C. and found that it could be expressed by the equation

$$\frac{d[2\,HBr]}{dt} = \frac{k[H_2]\sqrt{[Br_2]}}{m + \dfrac{[2\,HBr]}{[Br_2]}},$$

m being a constant, independent of temperature and having the value 5.

* *Z. physikal. Chem.*, 1906, **57**, 168.

The interpretation of this curious result was given by Christiansen,* Polanyi,† and Herzfeld.‡ The reaction takes place in the following steps:

$$(1) \quad Br_2 = 2\,Br.$$
$$(2) \quad Br + H_2 = HBr + H.$$
$$(3) \quad H + Br_2 = HBr + Br.$$
$$(4) \quad H + HBr = H_2 + Br.$$

(1) is the ordinary thermal dissociation of bromine, which, at 200° to 300°, can only give rise to a very small concentration of bromine atoms. Expressing the fact that the rate of formation of hydrogen bromide is the sum of its rates of production in (2) and (3) less its rate of destruction in (4) we have

$$\frac{d[2\,HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][2\,HBr].$$

Further, the concentration of hydrogen atoms must be constant after the first few instants of the reaction, or the rate of reaction would steadily increase. This stationary state is expressed by the equation

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0.$$

Finally, we have for the bromine dissociation

$$[Br]^2 = k_1[Br_2].$$

Eliminating [H] and [Br] we obtain the experimentally found formula.

The Thermal Decomposition of Phosgene.

This is, in a sense, a bimolecular reaction, since it has been found by Christiansen § and by Bodenstein and Plaut || to proceed at a rate directly proportional to the concentration of the phosgene, and to the square root of the concentration of the chlorine, formed in the reaction or initially

* *Dansk. Vid. Math. Phys. Medd.*, 1919, **1**, 14.
† *Z. Elektrochem.*, 1920, **26**, 49. ‡ Ibid., 1919, **25**, 301.
§ *Z. physikal. Chem.*, 1922, **103**, 99. || Ibid., 1924, **110**, 399.

added. In the absence of chlorine there is a long induction period. The reaction seems, therefore, to be determined by collision between molecules of phosgene and atoms of chlorine—an unexpected result, fully discussed by Bodenstein and Plaut. They conclude that both velocity and equilibrium in the system

$$CO + Cl_2 \rightleftharpoons 2\,COCl_2$$

can be represented by the scheme

$$(1)\ Cl_2 \rightleftharpoons 2\,Cl,$$
$$(2)\ Cl + Cl_2 \rightleftharpoons Cl_3,$$
$$(3)\ Cl_3 + CO \rightleftharpoons COCl_2 + Cl,$$

the processes (1) and (2) being rapid in both directions, and (3) determining the observed velocity of the change.

It is interesting to note in comparison that the thermal decomposition of bromphosgene is a wall reaction of the first order.*

The Combination of Bromine Atoms $2\,Br = Br_2$.

An ingenious method of finding the velocity of this reaction was employed by Bodenstein and Lütkemeyer.† The results, although provisional only, afford the first information that has ever been obtained about the kinetics of reactions between free atoms. The method depends upon the conclusions outlined in the previous section relating to the hydrogen bromide formation.

It is based upon a comparison between the rate of hydrogen bromide formation in the dark and the rate of formation under the influence of light. The photochemical reaction proceeds in accordance with the equation

$$\frac{d[HBr]}{dt} = \frac{k\sqrt{\text{Light absorbed}}\,[H_2]}{m' + \dfrac{[HBr]}{[Br_2]}}.$$

The mechanism, therefore, appears to be exactly analogous

* Lenher and Schumacher, *Z. physikal. Chem.*, 1928, **135**, 85.

† *Z. physikal. Chem.*, 1924, **114**, 208.

to that of the thermal reaction, except that the bromine atoms are now provided in much larger numbers than before, being produced not merely by the ordinary thermal dissociation but by the reaction

$$(1)\ Br_2 + h\nu = 2\,Br,$$

$h\nu$ being the quantum of light absorbed in the photochemical dissociation of the bromine. This reaction is regarded on good grounds as the primary photochemical process, and is followed as before by the series of purely thermal reactions

$$(2)\ Br + H_2 = HBr + H,$$
$$(3)\ H + Br_2 = HBr + Br,$$
$$(4)\ H + HBr = H_2 + Br.$$

Simultaneously there occurs the reaction

$$(5)\ Br + Br = Br_2.$$

These assumptions lead, by the same method of calculation as that used in the case of the thermal reaction, to the correct velocity equation. It is to be noted that since (2) is followed by either (3) or (4) the actual formation of hydrobromic acid does not use up the supply of atomic bromine, and a stationary concentration of bromine atoms is established by the balancing of the rate of their photochemical formation (1) and the rate of their thermal recombination (5).*

* An interesting point connected with the processes $Cl_2 = 2\,Cl$ and $Br_2 = 2\,Br$ arises from a comparison of the photochemical formation of hydrogen chloride and that of hydrogen bromide. The rate of the former reaction is proportional to the first power of the light intensity, that of the latter to the square root of the intensity. This difference is due to the fact that the chlorine atoms formed by the process $Cl_2 + h\nu = 2\,Cl$ are used up as quickly as formed; thus the rate of reaction is determined by the rate of dissociation of the chlorine which in turn is proportional to the light intensity. On the other hand, the bromine atoms formed by the process $Br_2 + h\nu = 2\,Br$ are not used up nearly so efficiently, and much recombination occurs. The rate of reaction with hydrogen is proportional to the concentration of Br atoms at any

This stationary concentration determines the rate of hydrogen bromide formation. The photochemical reaction is about 300 times as fast as the thermal reaction at the same temperature (160° to 218° C.).

This means that in the photochemical reaction the concentration of the bromine atoms which prevails is about 300 times greater than in the dark reaction, since all other parts of the reaction mechanism are identical. The rate of combination is simply an indicator of the concentration of atomic bromine. Thus this concentration is found by the relation

$$\text{(conc. Br at any stage of photo reaction)} = \text{(conc. Br in dark reaction)} \times \left[\frac{\text{speed of light reaction}}{\text{speed of dark reaction}}\right].$$

The concentration of bromine atoms in the dark reaction is known from the concentration of molecular bromine and the thermal dissociation constant of bromine, hence that prevailing at any stage of the photochemical reaction is found.

The rate of production of bromine atoms by light is estimated on the basis of Einstein's law, which requires one molecule of bromine to be dissociated for each quantum of light absorbed. In the stationary state the number of bromine atoms recombining thermally in unit time is equal to this rate of photochemical formation. Thus the number of bromine atoms which recombine per second at a known atomic concentration is found. In this way Bodenstein and Lütkemeyer find that about one collision in a thousand between bromine atoms results in combination. This number is of the right order of magnitude only, since the estimation of the number of light quanta absorbed was not very certain, and a value based only on analogy had to be assumed for the diameter of the bromine atom.

moment. Since the rate of dissociation is proportional to $[Br_2] \times$ Intensity and the rate of recombination to $[Br]^2$, we have [Br] proportional to $\sqrt{[Br_2] \times \text{Intensity}}$.

Bodenstein and Müller* attempted to employ a second method depending upon the marked retardation of the hydrogen bromide formation by iodine. The iodine was assumed to react with the atomic hydrogen and thus prevent the main reaction. If sufficient iodine were added to remove practically all the hydrogen atoms produced, the rate of hydrogen bromide formation would be reduced to the rate of thermal formation of bromine atoms from molecules. This, in conjunction with the equilibrium constant of the bromine dissociation, would give the rate of reunion of the atoms. Further investigation† showed that the retardation by iodine had a cause other than the removal of hydrogen atoms: the reaction $I_2 + Br_2 = 2\,IBr$ takes place, and thus diminishes the concentration of the bromine atoms.

The Interaction of Alkali Metal Vapours with Halogens and Halogen Compounds.

When the vapour of alkali metals is mixed at low pressures, of the order 10^{-3} mm., with certain halogen compounds, a cold, highly diluted flame is produced. A deposit of alkali halide is formed on the wall of the tube in which the reaction takes place, and from the distribution of this deposit and the velocity of the gas stream the partial pressures of the reacting substances and the reaction velocity can be inferred. A number of investigations with various modifications of this method have been carried out by Polanyi and others,‡ and a careful analysis and interpretation of the results has yielded much interesting and valuable information about the speed of the chemical reactions involved.

* *Z. Elektrochem.*, 1924, **30**, 416.

† Müller, *Z. physikal. Chem.*, 1926, **123**, 1.

‡ Beutler and Polanyi, *Z. physikal. Chem.*, 1928, B, **1**, 3.
Bogdandy and Polanyi, ibid., 1928, B, **1**, 21.
Polanyi and Schay, ibid., 1928, B, **1**, 30.
Ootuka and Schay, ibid., 1928, B, **1**, 62, 68.

Two types of reaction may occur. The first type is exemplified by the action of sodium or potassium vapour with chlorine, bromine, iodine, cyanogen chloride, and cyanogen bromide. Taking sodium and chlorine as an example, it is found that the primary reaction is $Na + Cl_2 = NaCl + Cl$. In this primary reaction it appears that every collision is effective in leading to chemical change. Indeed, it appears probable that in all the primary reactions of this type each collision is effective, and Polanyi suggests that wherever an atom can undergo an exothermic reaction with a molecule the collisions will all be effective. This amounts to saying that in such reactions no activation is required.

Most of the chlorine atoms formed in the primary process appear to unite with sodium atoms at the wall of the vessel. This process is not accompanied by the emission of any light. Some chlorine atoms, however, react in the gas with sodium, but according to the equation

$$Na_2 + Cl = NaCl + Na$$

the NaCl molecules thus formed are activated, and on collision with Na atoms stimulate them to light emission.

An increase in the temperature of the reaction zone weakens the light emission, as a result of the dissociation of the sodium molecules, and this weakening can be used to determine the heat of dissociation of the sodium molecule (the value obtained is in approximate agreement with an independently determined value). Increase in the pressure of the sodium vapour increases the light emission. Both of these facts support the view that chlorine atoms react in the gas phase with molecular rather than atomic sodium.

While every collision between Na and Cl_2 appears to be effective in the gas, not more than one collision in 10,000 between Na and Cl in the gas phase appears to lead to the formation of an NaCl molecule.

In the second type of reaction sodium or potassium vapour reacts with the vapour of such compounds as mercuric chloride or bromide.

In these reactions heating the reaction zone does not diminish the light emission, and this increases much less rapidly with the pressure of the alkali metal than in the first type of reaction. Thus the molecules of the alkali metal apparently do not play the same important part. The primary reaction with sodium and mercuric chloride is

$$Na + HgCl_2 = NaCl + HgCl$$

followed by $HgCl + Na = Hg + NaCl$

in the gas.

One of the most interesting results of these studies is the establishment of the fact that certain reactions between atoms and molecules take place, without activation, at every collision.

Miscellaneous Reactions. Catalysis by the Walls of the Reaction Vessel.

When a discharge is passed through hydrogen under such conditions that the Balmer series is developed strongly—this is the spectrum known on theoretical grounds to be due to the free hydrogen atom—the tube becomes charged with atomic hydrogen, which possesses abnormal chemical properties.* The recombination of this to the molecular form might have been expected to be a homogeneous reaction, but in fact it takes place predominantly on the walls of the discharge tube, and with greater readiness at certain 'infected spots'. The catalytic recombination on the surface of a tungsten wire is so rapid that the wire is raised to incandescence.

The influence of moisture is interesting. It 'poisons' the walls of the tube and hinders the catalytic recombination of the hydrogen atoms. This produces the illusion that water vapour favours the production of the atoms in the discharge.

* R. W. Wood, *Proc. Roy. Soc.*, 1922, A, **102**, 1.

The decay of active nitrogen presents certain features of interest from the point of view of reaction kinetics. When a stream of nitrogen is drawn through a region where an electric discharge is taking place it acquires abnormal chemical activity, and, in addition, continues to glow after it leaves the region of the discharge.*

The production of the glow seems to demand the presence of a little oxygen or of some gas which readily takes up electrons to give negative ions.

Spectroscopic evidence shows conclusively that the glow is emitted by a neutral nitrogen molecule in an excited condition, and that the actual emission process is one in which nitrogen alone is concerned.† Different stages of activity are possible, and chemical activity may be shown by nitrogen which does not glow.‡ Nearly all the kinetic measurements deal, however, with the glowing gas.

Three views may be held about the nature of the process giving rise to the glow: (*a*) molecules of nitrogen excited in the discharge to a high energy level are 'metastable' and can continue to exist for some time after leaving the discharge, when they slowly revert to their normal state with emission of light; (*b*) atomic nitrogen emerges from the discharge, and then recombination takes place to give molecules at a high enough energy level to emit the spectrum; (*c*) nitrogen atoms emerge from the discharge and cause excitation of normal molecules in a ternary collision ($2\,N + N_2$).

The purely kinetic evidence seems to favour (*c*). Measurement of the rate of decay for a constant total pressure shows that the process is bimolecular with respect to the decaying substance, § i.e. the two atoms on this view. The rate of decay is proportional to the total pressure of

* Strutt, *J. Chem. Soc.*, 1918, **113**, 200.
† Cf. *Z. physikal. Chem.*, 1927, **127**, 385.
‡ Willey, *J. Chem. Soc.*, 1927, 2831.
§ Angerer, *Physikal. Z.*, 1921, **22**, 4, 97.

nitrogen.* (There is, moreover, theoretical reason for believing that free atoms cannot combine unless they suffer a collision with a third molecule which can remove the excess energy liberated by their union (see p. 111).) Finally, Rayleigh found that active nitrogen decays more rapidly at low temperatures than at high temperatures. If the decay depends upon a ternary collision, this is natural, since the chance of such encounters decreases with increasing speed of the molecules.

With regard to the part played by foreign electronegative gases in the production of active nitrogen, two suggestions have been made. Birge suggests that if the glow is emitted by metastable molecules, these could only escape from the discharge at all in the absence of the disturbing fields of free electrons. The function of the foreign gas is to 'clean up' these and permit the metastable molecules to persist for a long enough time to leave the discharge. The other explanation, a much more satisfactory one, is that the foreign gases 'poison' the walls of the vessel, and so prevent the destruction of atomic nitrogen in a glowless wall reaction. Rayleigh found the decay to be much influenced by the walls of the vessel, while Bonhoeffer and Kaminsky showed that in particular the effect of the different foreign gases was very much a function of the walls.

It seemed just possible that some of the common reactions which take place very rapidly at ordinary temperatures might prove to be homogeneous more often than slower changes. Stewart and Edlund,† however, found that the rapid combination of ethylene and bromine in a glass vessel took place almost entirely on the walls. This is a rather surprising result and shows how little justified the expectation that rapid reactions would be homogeneous really is.

* Willey, *J. Chem. Soc.*, 1929, 228.

† *J. Amer. Chem. Soc.*, 1923, **45**, 1014.

Norrish * has made experiments on the effect of the nature of the material of the vessel on the combination of ethylene and bromine. In a glass vessel covered internally with paraffin wax, the combination proceeded with extreme slowness, and even such as was observed could be attributed mainly to the glass surface exposed by the imperfections in the film of wax. Other surfaces were used, and it was found that surfaces coated with stearic acid were more active than glass, with cetyl alcohol less active than glass, but that all these are much more active than paraffin wax.

H. A. Taylor † made a similar experiment with phosphorus trichloride vapour and chlorine, which in glass vessels combine almost instantaneously to give the solid pentachloride. In this instance the combination still took place with immeasurable rapidity in a vessel of paraffin wax. This combination, unlike that of ethylene and bromine, appears to be a homogeneous reaction, since when the trichloride and chlorine are mixed there is a delay of a few seconds due to supersaturation, and then the solid is formed as a cloud which settles slowly to the bottom of the vessel. Some solid formation also takes place on the walls.

* *J. Chem. Soc.*, 1923, **123**, 3006.

† *J. Physical Chem.*, 1924, **28**, 510.

III

THE ENERGY OF ACTIVATION

Introduction.

It will be seen from the foregoing survey that although well-defined examples of homogeneous unimolecular reactions exist they are not as numerous as might have been expected. Many reactions which would merit investigation cannot be studied owing to the predominance of a wall reaction. The thermal decomposition of ammonia, $2\,NH_3 = N_2 + 3\,H_2$, for example, appears highly suitable for a kinetic study, but is found to take place almost entirely in a heterogeneous manner up to about 1,200° C., where the speed becomes too great to be measured.

Of homogeneous reactions, the number which follow a quite simple course is still further limited. The combination of hydrogen and bromine, for example, takes place by a quite complicated mechanism. Of those which are bimolecular in a fairly well-defined manner we have the thermal decomposition of hydrogen iodide, of nitrous oxide, of acetaldehyde, of nitrogen peroxide, and probably of ozone; the interaction of hydrogen and iodine, and, except for the complication of its occurrence in consecutive stages, the thermal decomposition of chlorine monoxide. In some of the more complex changes, moreover, one or other of the stages has several times involved a bimolecular reaction between an atom and a molecule, or the formally bimolecular combination of two atoms.

Examples of unimolecular and termolecular homogeneous reactions will appear in subsequent chapters: but the interpretation of the results yielded by kinetic studies of these reactions is much facilitated if the application of the theory of activation to the simpler example of bimolecular reactions is first considered in detail.

General discussion of the theory of activation.

There are several reasons why a chemical reaction might take place at a rate which is less than that at which the molecules can come together. The molecules might have to be in a suitable orientation or a suitable internal phase before they can react, or they might have to wait their turn to come into contact with a catalyst present in small concentration, or they might have to be 'activated' by the acquisition of energy. Since Arrhenius explained the law of variation of reaction velocity with temperature in terms of 'active molecules' it has been recognized that the third condition is the most essential one.

The number of molecules which react in unit time is far smaller than the number entering into collision: this shows that those which suffer transformation are in some way in an exceptional state. The attainment of this exceptional state is very much favoured by increase of temperature: molecules of high energy content are thus indicated, since the assumption of specific tautomeric changes* into an active form is impossible in the case of quite simple molecules. The law of variation with temperature of the number of molecules the energy of which exceeds an assigned value is, moreover, precisely the same as that of the change in reaction velocity.

The law in question is $\log k = C - E/RT$, or $k = \chi e^{-E/RT}$, where C and χ are constants. The exponential factor $e^{-E/RT}$ occurs frequently in physical problems, and almost

* Rice, Fryling, and Weselowski (*J. Amer. Chem. Soc.*, 1924, **46**, 2405) make all reaction rates proportional to the concentration of what they call residual molecules, which have to be formed endothermically from one of the reactants. The proportion of these increases with temperature and accounts for the increase in reaction rate. Something of this kind may be true in special cases, for example, in the formation of HBr the residual molecule would be the bromine atom. But this resolution into atoms is only the limiting case of ordinary activation, and it is difficult indeed to see what the residual molecule could be, or what tautomeric change could occur in the simple decomposition of hydrogen iodide or nitrous oxide.

invariably denotes the probability that the energy exceeds E.

This is the theory in its most general form ; nothing is so far specified about the nature of the energy. It may be remarked that the idea of an energy increment being in general necessary for chemical change is in accordance with our views on molecular structure, and the existence of higher vibrational quantum states.

In the special application to bimolecular reactions, as shown in the last chapter, the actual rate of reaction can be calculated from the equation

$$\textit{number of molecules reacting} = \textit{number entering into collision} \times e^{-E/RT}.$$

In six out of the seven examples of bimolecular reactions this expression allows the absolute rate of reaction to be calculated from the value of E, determined independently from the temperature coefficient, with an accuracy which is within the limits of experimental uncertainty.

The most striking evidence, however, of the significance of the energy of activation is provided by a comparison of the values of this energy for different bimolecular reactions.

Since all molecular diameters and velocities are of the same order of magnitude, and since the rates of different chemical reactions at a given temperature vary by many powers of ten, the absolute rate of a reaction is principally determined by the exponential term $e^{-E/RT}$. Thus the higher the value of E, the higher should be the temperature at which the reaction can obtain a given speed. This conclusion is strikingly verified, as shown by the following table.

Reaction	E_1	E_2	T (abs.)
Thermal Decomposition of			
$2\,N_2O$	55,500	58,500	956°
$2\,HI$	45,400	44,000	760°
$2\,NO_2$	33,500	32,000	575°
$2\,Cl_2O$	22,000	21,000	384°

E_1 is the heat of activation calculated from the equation

$$\frac{\text{number of effective impacts}}{\text{total number of impacts}} = e^{-E/RT}$$

E_2 is that obtained from the Arrhenius equation for the temperature coefficient.

T (abs.) is the temperature at which the bimolecular velocity constant has an arbitrarily chosen value for each reaction (namely 0·0914 gram mol. per litre per second).

The parallelism between E and the absolute temperature at which the reaction attains the assigned speed is evident. With minor variations, quantitatively accounted for by the differences in molecular diameters and velocities, the fraction $e^{-E/RT}$ has the same value for the different reactions. This is one of the most striking pieces of evidence for the reality of the energy of activation.

The decomposition of acetaldehyde and the union of hydrogen and iodine fit equally well into their places in this table. The decomposition of ozone, however, appears to have a greater value of E than would be expected from its velocity, and will be considered further in a subsequent section.

It is desirable that examples should be found of homogeneous bimolecular reactions which proceed with measurable velocity only at still higher temperatures than any of those recorded above. The decomposition of ammonia would be a good example if it could be measured. The heat of activation should be over 70,000 calories, since the velocity constant does not attain a measurable value up to about 1,200° C.

More detailed consideration of the equation for the rate of bimolecular reactions.

From quite general considerations about the nature of linkings between atoms, and from the fact, revealed by band spectra, that a whole sequence of vibrational quantum states leads up to complete dissociation of a molecule, it

might be expected that activation of two molecules AB and CD would consist in the acquisition by each of a number of quanta of vibrational energy. The molecules so loosened can then rearrange themselves to give AC and BD.

In a bimolecular reaction the two molecules must be in collision at the moment of transformation, so that the activating process might be the collision itself.

We thus have two possibilities, (a) a collision between two molecules, of sufficient violence to provide the energy E, (b) a collision of any kind between two molecules endowed with the right amount of vibrational energy. We will consider these in turn.

(a) Let Z be the number of molecules entering into collision in unit time, i.e.

$$Z = \sqrt{2}\,\pi\,\bar{u}\,\sigma^2 n^2.$$

If activation is brought about by a collision of sufficient violence, and the energy of activation is simply the kinetic energy of translation, there seems to be no good reason why it should not be simply the sum of the two energies without any conditions about separate values E_1 and E_2 for the two molecules. But since only the 'head-on' components of the velocities will be effective, we must take only *one* degree of freedom of translational motion for each molecule. Then the chance of an energy sum exceeding E in a collision comes out to

$$\int_E^\infty \int_0^E \frac{1}{(\pi RT)^{1/2}} Q^{-1/2} \,.\, e^{-Q/RT} \,.\, dQ \times \frac{1}{(\pi RT)^{1/2}} (E-Q)^{-1/2} \,.\, e^{-(E-Q)/RT} \,.\, dE$$

as shown on page 22. The result is $e^{-E/RT}$.

(b) If one internal degree of freedom in each molecule needs to be activated, the chance of an energy greater than E_1 in one molecule is $e^{-E_1/RT}$ and of an energy greater than E_2 in the other molecule is $e^{-E_2/RT}$, since the vibra-

tional energy involves two quadratic terms. If the two molecules participating in the reaction require independent activation to the extents E_1 and E_2 respectively, the number of molecules colliding, with this condition satisfied, is

$$Z \cdot e^{-E_1/RT} \times e^{-E_2/RT} = Ze^{E/RT}, \text{where } E = E_1 + E_2.$$

This is essentially the proof given in the last chapter.

If we do not assume the existence of the separate energies of activation E_1 and E_2, but allow the sum E to be made up in all possible ways, with a contribution of from zero upwards from either molecule, then the result assumes a different form. The chance that two molecules in a collision have a total energy E, in the vibrational form, between E and $E+dE$ is

$$\int_0^E \frac{1}{RT} e^{-Q/RT} \times \frac{1}{RT} \cdot e^{-(E-Q)/RT} \cdot dE$$

the integral being taken over all values of Q from 0 to E.

The result is $$\frac{E}{R^2T^2} e^{-E/RT}\, dE.$$

The number of molecules colliding with a joint vibrational energy greater than E is

$$Z\int_E^\infty \frac{E}{R^2T^2} e^{-E/RT} \cdot dE = Z\left(\frac{E}{RT}+1\right)e^{-E/RT}.$$

From the actual values of E we see that this expression is 20 to 30 times greater than that previously derived.

To sum up, the expression $Ze^{-E/RT}$ gives the number of molecules colliding with a total energy exceeding E, when the energy is not allowed to vary independently in more than two quadratic terms. Thus for example we may take the energy to be vibrational energy (two quadratic terms) and impose an independent critical limit for each molecule, or kinetic energy of translational motion along the line of centres (one quadratic term for each molecule), and make no restriction about how it is shared between the two molecules.

The second way of regarding the matter is so simple and satisfactory that we shall adopt it as a working hypothesis, in preference to the hypothesis made in the last chapter.

Two matters now demand consideration. First, if translational energy is concerned, and if more or less ' head-on ' collisions are necessary, then $\bar{u}$ should, for the collisions among molecules of high energy, be replaced by a greater value. This would make the calculated number of activating collisions greater in about the ratio $\sqrt{\frac{E}{RT}}$, or about five or six times greater.

Secondly, the orientation of the molecules at the moment of impact may be of importance, in addition to which, in assuming one degree of freedom for each molecule in calculating the energy of collision, we made only an approximate allowance for the influence of the direction of approach. This would all tend to reduce the effectiveness of the collisions, perhaps by 2 or 3 times.

Combining this with the 5- to 6-fold increase to be expected from the greater velocities, we may make an estimate that the expression $Ze^{-E/RT}$ should be multiplied by about 2·5 to give the number of molecules which would react. This factor has been used in the calculations of the last chapter and of this.

Its magnitude, however, is unimportant, since the uncertainties in the values of the molecular diameters, and of the exponential term, where the experimental errors in E are greatly magnified, are greater than the whole factor.

What we may say with some certainty, however, is that the rate of most bimolecular reactions can be expressed by the equation: number of molecules reacting $= P.Ze^{-E/RT}$, where P is a factor of the *order of magnitude* unity, i. e. within a power of ten.

There is no *a priori* reason why P should not vary by

many powers of ten from reaction to reaction, for all kinds of internal phase conditions might have to be favourable. If this had been found to be the actual state of affairs we should have been unable to make much progress.

But the fact that P is of the order of magnitude unity, combined with the parallelism between E and the temperature required to give an assigned rate of reaction, indicates that activation is the fundamental process in bimolecular reactions. The general coherence of the results would seem to justify the statement that an activating collision is not merely a necessary but a sufficient condition for chemical transformation.

More exact determinations of P may show that this is only a rough statement of the truth. It is quite possible that molecules may sometimes be reflected unchanged when in particular states, although the activation conditions are satisfied. It has also been suggested that P might be a function of the excess of energy over the minimum required for activation*—although this amounts rather to an elaboration of the idea of the simple critical energy limit than to the kind of factor we are dealing with here.

Kistiakowsky,† discussing the velocity of decomposition of hydrogen iodide, a reaction probably more free from complicating factors than any of the others, and therefore with more accurately known constants, concludes that 'the effective cross-sections of activated molecules in collisions leading to reaction are smaller than the average kinetic cross-sections of molecules'; in other words, the calculated rate, using the ordinary molecular diameters, is really slightly too large, or P is less than unity. This may well be true, but how far the effect is real is not quite easy to judge, since quite small variations in E make a considerable difference to the results.

* Garner, *Phil. Mag.*, 1925, **49**, 463.

† *J. Amer. Chem. Soc.*, 1928, **50**, 2315.

Activation of molecules with many degrees of freedom: energy of activation and 'critical increment'.

The simple exponential factor $e^{-E/RT}$, as we have seen, is only applicable strictly to represent the probability of a total energy E of the colliding molecules in two quadratic terms. As an approximation it may be used for any quite small number of terms. In fact its applicability with such success to bimolecular reactions might be taken to show that the activation process in such reactions was a relatively simple one, whatever its exact nature might be.

If we regard the two colliding molecules as one system, the fraction of such systems which possess energy greater than E in n quadratic terms is

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

which is much larger than $e^{-E/RT}$ when n becomes considerable. In the decomposition of ozone * the heat of activation appears to be rather greater than could be supplied to the molecules by simple impact at the required rate, and it is possible that the activation process is more complex, involving several degrees of freedom. This we shall see to be characteristic of unimolecular reactions. The possibility of a chain mechanism in an exothermic reaction like the decomposition of ozone must not be forgotten (see Chapter VI).

It might be suggested that the rates of the other bimolecular reactions which have been considered could be accounted for by assuming a larger value of n for the activation process, giving a much greater rate of activation, and a much smaller value of P, indicating 'inelastic' reflection of many of the molecules which have enough energy to react. The very great objection to this is that the coherent set of relationships between the energies of

* Belton, Griffith, and McKeown, *J. Chem. Soc.*, 1926, 3153.

activation and the temperatures of equal reaction velocity for different reactions on the one hand, and the calculated and observed rates of the same reaction on the other, could then only come about as a result of an accidental compensation of the two factors. This is improbable.

The form of the Arrhenius equation for the variation of the velocity constant with temperature requires some consideration when n is large.

If k is proportional to $\dfrac{e^{-E/RT}\left(\dfrac{E}{RT}\right)^{1/2n-1}}{\left|\frac{1}{2}n-1\right.}$ we have

$$\log k = \text{constant} - \frac{E}{RT} - (\tfrac{1}{2}n-1)\log T,$$

whence

$$\frac{d\log k}{dT} = \frac{E}{RT^2} - \frac{(\frac{1}{2}n-1)}{T}$$
$$= \frac{E-(\frac{1}{2}n-1)RT}{RT^2}.$$

Since the average energy of the molecules is $\frac{1}{2}RT$ for each of the n terms, $\frac{1}{2}nRT$ is the average energy of all the molecules. Thus we have $\dfrac{d\log k}{dT} = \dfrac{E+RT-\bar{U}}{RT^2}$, where $\bar{U}$ is the average energy. The formula $\dfrac{e^{-E/RT}\left(\dfrac{E}{RT}\right)^{1/2n-1}}{\left|\frac{1}{2}n-1\right.}$ is only an approximation formula itself, the more correct expression being $\dfrac{1}{\left|\frac{1}{2}n-1\,(RT)^{1/2n}\right.}\int_E^\infty e^{-E/RT}E^{1/2n-1}.dE.$ By employing this we may show that the really correct form of the Arrhenius equation is

$$\frac{d\log k}{dT} = \frac{\text{Average energy of the activated molecules} - \text{Average energy of all the molecules}}{RT^2}$$
$$= \frac{\bar{E}-\bar{U}}{RT^2}$$

For $k = \frac{A}{\lfloor \frac{1}{2}n - 1} (RT)^{-1/2n} \int_E^\infty e^{-E/RT} . E^{1/2n-1} . dE$

where A is constant.

Differentiating under the integral sign with respect to T we find

$$\frac{dk}{dT} = \frac{A}{\lfloor \frac{1}{2}n - 1} (RT)^{-1/2n} . \int_E^\infty \frac{E}{RT^2} . e^{-E/RT} . E^{1/2n-1} dE - \frac{\frac{1}{2}n . A . R^{-1/2n} . T^{-1/2n-1}}{\lfloor \frac{1}{2}n - 1} \int_E^\infty e^{-E/RT} . E^{1/2n-1} dE$$

$$\frac{1}{k}\frac{dk}{dT} = \frac{\int_E^\infty E . e^{-E/RT} . E^{1/2n-1} dE}{RT^2 \int_E^\infty e^{-E/RT} . E^{1/2n-1} dE} - \frac{\frac{1}{2}n}{T}$$

$$\frac{d \log k}{dT} = \frac{\int_E^\infty E . e^{-E/RT} . E^{1/2n-1} . dE}{\int_E^\infty e^{-E/RT} . E^{1/2n-1} dE} - \frac{\frac{1}{2}nRT}{RT^2}$$

$$= \frac{\text{Average energy of all molecules with energy greater than } E - \text{Average energy of all molecules}}{RT^2}$$

$$= \frac{\bar{E} - \bar{U}}{RT^2}$$

For this reason the constant of the Arrhenius equation is sometimes called the critical increment of energy. When n is small E and $\bar{E} - \bar{U}$ are very nearly equal.*

Modification of the Arrhenius equation for reactions depending on molecular collisions at high temperatures.

We have for a simple bimolecular reaction the equation

$$k = \text{constant} . \bar{u} . e^{-E/RT}.$$

* For a fuller discussion cf. Tolman, *J. Amer. Chem. Soc.*, 1925, **47**, 2652.

The term $e^{-E/RT}$ is the only one which varies considerably with temperature.

Differentiation of the equation

$$k = \text{constant} \,.\, e^{-E/RT}$$

leads to the Arrhenius equation

$$\log k = \log \text{constant} - E/RT,$$
$$d\log k/dT = E/RT^2.$$

Strictly, however, the variation of $\bar{u}$ should be taken into account.

Since $\bar{u}$ varies at $T^1/^2$,

$$k = \text{constant.}\sqrt{T} \,.\, e^{-E/RT},$$
$$\log k = \log \text{constant} + 1/2 \log T - E/RT,$$
$$d\log k/dT = 1/2\,T + E/RT^2,$$
$$= \frac{E + 1/2\,RT}{RT^2}.$$

The term E of the Arrhenius equation is thus not really quite constant, but the deviations from constancy are numerically too small to be observable when $\log k$ is plotted against $1/T$ in the usual way. This may be seen by reference to the data given in the last chapter for the decomposition of nitrous oxide. The slope of the $\log k$, $1/T$ curve gives an uncorrected value E equal to 59,500 calories. The temperature varied by about 150 on either side of 1,000° abs. The corresponding values of $1/2\ RT$ varied therefore between 850 and 1,150 approximately. $1/2\,RT$ thus equals $1{,}000 \pm 150$. The uncorrected value of E, obtained directly from the Arrhenius equation, must therefore be diminished by this amount. Since 150 in 59,500 is considerably smaller than the experimental error, it is easily seen that no deviation of the curve from a straight line could have been detected. Nevertheless the mean correction amounting to 1,000 calories is appreciable, and reduces the value of E to that given, namely 58,500 calories. At temperatures below about 500° abs. the correction would be hardly worth applying.

In principle it might be better to plot $\log k/\sqrt{T}$ instead of $\log k$ against the reciprocal of the temperature, but since the distribution law $e^{-E/RT}$ is already an approximation it is perhaps not worth while to depart from the simple classical equation for the representation of experimental results.

Rate of reaction and rate of activation.

When molecules are activated in the actual collision by which they are transformed chemically, there is no distinction between rate of activation and rate of reaction. This corresponds to the simplest interpretation of bimolecular reaction velocities, namely, that reaction follows collisions of sufficient violence.

If the activation process is an independent one for the two molecules, such, for example, as the absorption of radiation, ' active molecules ' exist in definite concentration, and have a definite average life, which may be terminated either by chemical transformation or by simple loss of energy, a process conveniently called deactivation.

In general we may distinguish two extreme cases : where all the molecules which are activated are transformed at once or at least before they lose their energy again, and, at the other extreme, where only a small proportion of the molecules which possess enough energy to react are actually transformed, most of them being deactivated again. When the second state of affairs prevails there is a definite concentration of active molecules in the system expressed by the appropriate energy distribution law.

The relations actually existing between rate of activation and rate of reaction may be roughly analysed as follows.

(*a*) In some reactions no activation of the molecules is required : this applies particularly to certain reactions involving free atoms, which are discussed further in a later section.

(*b*) The chemical transformation takes place in the activating collision. The efficiency of the process need not be unity, since some of the collisions, even though violent enough, may merely lead to 'reflection'. But with bimolecular reactions in gases the efficiency appears to approach unity.

(*c*) The production of the activated molecules may be quite independent of the collision in which they are chemically transformed, or indeed the final transformation may not depend upon a collision. The rate of activation and deactivation may both be great compared with the rate of reaction: this will appear to be characteristic of many unimolecular reactions (Chapter V).

(*d*) In exothermic reactions the energy liberated may be handed on to molecules of the reacting substance and activate them more rapidly than the normal process of collision. This gives rise to what is called a 'chain-reaction' (Chapter VI).

Bimolecular reactions in solution.

The study of reactions in solution is outside the scope of this book, but a general comparison between bimolecular reactions in solution and those in the gaseous state is interesting as a commentary on the preceding section.

The first important fact is that, as Menschutkin showed, the velocity of a reaction may vary several hundredfold with change of solvent. No general explanation of this has been found, and it must be concluded that reaction rates are subject to highly specific influences of solvent molecules.

Secondly, with regard to the relation between rate of activation and rate of reaction, if we assume that the frequency of collision between molecules A and B is of the same order of magnitude in solution as at corresponding concentrations in the gaseous state, and further that the heat of activation is a simple quantity determinable

directly from the temperature coefficient, then, as Christiansen * has pointed out, the effectiveness of collisions in bimolecular reactions is several powers of ten smaller in solution than in gases. The assumptions, especially the second, are, of course, not free from uncertainty as regards any single example, but from the fact that the result is a general one we must conclude that a large proportion of deactivations occur in solution.

Norrish and Smith † have studied two reactions, namely, the interactions of trimethylamine with *m*- and with *p*-nitrobenzyl chloride in non-polar solvents, with a view to correlating the absolute rates of change with the values for the energy of activation as calculated from the temperature coefficients. They find here also that there is a marked deactivating effect of the solvent, which, as they point out, is not surprising, since in solution the mean free path is of the same order as the molecular diameter, and 'nearly every collision between potentially reactant solute molecules must therefore of necessity partake of the nature of a ternary collision at least, in which the third body is a solvent molecule'.

Reactions involving free atoms.

Is is noteworthy that many chemical reactions, especially those in which halogens play a part, involve the intervention of free atoms. Atomic chlorine is involved at some stage of the reaction between hydrogen and chlorine and in the reaction between carbon monoxide and chlorine. Atomic bromine is involved in the reaction between hydrogen and bromine. In a number of photochemical reactions in solution, between halogens and other substances the rate of reaction is proportional to the square root of the light intensity which indicates, as shown on page 86, that the primary process is the resolution of the halogen molecule into atoms. In the interaction of hydrogen and sul-

* *Z. physikal. Chem.*, 1924, **113**, 35. † *J. Chem. Soc.*, 1928, 129.

phur vapour Norrish and Rideal have suggested that the sulphur atom rather than the sulphur molecule attacks the hydrogen. In addition to these examples we have the reactions, studied by Polanyi, between alkali metal atoms and halogen compounds. Some typical examples of these reactions may be tabulated for reference.

(1a) $Cl_2 = Cl + Cl$ (1b) $Cl + Cl = Cl_2$
(2a) $Br_2 = Br + Br$ (2b) $Br + Br = Br_2$
(3) $Cl + Cl_2 = Cl_3$
(4) $H + HBr = H_2 + Br$
(5) $S + H_2 = H_2S$
(6) $Na + Cl_2 = NaCl + Cl$

It is quite understandable that resolution into atoms should sometimes occur, since this is nothing but the limiting case of ordinary activation. Ordinarily activation of two molecules, AB and CD, consists in a loosening of the attachment of A to B and of C to D by a collision of sufficient violence to impart a considerable number of vibrational quanta to each molecule—normal heats of activation correspond to about 10 such quanta. AB and CD usually rearrange themselves to AC and BD without first being completely resolved into atoms. Resolution into atoms, however, as the study of band spectra shows, is the natural limit of the activation process, and indeed the amount of energy required to resolve the halogens into their atoms is of the same order of magnitude as the usual heats of activation.* Thus the occasional appearance of free atoms, especially as part of a complex series of changes, is far from being anomalous, or from constituting a sharp contrast with the rather commoner class of reaction where complete resolution does not occur.

For a reaction between two atoms such as (1b) or (2b) no activation can be required. This is not necessarily true of reactions between an atom and a molecule, such as (4),

* Cf. the heat of dissociation of chlorine, 57,000 calories, with the values of E in the table on page 96.

(5), or (6), although it is certainly fair to expect that the extent of the activation demanded, if any is demanded, will be much smaller. This anticipation is fully confirmed for exothermic reactions of this type.

Polanyi finds that in reaction (6) every collision is effective.* Bodenstein,† by more indirect methods, concludes that this is also true of reaction (3). The results are not by any means exact enough to show whether the orientation of the colliding atoms and molecules is of any significance, but they prove that no appreciable degree of thermal activation is required for reaction to occur. The method of calculation depends upon a comparison of the thermal and photochemical formation of phosgene. The thermal formation of phosgene yields another relevant result: the process determining the rate is $Cl_3 + CO = COCl_2 + Cl$. The amount of Cl_3 in equilibrium with Cl_2 can be calculated from Nernst's heat theorem if the heat of formation be known. The number of collisions between Cl_3 and CO molecules can then be calculated. If the whole temperature coefficient of the reaction velocity be attributed to the shift in the equilibrium between Cl_3 and Cl_2—an assumption justified by the result—the calculation can be made, and leads to the conclusion that the number of collisions between Cl_3 and carbon monoxide is of just the same order of magnitude as the number of molecules of phosgene formed. This being so, no activation is necessary, and the assumption about the temperature coefficient is justified *a posteriori*. Cl_3, as Bodenstein points out, may, owing to its very great instability, be regarded as an 'atom-like' substance from this point of view. In the reaction between hydrogen and sulphur vapour, the heat of activation is equal to the heat of dissociation of the sulphur molecule into atoms. This indicates, as in the previous example, that the subsequent processes do not demand any considerable degree of activation.

* p. 88. † *Sitzungsber. Preuss. Akad. Wiss.*, 1926, **13**, 104.

Formally, we might express the extreme types of behaviour thus:

$$(a)\quad A_2 + B_2 + \text{energy} \rightarrow 2AB$$

$$(b)\begin{cases} A_2 + \text{energy} & \rightarrow A + A \\ A + B_2 & \rightarrow AB + B \end{cases}$$

There is no theoretical reason why the second stage of (*b*) should not require some energy, though we expect it to be small. Actually a number of experimental results indicate that the amount required approaches zero in exothermic reactions.*

Processes in which two atoms combine to give a single molecule demand further consideration. No activation is required, but another condition has to be fulfilled, as Herzfeld † and Polanyi ‡ have pointed out. When two atoms collide, the nascent molecule which is formed contains all the energy of formation, and this, moreover, must be exactly quantized. Unless therefore its energy can be adjusted by a collision with a third molecule or with the wall of the vessel it will be incapable of continued existence and will fall apart again. This view about the necessity of collision with a third molecule is often referred to as the 'Dreierstoss' theory. Reactions of the type $A + BC = AC + B$ are not affected by these considerations, since the kinetic energy with which the two products of the reaction fly apart adjusts itself in accordance with the quantum demands of the molecule AB.

In the reaction between hydrogen and bromine Bodenstein found that a fraction of the order 1/1,000 of the collisions between bromine atoms leads to combination at about 200° C., but how exact this estimate is cannot easily

* If the change were endothermic, a heat of activation equal to, but no greater than, the heat of reaction would correspond to the zero activation of the exothermic case.

† *Z. Physik*, 1922, **8**, 132.

‡ Ibid., 1920, **1**, 337. Compare also Born and Franck, *Ann. Phys.*, 1925 [IV], **76**, 225.

be judged. At quite low gas-pressures, however, a still smaller value was found, which indicates that the 'Dreierstösse' were here beginning to be insufficient to stabilize all the potential bromine molecules.

The re-combination of hydrogen atoms is essentially a wall reaction, where the requirements of the theory are automatically fulfilled. There is also, as we have seen, a good deal of evidence that a process $2N + N_2 = 2N_2$ plays a part in the decay of active nitrogen.

Ionization and chemical change.

Since the nature of chemical combination is electrical it is natural to inquire whether there is any essential connexion between chemical activation processes and ionization. From the early days of the electron theory experiments have been made with the object of establishing such a relationship, but most of the evidence seems to indicate that any ionization accompanying ordinary chemical reactions is very small and probably of a purely secondary character.*

A. K. Brewer has measured the ionization accompanying a number of gas reactions, and found that on the average one pair of ions was always formed for the reaction of about 10^{13} molecules.

The measurements by Garner and others of the amount of ionization attending gaseous explosions show that it corresponds fairly closely to the purely thermal ionization which might be expected at the maximum temperature of the explosion.

Theoretical consideration, moreover, of the physical nature of the activation process, and its limit, the resolution of the molecule into atoms, suggests that there is no direct or necessary connexion between ionization and

* Discussions of this matter, to some extent from opposing points of view, are to be found in the Annual Reports of the Chemical Society, 1927 (Chemical Kinetics) and 1928 (Catalysis), where full references are also given.

stimulation of the vibrational degrees of freedom of the molecule. Physical evidence indicates two kinds of molecule, 'atom-molecules' and 'ion-molecules': the former, even on complete resolution, giving uncharged atoms.

For all these reasons it seems preferable to regard the ionization phenomena as secondary. Although the opposite view has not infrequently been stated, and must be given every consideration, it appears at all events to be clear that electrical phenomena of a measurable kind actually manifest themselves in gaseous reactions to an insignificant extent.

The influence of moisture.

Examples have not infrequently been found of reactions which involve the intervention of some impurity in the system, not at first imagined to be playing any part in the chemical change. For example, the rate of decomposition of hydrogen peroxide in aqueous solution is very variable, and Rice and Kilpatrick * traced the cause of this behaviour to the fact that the decomposition is mainly determined by the catalytic action of dust particles. As a result, the view has sometimes been held that pure substances are in general very unreactive, and that velocity measurements have no absolute significance, because the reaction mechanism is quite different from what it appears to be, and involves the participation of accidental impurities. Among such impurities water occupies the most prominent position.

The phenomena attending the complete desiccation of chemical systems, interesting and important as they may be, can, however, be regarded in a quite exaggerated perspective. The objections to the view that moisture, or indeed 'impurities' generally, are necessary to chemical change in general, or that the rate of chemical reactions is determined by the rate at which molecules can come into

* *J. Physical Chem.*, 1927, **31**, 1507.

association with such catalysts, can be summarized as follows.

Where the rate of reaction depends upon the presence of an accidental catalyst, measurements are characterized by great lack of reproducibility. Many homogeneous reactions, on the other hand, have quite definite and reproducible rates. For example, the measurements of Bodenstein and of Kistiakowsky on the rate of decomposition of hydrogen iodide agree excellently, as do those of numerous investigators of the rate of decomposition of nitrogen pentoxide.

The general coherence of the whole picture of chemical reactions which can be constructed without the aid of such an hypothesis makes it superfluous.

Finally, the insufficiency of any positive evidence for the hypothesis has to be admitted. Most of the reactions where, for example, inhibition by drying has been described are kinetically of a fundamentally different type from the homogeneous reactions we have been considering. No claim has ever been made to have retarded by drying any one of the reactions described in the last chapter, with the exception of the combination of hydrogen and chlorine. Of the examples where inhibition by drying has been reported the great majority are interactions between substances in two different phases, where the great influence of an adsorbed film in poisoning or promoting the activity of a boundary surface, or of nuclei, can be understood. Some others, which appear at first sight to be homogeneous reactions, are really heterogeneous, as, for example, the union of ethylene and bromine, where the 'polar' nature of the surface is known to be of great influence. Retardation of such reactions by drying is an interesting and important fact, but not one on which generalizations about homogeneous reactions should be based. Apart from the photochemical reaction between hydrogen and chlorine, the only reaction on which normal velocity measurements

have been made, and which is said to have been retarded by drying, is the union of nitric oxide and oxygen.* But this is equally definitely stated to proceed just as well in the absence of water.†

It will be interesting to consider a few typical reactions where inhibition by drying has actually been found.

The homogeneous reaction between carbon monoxide and oxygen has only been observed in the explosion wave. The explosion takes place much more readily in the presence of steam than in its absence.‡ Dixon explained this by showing that the series of reactions

$$CO + H_2O = CO_2 + H_2$$
$$2H_2 + O_2 = 2H_2O$$

takes place much more readily than the direct oxidation $2CO + O_2 = 2CO_2$. More recently Weston§ showed that both direct and indirect oxidation of the carbon monoxide occur, the direct oxidation tending to predominate at high pressures.

The union of hydrogen chloride and ammonia is typical of another class of reaction. When not 'completely dry' the gases combine immeasurably fast; when dried beyond a certain point they are said not to react at all.|| There is no stage of 'dryness' at which a reaction with measureable velocity occurs.

The union of hydrogen and chlorine under the influence of visible light¶ is analogous to the extent that when the partial pressure of water vapour is 10^{-7} mm. the reaction is said to be inhibited, while at all higher pressures it proceeds normally.

The two remarkable characteristics of the action in

* Baker, *J. Chem. Soc.*, 1894, 611.
† Briner, *J. Chim. physique*, 1926, **23**, 848.
‡ Dixon, *Phil. Trans. Roy. Soc.*, 1884, **175**, 617.
§ *Proc. Roy. Soc.*, 1925, A, **109**, 176, 523.
|| Tramm, *Z. physikal. Chem.*, 1923, **105**, 397.
¶ Coehn and Jung, loc. cit.

these examples are first the small trace which apparently exerts the maximum effect, and secondly the 'all or nothingness' of the effect.

Two explanations are possible of the first phenomenon: either the water might form a catalytically active film over a surface, saturation of this film being complete at a very low partial pressure of the vapour; or the water might combine with some reactant, such as a chlorine atom in the hydrogen-chlorine combination, present in such small amount, and having such a long life, that all of it would be certain to meet with water molecules before being destroyed in any other way. This being so, the concentration of the water would only have an influence up to a certain point. If the chlorine atoms had to associate themselves with water in this way, their life, according to Chapman, would have to be about 1/50 second.

A possible explanation of the 'all-or-nothingness' effect is provided by the theory that the water may be concerned in the initiation of a 'chain-reaction' which, once started, proceeds explosively. Certain exothermic reactions which proceed explosively or not at all are known, and will be dealt with more fully in Chapter VI.

Relation of heat of activation to heat of reaction. Influence of homogeneous catalysts on the heat of activation and on the position of equilibrium.

Thermodynamically the heats of activation* of the direct and inverse reactions in a balanced change must be related to the heat of reaction by the equation

$$E_1 - E_2 = Q$$

The separate values bear, however, no relation to Q.

Unless a catalyst actually combines with an appreciable amount of one of the substances present it can have no influence on the position of equilibrium in a reversible

* More exactly the 'critical increments'.

reaction. When the change $AB \rightleftharpoons A + B$ has reached equilibrium the product

$$\frac{[AB]}{[A]\,[B]}$$

is constant at a given temperature and entirely independent of the mechanism by which equilibrium is established.

Otherwise it would be possible to circumvent the second law of thermodynamics in the following manner. The system is allowed to reach equilibrium in the presence of one catalyst. This can now be removed from the system without performance of work and replaced by another. The system is no longer in equilibrium, and undergoes a spontaneous change to another state. Whenever a system not in equilibrium passes to a state of equilibrium it can be made to yield work. Hence by alternately adding and removing catalysts an indefinitely large supply of work can be obtained at the expense of nothing except the heat of the surroundings.

Certain supposed shifts of equilibrium are all attributable to an actual finite alteration in the concentration of one or more of the substances, owing to combination with the catalyst. If this alteration is not taken into account, incorrect values of the concentrations are used in the expression for K, which then appears to be changed.

So many different catalytic mechanisms are possible that the kinetic interpretation of this simple thermodynamical result is rather complex, but the general principle is easily illustrated by simple instances. Suppose the reaction $AB \rightarrow A + B$ is accelerated by a homogeneous catalyst, which forms a complex with the molecule AB.

The reaction would be accelerated if the molecular compound $AB \,.\, C$ had a much lower energy of activation for the change $AB \,.\, C \rightarrow A + B + C$ than the molecule AB had for the simple decomposition.

Let the energy of activation of the simple reaction be E_1 and that of the catalysed reaction be $(E_1 - e_1)$. Now at equal

concentrations the complexes will decompose more rapidly than the molecules of AB in the ratio $e^{-(E_1-e_1)/RT}/e^{-E_1/RT}$ which equals $e^{e_1/RT}$.

Now, it is important to remember that the activated state of AB is identical with the activated state of $(A+B)$ in collision, the reactant and the products being probably indistinguishable in the condition corresponding to activation. Hence if activated AB molecules are capable of being attached to C molecules, the colliding complex of $A+B$ is also capable of being so held. Moreover, the activated systems have equal chances of meeting molecules of C, whether they are formed from AB molecules or by the collision of A and B.

Further, if E_2 be the energy of activation of the uncatalysed reaction $A+B \rightarrow AB$, and that of the catalysed reaction be (E_2-e_2), then, since $E_1-E_2=Q$ and

$$(E_1-e_1)-(E_2-e_2)=Q$$

also, it follows that e_1 is equal to e_2.

Thus, for equal concentrations the catalysed reaction is accelerated in the same ratio $e^{e_1/RT}$ as the direct reaction. The equilibrium position is thus unaltered. Other more complex mechanisms may be analysed in the same way.

Heterogeneous catalysis will be referred to again in another place.

IV

TERMOLECULAR REACTIONS

If, in bimolecular reactions, any considerable proportion of the collisions taking place at atmospheric pressure led to reaction, the velocity of transformation would be too great to be measured experimentally. Indeed, in reactions proceeding at conveniently measurable rates about one collision in 10^{10} to 10^{12} is effective. The value of E/RT in these instances is 25 to 30. Reactions with much smaller values than this will appear almost instantaneous.

With termolecular reactions the position is quite different. An appropriate ternary collision is an event of such rarity that, if in addition to a molecular encounter considerable activation is required, the velocity of reaction will be negligibly small. Conversely, it may be anticipated that if any termolecular gaseous reactions are observed to take place with measurable speed at ordinary pressures, they must be associated with a very small heat of activation. These theoretical anticipations are confirmed by experiment.

With regard to the probability of ternary collisions in gases, Trautz * suggested that it was so small as to render true termolecular reactions impossible.

It is true that they are very rare. The reaction $2CO + O_2 = 2CO_2$ proceeds, not homogeneously, but as a wall reaction under ordinary conditions. The explosion wave, which is set up at higher temperatures, must indeed depend upon a homogeneous change, but this, as Dixon has shown, requires the presence of water, whereby the termolecular reaction is probably replaced by a series of bimolecular changes

$$CO + H_2O = CO_2 + H_2,$$
$$H_2 + O_2 = H_2O_2,$$
$$2H_2O_2 = 2H_2O + O_2.$$

* Trautz, *Z. Elektrochem.*, 1916, **22**, 104.

Bodenstein has, however, shown that the combination of nitric oxide and oxygen $2NO + O_2 = 2NO_2$ is a homogeneous change which is kinetically of the third order, and the same appears to apply to the combination of nitric oxide with chlorine * and with bromine † and to the reaction between nitric oxide and hydrogen.‡

$$2NO + Cl_2 = 2NOCl$$
$$2NO + Br_2 = 2NOBr$$
$$2NO + H_2 = N_2O + H_2O$$
$$(\text{or } N_2 + H_2O_2)$$

Bodenstein, in the course of a comprehensive study of the formation and decomposition of the higher oxides of nitrogen,§ showed, in conjunction with Lindner, that the reaction between nitric oxide and oxygen proceeds in accordance with the equation

$$\frac{d[NO_2]}{dt} = k[2NO]^2[O_2].$$

The velocity was measured manometrically, definite quantities of nitric oxide and oxygen being allowed to stream into a vacuous vessel, which was provided with a bromnaphthalene manometer, protected from the oxides of nitrogen by an air-buffer.

The remarkable fact about the velocity of reaction was the negative temperature coefficient. The following figures are taken from Bodenstein's paper, and illustrate the way in which the rate of reaction decreases as the temperature rises.

T (abs.)	$k \times 10^{-6}$
273	2·09
333	1·33
470	0·80
564	0·68
662	0·61

* Trautz, *Z. Anorg. Chem.*, 1914, **88**, 285.
† Trautz and Dalal, *Z. Anorg. Chem.*, 1918, **102**, 149.
‡ Hinshelwood and Green, *J. Chem. Soc.*, 1926, 730.
§ *Z. physikal. Chem.*, 1922, **100**, 68.

The temperature coefficient, expressed as the relative increase in velocity for a ten-degree rise in temperature, k_{t+10}/k_t, changes gradually from 0·912 to 0·997 with rising temperature.

A comparison between this and the usual temperature coefficient of a two- to threefold increase for ten degrees shows the expectation of a very low heat of activation to be realized.

But the existence of a very low heat of activation would mean a temperature coefficient of just over unity. It would not account for an actual inversion of the normal effect. The depression of the coefficient below unity is due to another factor. This is the diminished 'duration of collisions' at higher temperatures, which lessens the chance of ternary collisions. Owing to the increasing molecular speeds, there is less and less chance, at greater temperatures, that two molecules shall still be within range of each other when a third one approaches. It is to be noted that the velocity of reaction falls off only very slowly, so that the diminishing frequency of the right kind of collision can account for the retrogression without undue strain.

With regard to the molecular statistics of the reaction, at 0° C., and 1/3 atmosphere pressure of oxygen, and 2/3 atmosphere of nitric oxide, the number of molecules reacting in one second is 7×10^{19} per c.c. It is now necessary to find whether the number of ternary collisions is sufficient to account for this rate of reaction.

Bodenstein makes the calculation in the following way, which is probably sufficiently accurate. The chance that an oxygen molecule hits a nitric oxide molecule actually in collision with one of its own kind bears the same ratio to the chance that it hits a single nitric oxide molecule as the molecular diameter bears to the mean free path. This gives the ratio of ternary to binary collisions as $10^{-8}/10^{-5}$ or 1 to 1,000. The number of collisions between oxygen and nitric oxide molecules under the experimental condi-

tions is 3×10^{28}. Thus there would be about 3×10^{25} ternary collisions to provide for 7×10^{19} cases of transformation.

In ternary collisions it is probable that the orientation of the molecules at the moment of impact is much more important than in bimolecular processes, so that it is probably necessary to reduce the number of collisions likely to lead to reaction to 3×10^{24}. In this way the ratio of the number of molecules reacting to the number suffering collisions of suitable orientation is found to be about 10^{-4} to 10^{-5}.

Now if we write, in the usual way, $e^{-E/RT} = 10^{-4}$ or 10^{-5}, we find a value for the heat of activation of a few thousand calories only. Thus a very small temperature coefficient is to be expected.

Nevertheless, it is remarkable that the diminished chance of ternary collisions at higher temperatures should actually invert the small positive effect which would otherwise be expected.

Two other termolecular reactions, namely, the formation of nitrosyl chloride and nitrosyl bromide, have in fact small positive coefficients, but very little above unity.

Trautz and Schueter * show that the whole matter can be envisaged from a formally different point of view. The termolecular reaction between nitric oxide and chlorine is assumed to proceed in the following two stages:

$$NO + Cl_2 \rightleftharpoons NOCl_2,$$
$$NOCl_2 + NO = 2NOCl.$$

The concentration of $NOCl_2$ is always small, the equilibrium in the first reaction being well on the side of dissociation. In this equilibrium

$$[NOCl_2] = k[NO][Cl_2].$$

The rate of formation of $2NOCl$ in the second reaction is proportional to $[NOCl_2][NO]$ and therefore to $[NO]^2[Cl_2]$.

* *Z. Anorg. Chem.*, 1924, **136**, 1.

If the speed of the second reaction determines the measured speed of the whole change, then the reaction is purely termolecular in the kinetic sense.

The increasing dissociation of the intermediate compound with rising temperature accounts for the low temperature coefficient of the resultant velocity.

The decrease in rate resulting from the diminishing concentration of this compound might indeed be greater than the normal increase with temperature in the rate of the second reaction, and the temperature coefficient would then actually be negative as in the example of the nitric oxide oxidation.

Bodenstein rejects a similar suggestion in relation to this reaction as artificial. It involves the assumption of an unknown oxide of nitrogen. This, if formed, is so unstable that there seems to be little distinction to be drawn between it and a molecule of nitric oxide in a collision of finite duration with an oxygen molecule. As we must think of collisions as possessing duration, this being roughly the time during which the two molecules are within molecular distances of each other, there seems to be little essential difference between the points of view of Trautz and of Bodenstein, as indeed both authors seem to realize.

Nevertheless, it is a rather striking fact that all the four termolecular reactions which are known involve the participation of two molecules of nitric oxide. This may be simply a coincidence, but it may also indicate that collisions between two molecules of nitric oxide, even if they do not result in the formation of N_2O_2, have a rather more 'inelastic' character and a longer duration than most molecular impacts.

The reaction between nitric oxide and hydrogen is interesting because it takes place at much higher temperatures than the other three termolecular reactions. Its speed at 1,100° absol. is more or less comparable with that of the oxidation of nitric oxide at the ordinary

temperature. The reaction takes place according to the equation

$$-\frac{d[\mathrm{NO}]}{dt} = k[\mathrm{NO}]^2[\mathrm{H_2}]$$

which shows that the primary reaction is between two molecules of nitric oxide and one of hydrogen. The subsequent decomposition of the nitrous oxide or hydrogen peroxide thus formed is very rapid in comparison.

The molecular statistics of this reaction are of some interest. The heat of activation, as measured directly from the temperature coefficient, is 44,000 calories.

A bimolecular reaction which would proceed with comparable velocity at the same temperature as this reaction would have a heat of activation of about 60,000 calories, as may be inferred from the table on page 96. Now termolecular collisions are about 1,000 times less frequent than bimolecular collisions at atmospheric pressure. Thus if we have a bimolecular reaction and a termolecular reaction with equal heats of activation, the rate of the latter should be at least 1,000 times smaller than that of the former at the same temperature. It will probably be more nearly 10,000 times slower, since a larger proportion of the ternary collisions are likely to be ineffective on account of unfavourable orientation of the molecules during impact. Conversely, if a termolecular reaction and a bimolecular reaction are to take place at equal rates at the same temperature, then the heat of activation of the termolecular reaction would need to be the smaller by an amount ΔE, such that $e^{\Delta E/RT} = 1{,}000$ to 10,000. Thus, other things being equal, the heats of activation of termolecular reactions ought to be about 5,000 calories less at the ordinary temperature, and about 15,000 calories less at 1,000° abs., than those of bimolecular reactions. We have also to allow for the diminished 'duration of collisions' at higher temperatures, which we can do by comparison with the nitric oxide oxidation.

A bimolecular reaction which would take place at a rapid but measurable rate at the ordinary temperature would have a heat of activation of 12,000 to 15,000 calories, a termolecular reaction might therefore be expected to have one of 5,000 to 10,000 calories. This would mean a very small temperature coefficient. The effect of the 'diminishing duration of collisions' is enough just to invert this.

The new factor, therefore, is equivalent to the reduction of the apparent heat of activation by 5,000 calories or so. Thus the termolecular reaction might be expected to have a heat of activation about 20,000 calories less than that of the bimolecular reaction at 1,000° abs. The predicted heat of activation is thus about 40,000 calories, the observed value being 44,000.

This result is of a very rough character, but it shows that termolecular reactions can reasonably be interpreted in terms of simple kinetic mechanisms.

More experimental material is much to be desired.

V

UNIMOLECULAR REACTIONS

General.

A UNIMOLECULAR reaction is one in which the absolute rate of change is proportional to the first power of the concentration of the reacting substance. The fraction of the total number of the molecules in the system which change in unit time is therefore independent of the concentration, and thus, in gaseous systems, cannot be proportional to the number of collisions undergone in unit time by the molecules. It must therefore be concluded that, whether or not previously received collisions have done anything to put the molecule into an abnormal condition, the actual chemical transformation is an event happening to the isolated molecule.

At the present time a number of gaseous unimolecular reactions are known. The view that none exist, although it appeared plausible for a time, has now been definitely abandoned. Nevertheless, unimolecular reactions are rather exceptional and appear to be confined to molecules of rather complex structure. It is possible that the decomposition of diatomic molecules into atoms at high temperatures is unimolecular; but more probable that it is bimolecular, the reverse reaction of recombination being termolecular. Thus the rate of dissociation of chlorine would be $k_1[Cl_2]^2$ while the rate of recombination of the atoms would be $k_2[Cl]^2[Cl_2]$, according to the Herzfeld theory (p. 111).

These two expressions combine to give the correct equilibrium condition, $\frac{[Cl]^2}{[Cl_2]} = K$. Since the latter is thermodynamically necessary, if we adopt Herzfeld's theory we must also assume bimolecular decomposition.

Inquiry, then, branches in two directions, first that of

seeking an explanation of the comparatively exceptional character of unimolecular changes, and secondly that of discovering the mechanism by which molecules become activated for such reactions.

That activation is necessary is seen at once from the high temperature coefficients of all unimolecular reactions.

The theory of unimolecular reactions was at first based upon very scanty data and, until more experimental evidence was forthcoming, discussion of the mechanism tended to be a little unsatisfactory and inconclusive. The great theoretical interest of these changes will be made evident if we consider in turn the various theories about them which have been current.

For a reason which will soon be evident, we will redefine the unimolecular reaction as a transformation in which the fraction undergoing change in unit time is independent of the pressure over the ordinary range of pressures, without prejudice to what may happen at extremely low pressures. The reservation is very important.

Interest was focused on the problem in 1919 by Perrin,* who argued that since the rate of unimolecular reactions is independent of the pressure, it should be possible to expand the gas to infinite volume without influencing the number of molecules which undergo transformation in unit time. In some way, therefore, isolated molecules, cut off from all communication of energy by collision, become activated for chemical change. Perrin suggested that the cause of reaction was therefore to be sought in the action of radiation upon the molecules. This argument seemed to lend support to the general radiation theory of chemical change put forward originally in an obscure form by Trautz,† and

* *Ann. de Phys.*, 1919 [IX], **11**, 1.

† *Z. wiss. Photochem.*, 1906, **4**, 160. Compare also the reference given by Perrin, *Trans. Faraday Soc.*, 1922, **17**, 546.

considerably developed by W. C. McC. Lewis,* but since discredited in its original form.

Lindemann † diminished the force of Perrin's argument by showing that molecules might actually receive their energy of activation by impact from other molecules, and nevertheless be transformed chemically at a rate which was independent of the pressure over a very large range, though not to the limit of infinite dilution, as Perrin had postulated.

It is only necessary to assume that a certain period of time elapses between the moment when a molecule receives the energy by collision and the moment of chemical transformation. This assumption is quite reasonable, for, in virtue of the internal motions, molecules must pass through maxima and minima of stability.

Lindemann supposes the molecule to be activated by collision, and to decompose only when it passes through its next minimum of stability. If the average time elapsing between activation and chemical transformation is large compared with that between two impacts, most of the molecules activated by one collision will lose their energy again by a second collision before they have a chance to react. According to this view, rate of activation is a very different thing from rate of reaction. The state of affairs may be represented as follows :

$$\text{normal molecules} \rightleftharpoons \text{activated molecules} \downarrow \text{products of reaction}$$

The processes indicated by the horizontal arrows take place very rapidly compared with that indicated by the vertical arrow. A stationary state is thus set up, in which a constant fraction of the molecules, nearly proportional to $e^{-E/RT}$, possess the energy of activation, and are liable

* See, for example, *J. Chem. Soc.*, 1916, **109**, 796 ; 1917, **111**, 457 ; 1918, **113**, 471.

† *Trans. Faraday Soc.*, 1922, **17**, 598.

to suffer transformation if they pass through the phase of minimum stability before their next collision. A small fraction only are so transformed, the majority being deactivated. The chemical reaction, therefore, disturbs the concentration of active molecules very little. The fraction $e^{-E/RT}$ is independent of pressure, and the number of molecules reacting in unit time is a small constant fraction of this. Thus the number reacting in unit time is also independent of the pressure, and all the conditions of a unimolecular reaction are realized.

At sufficiently low pressures, however, the time between two collisions must become comparable with the period elapsing between activation and reaction, so that the removal of molecules by chemical change seriously diminishes the stationary concentration of activated molecules. When the pressure is very much reduced there must therefore ultimately come a point where the unimolecular velocity constant falls off.

The reason for our reservation in the definition of unimolecular reactions is now clear. Lindemann's mechanism would account for the independence over large ranges—and this corresponds to our experimental criterion of unimolecularity. Perrin seeks to extrapolate the experimental observations to infinite dilution, which may not be permissible.

The acceleration of many chemical reactions by light shows that there is nothing improbable in principle about the supposition that molecules are activated by the absorption of ordinary temperature radiation. Only the fact that the amount of radiational energy contained in a gaseous system is small in comparison with the molecular kinetic energy, except at very low pressures, as was long ago shown,* seems at first sight to render the hypothesis of activation by infra-red radiation rather superfluous, when Perrin's argument has once been met.

* At extremely high temperatures this is not true, however.

Another mechanism has been suggested by Christiansen and Kramers * in which activation is by collision and yet there is an apparently unimolecular reaction. It depends upon the possibility that the products of reaction, possessing the energy corresponding to the chemical heat of reaction as well as the original heat of activation, are able immediately to activate fresh molecules of reactant. In this way 'reaction-chains' are set up. The assumption is made that every molecule of product can at once activate by collision a fresh molecule of the reactant. In this way each activated molecule removed from the system by chemical transformation is replaced by a new activated molecule.

The supply of activated molecules is thus maintained (1) by the Maxwell distribution, according to which a constant fraction of the total number are in the active state when there is no removal by chemical change, and (2) by the complete replacement of all such removals in the way postulated. The number of active molecules is thus always a constant fraction of the total concentration of reactant, and the reaction is thus kinetically unimolecular (see also p. 173).

As products accumulate, however, or if inert gas is added to the system, the activated molecules of product, which would normally activate fresh molecules of the reactant, might to a greater and greater extent become deactivated by collisions with inert molecules, and the reaction would then depend more and more upon the ordinary kind of bimolecular activation.

To circumvent this difficulty Christiansen and Kramers made the assumption, which seemed at first sight a little arbitrary, that the 'activated reaction products' can give up their energy only to molecules of the reacting substance, and not to molecules of inert gas or of the products of reaction. Otherwise the reaction chains would be interrupted, and the mechanism breaks down completely.

* *Z. physikal. Chem.*, 1923, **104**, 451.

We shall return to the discussion of this assumption in Chapter VI, which deals in detail with chain reactions. It may be stated here that it proves to be a not unreasonable one. Nevertheless the chain theory does not appear to be the general explanation of unimolecular changes.

Before leaving general theoretical considerations we must briefly examine the consequences of the simple radiation theory of unimolecular reactions. The only unimolecular reactions to which, on purely *a priori* grounds, it would be necessary to apply this theory would be those in which the value of the velocity constant showed no diminution whatever as the concentration was indefinitely decreased.

The specific form of the theory which was elaborated chiefly by W. C. McC. Lewis and Perrin was of great beauty and simplicity.

In the activation of molecules a narrow band of infrared frequencies was assumed to be operative.

All matter at constant temperature is in equilibrium with radiant energy, which is being continually absorbed and re-emitted in quanta by the molecules.

A space entirely surrounded by material walls of sufficient thickness to be impenetrable to radiation is traversed in all directions by waves of every possible frequency. Unit volume contains a definite amount of radiant energy —the radiation density—determined only by the temperature of the walls, and distributed among the different frequencies in accordance with Planck's law.

This law states that if the quantity of energy lying between the frequencies ν and $\nu+d\nu$ be represented by $u_\nu d\nu$, where u_ν is called the radiation density for the frequency ν, then

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT}-1},$$

where c is the velocity of light.

Gas molecules bathed in this radiation absorb and

emit quanta of magnitude $h\nu$, if their internal structure permits.

For the frequency which is effective in activating the molecules chemically $N \cdot h\nu$ ought to be equal to E, the energy of activation. (N is Avogadro's number.) From the heat of activation, therefore, we calculate the activating frequency by the relation $\nu = E/Nh$. If the molecules really are activated by quanta of more or less monochromatic radiation the fact that the gas can absorb it should be manifested by the existence of an absorption band at this calculated frequency.

The temperature coefficient of the reaction is still given by the Arrhenius equation. It is reasonable to assume that the velocity constant of the reaction is proportional to the radiation density. Now chemical heats of activation correspond to frequencies in the short infra-red region, and for these values of ν the term $e^{h\nu/kT}$ in Planck's equation is large in comparison with unity. The expression for u_ν thus reduces to

$$\frac{8\pi h\nu^3}{c^3} \cdot e^{-h\nu/kT}.$$

Thus we have $k = \text{constant} \cdot e^{-h\nu/kT}$,

whence $$\frac{d\log k}{dT} = \frac{h\nu}{kT^2} = \frac{Nh\nu}{NkT^2} = \frac{E}{RT^2}.$$

E can thus be found from the Arrhenius equation in the usual way, and ν calculated from it. The presence or absence of an absorption band in the proper region is then a test of the simple radiation theory.

It may be stated at once that the theory does not survive this test. When matters are complicated by assuming that a complex spectrum of frequencies are operative the problem tends to elude experimental investigation.

Various modifications of the simple theory have been proposed, depending upon either the simultaneous or

successive absorption of several quanta, or upon the absorption of energy of a continuous range of frequencies superior to a certain limit.

We shall return to the discussion of these various mechanisms when the experimental material has been considered.

EXPERIMENTAL MATERIAL

The decomposition of nitrogen pentoxide.

In 1925 the only known gaseous unimolecular reaction was the decomposition of nitrogen pentoxide. The result of the decomposition is expressed by the equation

$$2\,N_2O_5 = 2\,N_2O_4 + O_2.$$

Since the reaction is unimolecular the primary change cannot be expressed by this equation, but must take place by a mechanism such as the following

$$N_2O_5 = N_2O_3 + O_2.$$

The nitrogen trioxide then decomposes almost instantaneously into nitric oxide and nitrogen peroxide

$$N_2O_3 = NO + NO_2.$$

Nitrogen peroxide has no influence on the thermal decomposition of nitrogen pentoxide, but an almost instantaneous reaction occurs between nitric oxide and the pentoxide*

$$NO + N_2O_5 = 3\,NO_2.$$

Thus each primary act of chemical change results in the decomposition of two molecules of the pentoxide, a fact which has to be taken into account in dealing with the molecular statistics of the reaction.

According to Schumacher and Sprenger† an oxide NO_3 is produced when nitrogen pentoxide reacts with ozone, but this does not appear to play any part in the thermal decomposition.

* Busse and Daniels, *J. Amer. Chem. Soc.*, 1927, **49**, 1257.

† *Z. physikal. Chem.*, 1928, **136**, 77 ; ibid, 1928, **140**, A, 281.

Daniels and Johnston* investigated the kinetics of the reaction, using an all-glass manometer of special construction.

They found the change to be completely homogeneous, applying the test of the addition of glass wool to the reaction vessel. It proceeds with conveniently measurable velocity at ordinary temperature. In calculating velocity constants corrections have to be applied for the changing dissociation of the N_2O_4 as its concentration alters.

The fraction of the total nitrogen pentoxide which is transformed in unit time is constant and independent of the initial concentration for ordinary variations of pressure. Satisfactory unimolecular constants are obtained.

The following table gives the velocity constants at different temperatures, and the value of the heat of activation :

Temperature ° C.	k (Time in minutes)	Heat of activation
65°	0·292	
55°	0·0900	25,830
45°	0·0299	22,750
35°	0·00808	25,370
25°	0·00203	25,100
0°	0·0000472	24,240
		Mean, 24,700 calories.

The velocity constants, with the time expressed in seconds, are given by the formula †

$$\ln k = 31{\cdot}45 - \frac{24{,}700}{RT}.$$

Taking this value for the heat of activation, and calculating the frequency to which it corresponds according to the simple radiation theory, it is found that light of wave-length 1·16 μ should be effective in decomposing nitrogen pentoxide. The amount of light of this wave-length present in the ordinary thermal radiation in an enclosure

* *J. Amer. Chem. Soc.*, 1921, **43**, 53.

† Kassel, *J. Amer. Chem. Soc.*, 1928, **50**, 1344.

at 0° to 65° C. is very small, so that if the theory is applicable illumination of the system from outside with light of this kind should have all the effects on the reaction velocity of a great increase of temperature. The short waves appear in thermal radiation with greater and greater relative intensity as temperature increases, and if chemical change is provoked by more or less monochromatic radiation, increase in the intensity of this one particular frequency is chemically equivalent to raising the temperature of the whole system to the point where the natural thermal intensity of this would be equal to the artificially produced intensity.

Exposure of a cell containing nitrogen pentoxide to strong sunlight, filtered through iodine solution, which is transparent to waves of length 1·16 μ but opaque to visible light, produced no detectable acceleration of the reaction.

It was found, on the other hand, that nitrogen pentoxide is decomposed under the influence of blue light, but only when some nitrogen dioxide is present.* This is an example of the phenomenon of photocatalysis.

Further tests of the influence of infra-red radiation on the reaction velocity have been made by Rice, Urey, and Washburne,† who exposed a 'molecular beam' of nitrogen pentoxide to black body radiation of high temperature with a negative result, and by Kassel,‡ who also found that radiation of wave-length less than 5 μ does not increase the reaction rate even at low pressures, where its effect relative to that of collisions might have been expected to be greater than at atmospheric pressure.

In the earlier experiments on the decomposition the nitrogen pentoxide had never been free from some nitrogen dioxide, since in the sealing off of the apparatus a certain amount of decomposition had been inevitable. Daniels,

* Daniels and Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 72.

† *J. Amer. Chem. Soc.*, 1928, **50**, 2402.

‡ Ibid., 1929, **51**, 54.

Wulf, and Karrer * attempted to repeat some of the previous work in the presence of ozone, which ensures the complete absence of lower oxides since it oxidizes them instantaneously to the pentoxide. In the decomposition of the pentoxide, therefore, there should be a period of induction during which the decomposition products are re-oxidized by the ozone. When all the ozone is used up brown fumes should appear and the decomposition of the pentoxide should go forward in the normal way. It appeared, however, that when the lower oxides were removed in this way the decomposition did not take place at all. This led to the conclusion that the reaction was not, after all, a simple unimolecular decomposition but a change depending on collisions between molecules of nitrogen pentoxide and molecules of nitrogen dioxide.

The matter was then reinvestigated by Hirst,† who repeated the experiments of Daniels, Wulf, and Karrer on the decomposition in presence of ozone and failed to confirm their result. On the other hand, the original work of Daniels and Johnston was confirmed.

More recently White and Tolman‡ have again shown that when nitrogen pentoxide is allowed to decompose in presence of ozone, as soon as the ozone is used up the pure nitrogen pentoxide left decomposes at the normal rate found by Daniels and Johnston in their first experiments.

Thus it seems most probable that the isolated result of Daniels, Wulf, and Karrer was due to error rather than a real anomaly in the reaction.

With regard to the influence of impurities and accidental catalysts in general on the rate of reaction it may be said to be of little account, and there can be no doubt that what is measured is the rate of the uncatalysed decomposition. The reaction has now been investigated under

* *J. Amer. Chem. Soc.*, 1922, **44**, 2402.
† *J. Chem. Soc.*, 1925, **127**, 657.
‡ *J. Amer. Chem. Soc.*, 1925, 47, 1240.

a great variety of circumstances by observers in different parts of the world, and with material of varying origin. The results are all in agreement. Hirst* found a velocity constant of $7{\cdot}11 \times 10^{-3}$ at 35·4° compared with the value $7{\cdot}71 \times 10^{-3}$ calculated for this temperature from the data of Daniels and Johnston. Some results of White and Tolman† can be compared with those of Daniels and Johnston over a range of temperatures:

Temperature	20° C.	25°	35°	40°
$k \times 10^5$ (W. and T.)	103	219	837	1480
$k \times 10^5$ (D. and J.)	117	203	808	1510

Rice and Getz‡ made a very complete study of the matter from this point of view. At 65° C. they found $k = 0{\cdot}286$, compared with the value 0·292 of Daniels and Johnston. In order to test the possibility that the reaction might depend on catalysis by dust, they compared the velocity constants for filtered and unfiltered nitrogen pentoxide and for gas which had been passed through an electrical dust precipitator. In some experiments the gas was dried with phosphorus pentoxide, in others not. In some it was prepared by the dehydration of nitric acid with phosphorus pentoxide and in others by the action of chlorine on silver nitrate. Nitric acid was found to have no catalytic effect on the decomposition. Some of the principal results are summarized below, all data referring to 65° C.

	k
'Ordinary' experiments	0·286
Gas filtered through blue asbestos . . .	0·284
Gas passed through electrical precipitator .	0·278
P_2O_5 in reaction vessel	0·278
N_2O_5 made from $AgNO_3$ and chlorine . .	0·291

It is of considerable interest that Lueck§ found the rate of decomposition in solution in carbon tetrachloride and

* *J. Chem. Soc.*, 1925, **127**, 657.
† *J. Amer. Chem. Soc.*, 1925, **47**, 1240.
‡ *J. Physical Chem.*, 1927, **31**, 1572.
§ *J. Amer. Chem. Soc.*, 1922, **44**, 757.

in chloroform to be practically the same as in the gaseous state.

Busse and Daniels* have, moreover, found that hydrogen, carbon monoxide, bromine, and chlorine are without influence on the reaction. Certain organic vapours, which are themselves attacked by nitrogen pentoxide, bring about rapid decomposition. Hirst found that argon exerted no influence, while Hunt and Daniels showed that the presence of a large excess of nitrogen did not alter the rate of reaction at all.

The rate of decomposition at low pressures is of special interest in connexion with Lindemann's views on the possibility that certain reactions might be independent of pressure over a wide range but reveal themselves as essentially bimolecular at very low pressures. Hunt and Daniels† showed that the unimolecular character of the reaction was preserved down to quite low partial pressures of nitrogen pentoxide, but they came to no definite conclusion as to the applicability of Lindemann's theory. Hirst and Rideal‡ found, on the other hand, that the velocity constant, so far from decreasing at low pressures, actually increased, but Hibben § again found a normal velocity constant between 0·2 and 0·002 mm. These discordant results seemed to suggest that at the low pressures interference by surface reactions must be more or less serious, but recent work by Sprenger ‖ in Bodenstein's laboratory suggests another explanation of the discrepancies, besides revealing the existence of what appears to be a very remarkable phenomenon. Sprenger finds that when nitrogen pentoxide is admitted to a vessel at low pressure the reaction begins at the normal rate and then stops completely, even though undecomposed nitrogen

* *J. Amer. Chem. Soc.*, 1927, **49**, 1257. † Ibid., 1925, **47**, 1602.
‡ *Proc. Roy. Soc.*, 1925, A, **109**, 526.
§ *Proc. Nat. Acad. Sci.*, 1927, **13**, 626.
‖ *Z. physikal. Chem.*, 1928, **136**, 49.

pentoxide is demonstrably present. He regards this as evidence for some kind of chain mechanism. The results of Hirst and Rideal, if Sprenger's result is correct, can now be explained. The initial concentration of nitrogen pentoxide had been inferred from the total increase of pressure attending the decomposition. If this stopped before completion, the inferred initial concentration would be too low, and thus the velocity constant for the early stages where the velocity is normal would be too high.

The decomposition of phosphine: the transformation of cyclo-propane into propylene.

For some time the thermal decomposition of phosphine at high temperatures was believed to be a homogeneous unimolecular reaction. It was studied by Trautz and Bhandarkar,* who concluded that under the conditions of their experiments, namely in a 3-litre porcelain bulb, the reaction on the walls of the vessel was negligible above 945° abs., in comparison with the homogeneous reaction.

This conclusion was based only upon a supposed increase in the heat of activation with temperature, which was interpreted as proof that the wall reaction which predominates at lower temperatures is superseded by a true gas reaction. Hinshelwood and Topley † found, by varying the ratio surface/volume, that the reaction taking place in a silica vessel was predominantly heterogeneous up to 1,044° abs. at least. Since the total velocity as measured in these experiments was actually rather less than that in the experiments of Trautz and Bhandarkar, it seems clear that the reaction measured by the latter observers must have been heterogeneous also. Re-examination of their experimental data, moreover, fails to substantiate the conclusion that there is any real increase in the heat of activation with temperature.

* *Z. Anorg. Chem.*, 1919, **106**, 95. † *J. Chem. Soc.*, 1924, **125**, 393.

It has also been held that the transformation of cyclopropane into propylene* tends to become predominantly homogeneous as the temperature is raised. But here again the data are of a very inconclusive kind.

The decomposition of gaseous acetone.

The decomposition of gaseous acetone at about 500° C. is a homogeneous reaction† the rate of which can be measured manometrically. The acetone decomposes primarily into carbon monoxide and two methyl groups, which at once interact to give various hydrocarbons. The time of half-change is independent of the initial pressure over a wide range, and the reaction is thus empirically unimolecular, but it has not been investigated at low pressures. The heat of activation is 68,500 calories, and the velocity constants are given by the expression

$$\ln k = 34{\cdot}95 - \frac{68{,}500}{RT}$$

(the time being measured in seconds).

The decomposition of gaseous propionic aldehyde.‡

This reaction also involves the elimination of carbon monoxide and the formation of a mixture of hydrocarbons, principally ethane and methane. It is homogeneous and conveniently measurable between 450° and 600° C. The decomposition is kinetically unimolecular over a considerable range of pressure, but at pressures below about 80 mm. Hg the velocity constant falls appreciably, in the manner which would be expected if Lindemann's theory were correct. In the region of pressure where the reaction is unimolecular the velocity constants (sec^{-1}) are given by

$$\ln k = 27{\cdot}93 - \frac{54{,}000}{RT}.$$

* Trautz and Winkler, *J. pr. Chem.*, 1922, [ii], **104**, 53.

† Hinshelwood and Hutchison, *Proc. Roy. Soc.*, 1926, A, **111**, 245.

‡ Hinshelwood and Thompson, ibid., 1926, A, **113**, 221.

In presence of an excess of hydrogen, which appears to have no direct chemical action on the aldehyde or its decomposition products, the velocity constant does not decrease for low partial pressures of the aldehyde as it does in the absence of hydrogen.*

The decomposition of gaseous diethyl ether.†

This is also homogeneous and attains a measurable rate at about 400° C. The decomposition is represented approximately by the equation

$$C_2H_5 . O . C_2H_5 = CO + 2CH_4 + 1/2C_2H_4.$$

At higher pressures of ether the reaction is unimolecular in the sense that the time required for any given fraction of the total change is independent of the initial pressure. Below about 150 mm., however, the time increases very considerably, that is to say the velocity constant falls, a behaviour exactly similar to that of propionic aldehyde. In the presence of hydrogen the constant retains its normal value at lower pressures. Helium and other inert gases do not exert this influence in maintaining the constant at its normal value. It should be remarked that the constant cannot be raised above its normal value by the presence of any amount of hydrogen.

In the region of unimolecular behaviour the constants (sec^{-1}) are given by

$$ln\,k = 26{\cdot}47 - \frac{53{,}000}{RT}.$$

The decomposition of dimethyl ether.‡

This reaction, which is homogeneous, may be investigated conveniently between 400° and 600° C. The changes involved are

$$CH_3 . O . CH_3 = [CH_4 + HCHO] = CH_4 + CO + H_2.$$

* Hinshelwood and Askey, *Proc. Roy. Soc.*, 1927, A, **116**, 163.

† Hinshelwood, ibid., 1927, A, **114**, 84.

‡ Hinshelwood and Askey, ibid., 1927, A, **115**, 215.

The intermediate formation of formaldehyde introduces a slight complication, which, however, can be adequately allowed for.

Kinetically the reaction resembles the decomposition of diethyl ether, being unimolecular at high pressures, but deviating markedly below about 350 mm. The same remarkable influence of hydrogen appears here also.

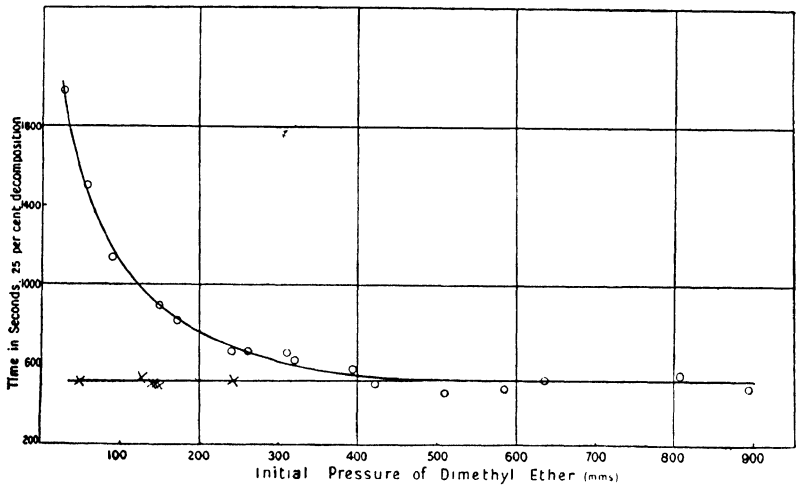


FIG. 3.

The variation with pressure of the time required for a given fraction of the total change is shown in fig. 3, which also shows the influence of hydrogen in keeping the velocity constant at its normal value at low pressures. The unimolecular velocity constants (sec^{-1}) are given by

$$\ln k = 30{\cdot}36 - \frac{58{,}500}{RT}.$$

The racemization of pinene in the gaseous state.

D. F. Smith* has shown that the racemization of pinene in the gaseous state, which can be observed by a polarimetric method, is a homogeneous reaction, and that it obeys the unimolecular law. Experiments were made

* *J. Amer. Chem. Soc.*, 1927, **49**, 43.

over the range 184° to 237° C. The value of the velocity constant at 491° abs. is $0{\cdot}88 \times 10^{-5}$ (sec^{-1}) and the heat of activation is 43,710 calories. The constants are expressed by the equation*

$$ln\,k = 33{\cdot}21 - \frac{43{,}710}{RT}.$$

The velocity of reaction was found to be the same in the gas phase, in the pure liquid state, and in solution in various solvents.

Experiments were not made with the gas at low pressures, so that data are not available to show whether the velocity constant falls.

Lewis and Mayer† made experiments to test whether the decomposition in the gas phase is accelerated by irradiation with the appropriate infra-red radiation. The pinene vapour was caused to stream at low pressure through a vessel intensely irradiated with infra-red radiation. The result was that none of the racemization which would have been expected on the basis of the radiation theory took place.

The decomposition of azomethane.

Ramsperger‡ found that between 278·6° and 327·4° C. azomethane decomposes principally in accordance with the equation

$$CH_3 . N : N . CH_3 = N_2 + C_2H_6.$$

The reaction is homogeneous and unimolecular, with a heat of activation of 51,200 calories.

The velocity constants fall with the pressure when this is reduced below a certain limit. Thus at 290° C. k at 0·259 mm. is one-fourth of the high pressure value at 707·9 mm. At higher temperatures the falling off is more marked. Thus over the same range of pressure at 330° the

* Kassel, *J. Amer. Chem. Soc.*, 1928, **50**, 1344.

† *Proc. Nat. Acad. Sci.*, 1927, **13**, 623.

‡ *J. Amer. Chem. Soc.*, 1927, **49**, 912, 1495.

constant falls to one-tenth. As the reaction proceeds the constant does not drop, as would be expected from the changing partial pressure of azomethane, indicating that the reaction products exert an influence in preventing the falling off. The value of the constant in the region of higher pressures is given by

$$ln k = 36{\cdot}73 - \frac{51{,}200}{RT}.$$

*The decomposition of azoisopropane.**

The principal chemical change involved in this decomposition may be expressed by the equation

$$C_3H_7N : N . C_3H_7 = N_2 + C_6H_{14}.$$

The change

$$C_3H_7N : N . C_3H_7 = N_2 + C_3H_6 + C_3H_8$$

is also thought to occur to the extent of about 15 per cent.

The reaction is homogeneous and unimolecular between the initial pressures of 46 mm. and 0·25 mm., in the temperature range 250° to 290° C. The velocity constant does not change over this range of pressures. The falling off in the value of the velocity constant, if it occurs as would be expected from analogy with the decomposition of azomethane, must begin therefore at a pressure lower than 0·25 mm. The heat of activation is 40,900 calories, and the velocity constants are given by the expression

$$k = 5{\cdot}6 \times 10^{13} \times e^{-40{,}900/RT}$$

or

$$ln k = 31{\cdot}65 - \frac{40{,}900}{RT}.$$

The decomposition of sulphuryl chloride.

This reaction, which proceeds in accordance with the equation $SO_2Cl_2 = SO_2 + Cl_2$, is not a homogeneous reaction in vessels of ordinary soda glass. Using vessels of Pyrex glass, however, D. F. Smith found that the reaction was

* Ramsperger, *J. Amer. Chem. Soc.*, 1928, **50**, 714.

not accelerated by an increase in the surface to anything like the extent which would be expected if the reaction were heterogeneous. Thus there appear to be two simultaneous reactions, one homogeneous and one heterogeneous under these conditions.

THE MECHANISM OF THE ACTIVATION PROCESS IN UNIMOLECULAR REACTIONS

The first problem is to decide between three possibilities: (1) activation by radiation, (2) activation by collision, (3) activation by both agencies simultaneously, always bearing in mind, however, that the activation process is not necessarily the same for all unimolecular reactions.

Activation by radiation.

Perrin's argument that the very nature of a unimolecular reaction demands independence of collisions, and therefore dependence on radiation, is adequately met both by the theory of Lindemann and by that of Christiansen and Kramers. Both these theories have the essential element in common that the distribution of energy among the molecules is not appreciably disturbed by the chemical transformation of the activated molecules: thus the rate of reaction is proportional simply to the number of activated molecules and therefore to the total number of molecules, since in statistical equilibrium the activated molecules are a constant fraction of the whole. Thus the radiation theory is not necessary to explain the existence of reactions which are unimolecular over a wide range of pressures.

Further, the calculated frequency of the radiation which should be effective in accelerating the reaction is found not to be in agreement with any frequency which is photochemically active. Moreover, in certain examples, the reacting substances have been shown to be quite insensitive to any infra-red frequency over a wide range. Pinene

and nitrogen pentoxide, for example, should be sensitive to short infra-red frequencies. The experiments of Daniels, of Rice, Urey, and Washburne, and of Kassel have all shown that nitrogen pentoxide is insensitive to infra-red radiation, even at low pressures, so that activation by radiation would appear not to play even a small part at ordinary pressures. The experiments of Lewis and Mayer on pinene have led to similar conclusions, as have those of T. W. J. Taylor on solutions of cane sugar, the inversion of which is not accelerated by sunlight as it should be according to the simple radiation theory. Hibben also has found that the decomposition of ozone and that of nitrous oxide are unresponsive to infra-red radiation.*

Nevertheless the fact that nitrogen pentoxide in presence of nitrogen peroxide is decomposed by blue light, and indeed, the whole of photochemistry, shows that there is nothing impossible in principle about the radiation theory, and examples in which infra-red radiation plays some part in molecular activation may yet be discovered.

But in addition to the considerations already mentioned there are objections of a more general kind to the radiation theory as a theory of universal applicability.

In the first place, except at very high temperatures, the amount of radiation present per unit volume of a gas at normal pressure is very small compared with the kinetic and internal energy of the gas molecules. This makes it appear probable that activation will occur by collision rather than by absorption of radiation. The argument is not quite conclusive, however, since, although the total amount of radiation in equilibrium with matter per cubic centimetre at a given temperature is known from Stefan's law, the rate of interchange of energy by radiation between molecules is not so certainly calculable. The methods available for estimating the number of molecules which could acquire the energy of activation in each second by

* *J. Amer. Chem. Soc.*, 1928, **50**, 937.

absorption of radiation are of a rather approximate character, but they seem to lead with sufficient certainty to the result that the possible rate of activation is not great enough to account for the observed rate of reaction. Calculations of this maximum rate of activation were made by Christiansen and Kramers in the paper to which reference has already been made, and also by Tolman * and others.

The methods depend upon measurements of the intensity of absorption lines where such measurements are available, and upon theoretical estimates of the rate of absorption and emission of energy. The rate of absorption and emission of energy by a vibrating electron can be calculated on the basis of the electromagnetic theory of light. These calculations can then be applied to determine the corresponding rates of absorption and emission of different frequencies according to the quantum theory with the help of Bohr's correspondence principle. The correspondence principle, roughly speaking, connects the probability of a given quantum transition, which determines the intensity of an absorption line, with the amplitude of the vibration, which, according to the classical electromagnetic theory, would have been responsible for the existence of the line. The order of magnitude of estimates made in this way is probably quite correct, and although the theory of the rate of energy exchange between atoms can doubtless be put in a more satisfactory form by the application of the Heisenberg or Schrödinger methods, it does not at the moment appear likely that the general result will be altered, namely, that activation by radiation cannot occur fast enough.

Numerous attempts have been made to modify the original radiation theory by assuming the mechanism of activation to consist in (1) the simultaneous absorption of several quanta of different frequencies or the absorption

* *Phys. Rev.*, 1924, **23**, 693.

of a range of frequencies, or (2) in the successive absorption of two or more quanta, or finally (3) in the absorption of radiation by a molecule already partially activated by collision. The first two of these alternatives meet the difficulty that the infra-red frequency calculated from the relation $E = Nh\nu$ is inactive, the third meets that of the insufficiency of the radiation density. But it is difficult to see how any of them survive in face of the fact that wide ranges of infra-red frequencies actually produce no acceleration of chemical reactions of different kinds. The possibility that several physical agencies such as radiation and collision, or two quanta of different frequencies, should be simultaneously responsible for the excitation of a molecule is discussed by Oldenberg * in connexion with the Raman effect and various spectroscopic phenomena. It appears that such a process is by no means inherently impossible. Phenomena may exist in chemical kinetics of a similar kind, but it is probably correct to say that they will appear only in exceptional reactions and not be in any sense representative.

Activation by collision.

If activation by collision is assumed two questions arise (i) how the velocity constant of the unimolecular reaction remains independent of pressure, and (ii) whether the number of collisions taking place in the gas is great enough to activate molecules sufficiently fast to account for the observed rate of chemical change even at the lowest pressures.

Two theories have been described which would account for the independence of rate and pressure, one involving the assumption of a time-lag between activation and transformation, the other involving a chain mechanism in which the activated products give their energy only to molecules of the reactant. Both theories have the

* *Z. Physik*, 1928, **51**, 605.

essential element in common that the normal statistical equilibrium in the gas is not appreciably disturbed by the chemical transformation of activated molecules.

The chain theory can obviously provide a rate of activation great enough to account for any observed rate of reaction. With Lindemann's theory it is necessary that the normal rate of production of activated molecules by collision should be at least equal to and indeed considerably greater than the number of molecules undergoing chemical transformation in unit time.

Lindemann's mechanism further demands that the velocity constant shall begin to fall at some pressure sufficiently low, but does not predict at what pressure the effect should begin to be observable, since this depends upon a specific factor, namely, the average life of an activated molecule.

The chain theory is not possible for endothermic changes and indeed is only probable for exothermic reactions in which the heat of reaction is moderately great. Further, some rather marked effect of foreign gases on a chain reaction is rather to be expected, although it is by no means absolutely inevitable.

The strongest support for Lindemann's theory is provided by observations on the falling off of the velocity constant of unimolecular reactions which is actually observed at low pressures in a number of examples. A few years ago the only unimolecular reaction known was the decomposition of nitrogen pentoxide. As we have seen, the statements about the behaviour of this reaction at low pressures are somewhat conflicting, but the most recent work seems to indicate definitely that a falling off in velocity constant really occurs. At the same time Sprenger's results seem to show that the falling off takes place in a curiously abrupt manner, as though at a certain pressure the propagation of chains ceased to be possible (see page 178). In this and in other respects the nitrogen

pentoxide reaction appears to possess peculiar characteristics of its own which are not shared by other unimolecular reactions.

The constant for the decomposition of gaseous propionic aldehyde falls away steadily below about 80 mm., that for the decomposition of diethyl ether below about 150 mm., that for the decomposition of diethyl ether below about 300 mm. Several other ethers, dipropyl ether, methyl propyl ether and methyl ethyl ether behave in a similar manner.* The velocity constant for the decomposition of azomethane also diminishes but not until lower pressures are reached: for example at 290° C. k at 0·259 mm. has one-fourth of its value at 707·9 mm. In several reactions, such as the racemization of pinene, and the decomposition of gaseous acetone the falling off of the velocity constant has not actually been looked for. The decomposition of azoisopropane is unimolecular down to pressures of 0·25 mm.

It is a very remarkable fact that in the presence of a sufficient concentration of hydrogen the velocity constant in a number of examples (propionic aldehyde, dimethyl, diethyl, and other ethers) does not diminish but retains its normal value exactly when the partial pressure of the reacting gas is reduced (see fig. 3). There is apparently no question of any reducing or other purely chemical action of the hydrogen, because it is without influence when the initial pressure of the reacting gas is above a certain limit, and, moreover, no pressure of hydrogen can increase the velocity constant to a value greater than the normal limiting value characteristic of higher pressures. (In keeping with this Busse and Daniels found that the nitrogen pentoxide reaction in the region where the constant does not show any diminution, is totally uninfluenced by hydrogen.) The hydrogen thus appears to act merely by maintaining the Maxwell distribution of energy among

* Unpublished observations.

the molecules of the reacting gas, when the supply of active molecules would otherwise begin to fall short of that required to keep the constant at its normal value.

All this is in complete accordance with Lindemann's theory ; but it is remarkable that the action of hydrogen is so specific, and that helium, nitrogen, and other gases do not have a similar effect. The molecular velocity of hydrogen is much greater than that of any other gas, being nearly four times as great, for example, as that of nitrogen. Thus the molecules of the reacting gas will suffer approximately four times as many collisions with hydrogen as they would with nitrogen at the same pressure. Helium, which is the only gas with a molecular velocity approaching that of hydrogen, has only three degrees of freedom as compared with the five of hydrogen and therefore could communicate less energy than hydrogen. Qualitatively therefore the exceptional position of hydrogen is understandable but quantitatively the differences seem to be greater than can be accounted for in this way. The advantage that hydrogen possesses in virtue of its great velocity over all gases except helium, and over helium in virtue of its five degrees of freedom, appears to be reinforced by some specific factor. This influence of hydrogen as a distributor of energy, although exceptional and specific, is not quite unique. The reaction products in the decomposition of azomethane appear to be able to keep the velocity constant at its normal value, since the constant does not drop in the course of the reaction in the way which would be expected from the falling partial pressure of the reacting gas. In the decomposition of methyl propyl ether,* which, like azomethane, yields ethane as one of the products, the reaction products have an effect similar to that of hydrogen, although somewhat less marked. This suggests the hypothesis that the ethane with its comparatively large number of internal degrees of freedom is the effective

* Glass and Hinshelwood, unpublished observations.

distributor of the energy in each example. The significance of the internal degrees of freedom will become evident when we have considered the nature of the activation process in unimolecular reactions in greater detail.

The facts that have just been described lend considerable support to the Lindemann theory. If this theory is to be applicable, the rate of activation and deactivation at higher pressures ought to be great compared with the rate of chemical change, in order that there may be little disturbance of the statistical equilibrium and hence an absolute rate of reaction directly proportional to the total concentration. At first some difficulty was felt about this point, but the solution appears to have been found, and indeed the solution itself constitutes a rather strong piece of evidence in favour of the theory.

With bimolecular gas reactions, as we have seen, it is plausible to assume that the kinetic energy of the impact between the two molecules provides the energy of activation, and on this assumption we find for the number of molecules reacting: *number of collisions* $\times e^{-E/RT}$. This equation in six out of seven known examples is as nearly true as experiment can decide. Thus there is no absolute necessity to look any further for the interpretation of bimolecular reactions. At first it seemed natural to apply an analogous method of calculation to determine the maximum possible rate of activation in unimolecular reactions: this led to the result that unimolecular reactions in general proceed at a rate many times greater than the expression $Ze^{-E/RT}$ requires,* e.g. about 10^5 times as many molecules of acetone decompose at 800° abs. in unit time as this method of calculation would admit to be possible.†

The difficulty can be surmounted by taking into account all the internal degrees of freedom of the molecule, and assuming that energy of all kinds in every possible distri-

* Christiansen and Kramers, *Z. physikal. Chem.*, 1923, **104**, 451.

† Hinshelwood and Hutchison, *Proc. Roy. Soc.*, 1926, A, **111**, 245.

bution in a large number of degrees of freedom can constitute or be converted into energy of activation.* The chance that a molecule contains in n 'square terms' an amount of energy greater than E is

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

which for large values of n is very much larger than $e^{-E/RT}$. The important thing, moreover, is that the temperature coefficients of the two expressions are not very different, so that the value of E derived from the Arrhenius equation is not very much altered in the new method of calculation.

A significant fact now appears, namely, that whereas most bimolecular reactions, which only require the simple exponential expression to account for their rate, are transformations of comparatively simple molecules, unimolecular reactions seem to be characteristic of more complex molecules possessing the requisite number of internal degrees of freedom.† The following table shows the influence of the complexity of the molecule on the type of reaction mechanism by which it decomposes or transforms itself thermally.

Bimolecular	Unimolecular
$2\,HI$	N_2O_5
	$CH_3 . CO . CH_3$
$2\,N_2O$	$C_2H_5 . CHO$
$2\,Cl_2O$	$C_2H_5 . O . C_2H_5$
$2\,O_3$	$CH_3 . O . CH_3$
$2\,CH_3CHO$	$CH_3 . N = N . CH_3$
$2\,NO_2$	$C_3H_7 . N = N . C_3H_7$
	$C_{10}H_{16}$
	$C_3H_7 . O . C_3H_7$

If suitable values are assigned to n, the number of energy terms in the molecule, the rate of activation

* G. N. Lewis and D. F. Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 1508.
Hinshelwood, *Proc. Roy. Soc.*, 1926, A, **113**, 230.
Fowler and Rideal, ibid., 1927, A, **113**, 570.

† Hinshelwood, ibid., 1926, A, **113**, 230; 1927, A, **114**, 84.

becomes great enough to account for the rate of reaction in all cases except that of nitrogen pentoxide.

The calculation of n can be best made for those unimolecular reactions where k decreases below a certain pressure. The following simple method of calculation is probably as accurate as is needed in the present state of our knowledge.

Let it first be assumed that no chemical reaction is taking place in the gas. Of N molecules present let N_1 possess energy greater than E, the energy being distributed in n 'square terms'. These are the active molecules

$$N_1 = N f(E)$$
$$= \frac{N \cdot e^{-E/RT}(E/RT)^{1/2n-1}}{\lfloor \frac{1}{2}n - 1}.$$

Let Z_1 be the number of molecules which enter the active state in unit time as a result of collisions, and Z_2 the number which leave it, also as a result of collisions.

For statistical equilibrium $Z_1 = Z_2$.

Active molecules are very exceptional ones, so that nearly every collision undergone by an active molecule results in its deactivation, rather than its activation to a higher degree. Thus Z_2 is very nearly equal to the number of collisions suffered in unit time by active molecules. Therefore

$$Z_2 = \text{total number of collisions} \times \frac{\text{number of active molecules}}{\text{total number of molecules}}$$
$$= \frac{Z \cdot N}{N} \cdot \frac{e^{-E/RT}(E/RT)^{1/2n-1}}{\lfloor \frac{1}{2}n - 1}$$

leaving out of account the very small number of collisions in which both the molecules have very high energy. This expression must also equal Z_1, since $Z_1 = Z_2$. If, now, the statistical equilibrium is disturbed by the removal of active molecules in chemical change, Z_1 is the maximum rate at which they can be re-formed. This determines the maximum rate that the chemical change can attain without the aid of chain mechanisms. According to Linde-

mann's theory this maximum rate of activation, in the region where k is constant, should be at least several times greater than the observed rate of reaction.

At the point where k begins to fall away from its normal value, it may be assumed that the rate of activation is just great enough to keep up the rate of reaction. By equating, therefore, the number of molecules reacting at the pressure where k begins to fall, to the expression for the rate of activation, the value of n may be found.

For the purposes of this calculation the value of E cannot be derived simply from the formula $d\log k/dT = E/RT^2$. Since the value of k is proportional to

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

we find by taking logarithms and differentiating

$$d\log k/dT = \frac{E-(\tfrac{1}{2}n-1)RT}{RT^2}.$$

Thus the value obtained from the Arrhenius equation must be increased by $(\frac{1}{2}n-1)RT$. This correction is, however, relatively small, though not negligible.

With dimethyl ether, for example, where k begins to fall at about 400 mm. at 800° abs., the number of collisions per c.c. per second under these conditions is $1{\cdot}73\times10^{28}$ and the number of molecules reacting per c.c. per second is $6{\cdot}8\times10^{15}$. The value of E is $58{,}500+(\frac{1}{2}n-1)RT$.

Thus $$\frac{e^{-\left\{\frac{58{,}500+(\frac{1}{2}n-1)RT}{RT}\right\}}\left(\frac{58{,}500+(\frac{1}{2}n-1)RT}{RT}\right)^{1/2n-1}}{\lfloor\tfrac{1}{2}n-1} = \frac{6{\cdot}8\times10^{15}}{1{\cdot}73\times10^{28}},$$

whence $$\frac{e^{-(\frac{1}{2}n-1)}\{36{\cdot}93+(\frac{1}{2}n-1)\}^{1/2n-1}}{\lfloor\tfrac{1}{2}n-1} = 4{,}300.$$

If $n=10$, the left-hand side is 2,140, while if $n=12$ it is 7,270. n may therefore be taken as 11.

To account for the behaviour of propionic aldehyde about 12 terms are needed, for diethyl ether 8, and for azomethane about 25.

Since each internal vibration contributes two square terms, kinetic energy and potential energy, 4 to 6 internal vibrations must be involved in the activation of the ethers, and about 12 in the activation of azomethane. For most of the molecules, the formulae of which are given in the above table, therefore, the result is very plausible.

The result is a particularly interesting one, since it is precisely for molecules of this complex internal structure, with several simultaneous vibrations, that complicated phase relations might be expected, leading to the time-lag between activation and reaction which is the essential condition of the Lindemann mechanism. There are two independent pieces of evidence. On the one hand the decrease of the velocity constant at lower pressures and its approach to a limiting value at higher pressures is most simply explained in terms of increasing deactivation by collision at higher pressures, and this can only occur when the time-lag exists. On the other hand the complexity of the activation process, as revealed by the number of degrees of freedom which have to be assumed to account for the rate, make the existence of such a time-lag appear very probable. The value of n required to account for the fact that the velocity constant for the decomposition of azoisopropane does not fall off at 0·25 mm. is from 45 to 50. This is rather a large value, but not by any means an impossible one. The specific heat of gaseous acetone, which contains 10 atoms, is about 20 calories per gram molecule at about 150° C.; azoisopropane contains 22 atoms to the molecule, and might therefore have a specific heat of 40 to 50 calories. Since each square term in the energy expression contributes $1/2R$ calories per gram molecule there is obviously nothing unreasonable about the value which must be assigned to n to account for the constancy of k. If the velocity constant were found not to diminish at still lower pressures serious difficulties would begin to arise.

The only example of all the unimolecular reactions known where such a difficulty has actually arisen in an acute form is the decomposition of nitrogen pentoxide. It appears that at low pressures nitrogen pentoxide reacts at a rate which is considerably greater than the maximum possible rate of activation by collision, however great a value of n be assumed. There is a limit to the maximum rate theoretically possible, since, when n is increased beyond a certain point, the increase in the term $E = E_{Arrhenius} + (\frac{1}{2}n - 1)RT$ produces a decrease in the calculated rate which more than compensates for the increase due to the term $(E/RT)^{1/2n-1}$ multiplying the exponential term.

The nitrogen pentoxide decomposition is the only reaction definitely known to be anomalous in this respect, but it is just possible that the azoisopropane decomposition may have to be added to the list. Several explanations of the anomaly have been offered. Fowler and Rideal suggested that all the energy of two molecules in collision might flow into one of the molecules, and activate it. By considering the statistical equilibrium between activated and unactivated molecules, it can easily be shown that if it is possible for all the energy of two molecules in collision to become concentrated in one, then the effective radius of a molecule for deactivating collisions must be very many times greater than for activating collisions. This result is not a very plausible one, though not definitely impossible. To explain, for example, the variation with pressure of the polarization of the resonance radiation of mercury vapour, the effective radius of the mercury atom has to be assumed considerably greater than that indicated by the kinetic theory.

It has also been suggested that the molecular diameter of nitrogen pentoxide is effectively much greater for activating collisions, as well as for deactivating collisions, than that calculated in the ordinary way from the kinetic theory. The difficulty about this suggestion is that the

calculation of bimolecular reaction rates can be carried out satisfactorily with the ordinary diameters ; it is therefore rather an *ad hoc* procedure to alter them to explain one or two anomalous unimolecular reactions.

The most satisfactory explanation is that the rate is increased beyond the maximum rate of activation by collision through the operation of a chain mechanism. The observations of Sprenger on the peculiar behaviour of nitrogen pentoxide at low pressures suggest strongly that chains are propagated. Moreover, if the rate of the azo-isopropane reaction at the lowest pressures should prove to be greater than can be accounted for on the basis of the simple collision mechanism, a chain mechanism can be assumed without difficulty since the reaction is quite markedly exothermic.

There is no reason why a combination of mechanisms should not operate in particular examples, e. g. the Lindemann mechanism followed by quite short chains. Moreover the results to be described in Chapter VI show that the ease of propagation of chains varies very much with pressure, so that it would be possible to have a normal reaction at higher pressures reinforced by chains at low pressures, or between certain limits of pressure.

The heat of activation of unimolecular reactions.

The velocity constant of a reaction can be expressed in the form $\chi e^{-E/RT}$. With bimolecular reactions the variations in χ, which depends on the collision number, are small from reaction to reaction compared with the variations of many powers of ten in the exponential term. Similarly, even in termolecular reactions the exponential term appears to play the principal part in determining the region of temperature in which the velocity of reaction shall attain an assigned value. The gaining of the energy of activation appears to be the principal determining factor in simple reactions, and it is often roughly true to

say that the gaining of this energy is not merely a necessary, but also a sufficient condition for chemical transformation.

In unimolecular reactions, where complex molecules are involved, a fraction only of the activated molecules react, and this fraction is determined by specific factors. Thus a rigid parallelism between the heats of activation and the temperatures at which different reactions attain some assigned rate cannot be expected. Nevertheless in any expression containing an exponential term that term tends to play a predominant role, and a definite, if rough, parallelism still exists, showing that even in the case of more complex reactions the value of E is perhaps the most important factor in determining the rate of reaction.

Reaction decomposition or transformation of	Temperature of equal reaction velocity (absolute)	Energy of activation (calories per gram molecule)
N_2O_5	328°	24,700
$C_3H_7 . N = N . C_3H_7$	545°	40,900
$C_{10}H_{16}$	556°	43,700
$CH_3 . N = N . CH_3$	599°	51,200
C_2H_5CHO	792°	54,000
$CH_3 . O . CH_3$	800°	58,500
$C_2H_5 . O . C_2H_5$	812°	53,000
$CH_3 . CO . CH_3$	835°	68,500

More detailed theories about the constant χ.

In so far as the parallelism between E and T, discussed in the last section, exists, it means that the factor χ multiplying the exponential term is always of the same order of magnitude.

Dushman* put forward the equation $k = \nu e^{-h\nu/kT}$ for the velocity constant of a unimolecular reaction. The values of E, which in this equation are equal to $Nh\nu$, vary by a factor of less than 3 from reaction to reaction. Thus it is not easy to differentiate in practice between Dush-

* *J. Amer. Chem. Soc.*, 1921, **43**, 397.

man's equation, which makes the factor χ proportional to E, and an equation which makes χ constant, since comparatively small errors in the experimentally determined values of E make a considerable difference in χ. The equation, however, undoubtedly gives the correct order of magnitude. By combining the equation with the equation for the rate of bimolecular reactions, Dushman has calculated equilibria in such systems as the following, $AB \rightleftharpoons A + B$, in many cases with good results.

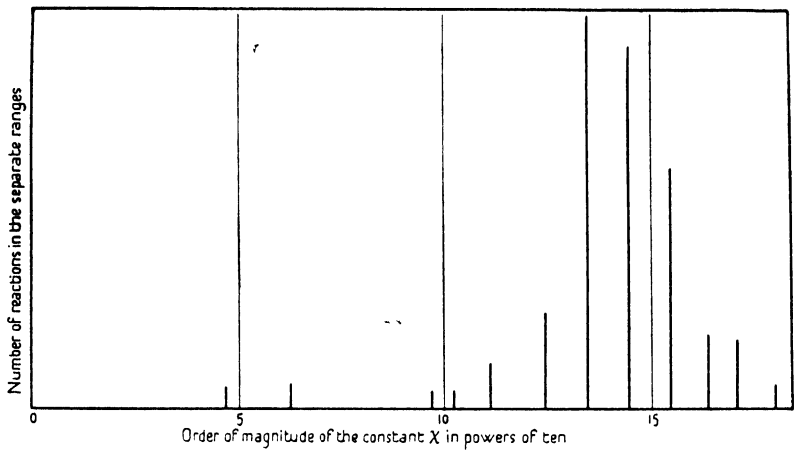


FIG. 4.

Several attempts at theoretical derivation of the equation have been made;* but if the energy of activation is distributed among a number of degrees of freedom, it is not easy to see how the relation $E = Nh\nu$ can have an exact meaning, justifying the proportionality of E and χ, though it may well be true that the order of magnitude of χ is that of E/Nh.

This matter has been discussed by Polanyi and Wigner.† Plotting a frequency distribution curve for the values of the constant multiplying the exponential term, for reactions in solution as well as in the gaseous state, they obtain fig. 4.

* E.g. Rideal, *Phil. Mag.*, 1920, **40**, 461.

† *Z. physikal. Chem.*, 1928, A ' Haber-Band ', 439.

It is evident that the value 10^{13} to 10^{14} occurs more often than any of the others. Polanyi and Wigner do not consider how the energy is communicated, but assume a large molecule containing already the necessary energy of activation, i.e. virtually they adopt the Lindemann theory, and fix their attention on the period between activation and transformation. They assume the energy to fluctuate in the molecule in 'elastic waves', and the transformation to occur when by 'interference' of these waves the amplitude at one of the linkings between the atoms reaches a critical value. Taking the velocity of propagation of a disturbance across the molecule as of the same order as the velocity of sound, they find that the order of magnitude of the factor χ should be that of the atomic frequency, which is the order of magnitude required.

The behaviour of unimolecular reactions at low pressures.

We have seen that the value of k should diminish when the pressure is sufficiently reduced. It remains to consider the relation between k and the pressure, p, in the region where the falling off occurs. Rice and Ramsperger* have shown that this relation varies somewhat according to whether the probability of transformation of the activated molecule is independent or not of the excess of energy which it possesses over the minimum required for activation. They consider two cases, the first, a state of affairs where the probability of transformation is independent of the energy as long as the latter exceeds E; and the second, one where a certain minimum of energy must reach a particular degree of freedom, the chance of this happening being proportional to the excess of energy over E possessed by the molecule as a whole.

The equations for the relation between k and p have been applied to the experimental results for various uni-

* *J. Amer. Chem. Soc.*, 1927, **49**, 1617; ibid., 1928, **50**, 617.

molecular reactions. The second assumption explains the course of the curve for the decomposition of azomethane considerably better than the first, and the curve for the decomposition of diethyl ether a little better. The data for propionic aldehyde are represented about equally well by either equation.

It is interesting to inquire how the point at which the velocity constant begins to fall away from its limiting value depends upon the temperature. The answer is that the influence of temperature on the k, p curve should not be considerable, but that theoretically the velocity constant should begin to fall at a higher pressure the higher the temperature. For the purpose of showing this we may adopt the simple theory, namely, that the probability of transformation of active molecules is constant.

Let $[a]$ = the actual number of activated molecules per c.c. and n = the total number of molecules per c.c.

At high pressures, where the rate of activation and deactivation are large compared with the rate of chemical change, the value of $[a]$ is simply $nf(E)$, where $f(E)$ is the fraction of the total number of molecules having energy greater than E.

The rate of change of these molecules is $b[a]$, where b is a constant. It is also equal to $k_\infty \,.\, n$, k_∞ being the limiting value of the velocity constant at high pressures. Thus

$$b[a] = bnf(E) = k_\infty\, n,$$

whence

$$b = \frac{k_\infty}{f(E)}.$$

At low pressures the rate of chemical transformation is comparable with the rate of deactivation. The rate of activation is still given by total number of collisions $\times f(E)$, i. e. by $\sqrt{2}\,\pi\,\bar{u}\,\sigma^2 \,.\, n^2 \,.\, f(E)$. The rate of deactivation is very nearly equal to the number of collisions between activated molecules and normal molecules, i. e. to $\sqrt{2}\,\pi\,\bar{u}\,\sigma^2 .\, n[a]$. The rate of chemical change is $b[a]$.

Since rate of activation = rate of deactivation + rate of transformation,

$$\xi \,.\, n^2 f(E) = \xi\, n[a] + b[a],$$

where $\xi = \sqrt{2}\,\pi\, \bar{u}\, \sigma^2$

and $b = k_\infty / f(E)$,

whence

$$k = \frac{b[a]}{n} = \frac{k_\infty \,.\, \xi \,.\, n}{\xi \,.\, n + k_\infty / f(E)},$$

since $p = nkT$,

where k = gas constant per molecule,

$$\frac{k}{k_\infty} = \frac{1}{1 + \dfrac{bkT}{\xi p}},$$

ξ varies as $\bar{u}$, and therefore as $\sqrt{T}$;

thus $$\frac{k_\infty}{k} = 1 + \frac{c\sqrt{T}}{p},$$

where c is a constant.

It is evident that k_∞ / k does not depend on $f(E)$ but only on $\sqrt{T}$; the variation with temperature will therefore, as far as the simple theory indicates, be inconsiderable. The effect of the $\sqrt{T}$ factor will actually be to give the same value of k_∞ / k for a higher pressure and a higher temperature as for a lower pressure and a lower temperature; in other words k falls more readily below k_∞ the higher the temperature. The physical meaning of this is that the relative ease of transformation and deactivation is shifted in favour of deactivation with increasing temperature, since rate of deactivation depends upon the molecular velocity, while transformation depends upon a factor, b, which we have assumed constant. But quantitatively the effect is not great. k, p curves almost identical at different temperatures have been found by Glass for the decomposition of methyl ethyl ether.

Rice and Ramsperger find that the constants for the decomposition of azomethane fall off sooner at higher

temperatures, and a similar result has been found by Glass for methyl propyl ether. These results therefore lend some support to the idea that b is not a simple constant; but the possibility of a distortion of the results by secondary effects in these rather complicated reactions should be borne in mind.

The problem of the behaviour of unimolecular reactions at lower pressures has also been considered theoretically by Kassel,* who concludes that the best assumption to make is that the probability of transformation increases with the excess of the activation energy over the minimum.

THE OCCURRENCE OF UNIMOLECULAR REACTIONS

In the light of what has been said about the mechanism of unimolecular reactions, the distinction between unimolecular and bimolecular changes becomes, in certain respects, one of degree only. A reaction such as $H_2 + I_2 \rightarrow 2\,HI$ naturally could not be unimolecular, for purely chemical reasons, but the decomposition of hydrogen iodide might be unimolecular or bimolecular. Molecules of simple structure, as we have seen, with a small enough time-lag between activation and transformation, will react on impact at a rate proportional to the number of activating collisions, and thus give second order changes; more complex molecules suffer many deactivations and thus give first order changes.

Another important factor determining the bimolecular course of simple homogeneous gaseous decompositions is that the unimolecular mechanism would result, in many instances, in the production of free atoms, thus

$$O_3 = O_2 + O, \quad N_2O = N_2 + O, \quad Cl_2O = Cl_2 + O.$$

These changes would be highly endothermic, the heat of dissociation of the oxygen molecule amounting to about 150,000 calories according to a rough estimate.

* *J. Physical Chem.*, 1928, **32**, 225.

The heat of dissociation of 2 HI is very small, but since the heat of dissociation of the hydrogen molecule is about 95,000 calories it is easily seen that the change $HI = H + I$ is highly endothermic also.

Now, although there is no real relation between heat of activation and heat of reaction, it is obvious that in an endothermic change the heat of activation must be at least equal to the actual energy which must be absorbed in the transformation, and will probably be a good deal larger than this. Hence many of the simple unimolecular changes will be associated with extremely high heats of activation.

For this reason they take place with much greater reluctance than the corresponding bimolecular changes.

These considerations do not, however, apply to examples such as the decomposition of acetaldehyde $2\,CH_3CHO = 2\,CH_4 + 2\,CO$, where the unimolecular change is under no disadvantage on purely thermochemical grounds.

The relation of homogeneous unimolecular changes to the corresponding catalytic reactions on surfaces will be discussed in a later section.

VI

CHAIN REACTIONS

THE significance of the process called activation has been abundantly illustrated in previous chapters. Ordinarily it is governed by the energy distribution laws prevailing in a system in thermodynamic equilibrium, but in exothermic reactions a special mechanism becomes possible, in which the energy set free is communicated to molecules which it immediately activates, a reaction chain being thereby established.

The idea of chain reactions originated in two ways, both of which have been referred to in the foregoing pages. In one form it was introduced to explain the enormous deviation of the hydrogen chlorine combination from Einstein's law; and chain reactions are now generally supposed to occur wherever many molecules are transformed per quantum absorbed in a photochemical change. In a different connexion the idea was used by Christiansen and Kramers not only to account for a kinetically unimolecular reaction when the activation is brought about by collision, but also to overcome the difficulty then felt about accounting for the rate of activation, which was apparently too great to be explained except by a chain mechanism. We have now to consider this mechanism in more detail.

The Nernst Chain.

Weigert and Kellermann* obtained direct evidence of the propagation of chains in mixtures of hydrogen and chlorine. By photographic methods they were able to show that when the mixture was illuminated momentarily the chemical change, as rendered visible by the changes in refractive index caused by the heat of reaction, did not

* *Z. physikal. Chem.*, 1923, **107**, 1.

develop to its full extent for a finite fraction of a second after exposure to the flash of light. This proved that the light set up a chain of processes which continued independently in the dark.

Porter, Bardwell, and Lind* found a rather striking piece of evidence of a somewhat analogous kind. Over a wide range of conditions the relative amounts of combination of hydrogen and chlorine provoked by light and by the passage of α-particles through the gas are the same. This is readily intelligible if a definite thermal chain is assumed to be propagated, for, as they say, we have 'two entirely distinct physical agents, light and α-particles, acting through different primary steps, excitation and ionization, producing total reaction greatly in excess of the unit quantities involved in the primary steps, and yet the total quantities of action referred back to the unit in each case are equal to each other'.

Polanyi † has shown that the Nernst chain

$$\mathrm{Cl} + \mathrm{H_2} = \mathrm{HCl} + \mathrm{H}$$
$$\mathrm{H} + \mathrm{Cl_2} = \mathrm{HCl} + \mathrm{Cl} \text{ and so on}$$

can also be initiated by reactions between chlorine and the atoms of alkali metals, thus

$$\mathrm{Na} + \mathrm{Cl_2} = \mathrm{NaCl} + \mathrm{Cl}.$$

The method of experiment was to pass hydrogen at a pressure of 5–15 mm. over the heated metal, whereby a definite small amount of the vapour was taken up, and then to introduce small amounts of chlorine. For each molecule of sodium chloride many molecules of hydrogen chloride are formed. The experiments are carried out at a temperature about 50° lower than that where there is an appreciable spontaneous reaction between the hydrogen and chlorine.

* *J. Amer. Chem. Soc.*, 1926, **48**, 2603.

† *Trans. Faraday Soc.*, 1928, **24**, 606; cf. also *Z. Elektrochem.*, 1927, **33**, 554.

Alkali metal vapours will also induce reaction between chlorine and a hydrocarbon, a process which presumably occurs in the following way:

$$\begin{aligned} Na + Cl_2 &= NaCl + Cl \\ Cl + CH_4 &= HCl + CH_3 \\ CH_3 + Cl_2 &= CH_3Cl + Cl \text{ and so on.} \end{aligned}$$

The chains are terminated by the union of the free halogen atoms, hydrogen atoms, or hydrocarbon radicles to form molecules, or by their reaction with impurities. The walls of the vessel play an important part in the breaking of the chains, as may be recognized from the fact that the chains may be lengthened ten times by covering the wall with a layer of sodium chloride, and also that admixture with nitrogen increases the chain length by keeping the free atoms or radicles out of contact with the wall for a longer time.

The chain length is shortened by the presence of bromine, which appears to react with the free hydrogen atoms or CH_3—radicles thus

$$H + Br_2 = HBr + Br; \quad CH_3 + Br_2 = CH_3Br + Br,$$

the bromine atoms being incompetent to continue the chain. By comparing the chain length in mixtures containing chlorine and bromine in various proportions, the relative probability of the reactions $H + Cl_2$ and $H + Br_2$ can be estimated. It appears to be about seven to one. Similarly, at equal concentrations, CH_3—radicles appear to react about thrice as rapidly with chlorine as with bromine.

Cadmium, zinc, magnesium, arsenic, and phosphorus have also an inducing effect similar to that of the alkali metals. With the divalent metals the mechanism whereby the chain is initiated is

$$Me'' + Cl_2 = Me''Cl + Cl$$

and not the production of an activated molecule of $Me''Cl_2$ which then collides with a chlorine molecule splitting it

up into atoms. One of the ways in which Polanyi establishes this is as follows. The reaction between hydrogen and chlorine as induced by zinc vapour is measured in the presence of a known proportion of bromine. From the way in which the bromine slows down the reaction the number of chains terminated in unit time can be calculated, and hence the number starting in unit time. Comparing this with the number of metal atoms which have reacted, it appears that approximately one chain is started for each metal atom which reacts. Polanyi considers that the proportion would be much lower if the primary process were the production of an activated molecule of $MeCl_2$, on account of the considerable chance this would have of being deactivated before it caused the splitting up of a chlorine molecule.

The Theory of Negative Catalysis.

The explanation of negative catalysis in terms of the chain reaction mechanism was given by Christiansen.*

There is no particular difficulty in understanding how a small trace of some foreign substance can accelerate a chemical reaction to a very marked extent: the molecules resort one after another to the catalyst where they undergo an extremely rapid change. But there is much more mystery about the converse process, known as negative catalysis, whereby a small trace of some substance may almost entirely inhibit a reaction which in the absence of the negative catalyst would be taking place quite rapidly. Molecules are known to exert appreciable forces only at distances which are not much greater than their own diameters ; if therefore the negative catalyst is present in small concentration only, most of the molecules will be quite outside the range of its influence, and there is at first sight no reason why they should not be undergoing their normal reactions.

* *J. Physical Chem.*, 1924, **28**, 145.

One suggestion made was that all reactions subject to the influence of negative catalysts were in reality reactions already catalysed by a trace of some other substance present in small enough amount to be more or less completely removed even by the small quantity of negative catalyst added. Examples of this kind of action are known: and indeed the 'poisoning' of a catalytic surface in a heterogeneous reaction is something of the kind. Nevertheless examples of inhibition are known which do not seem to be explicable in this way.

Christiansen shows that if a reaction takes place by a chain mechanism and if a molecule of the negative catalyst combines with or deactivates one of the atoms or molecules participating in the propagation of the chain, then not only is this one atom or molecule put out of action, but, virtually, all those which would normally have reacted in the rest of the chain. Since the chain might have been a very long one, it is evident that one molecule of the negative catalyst may thus stop the reaction of hundreds or thousands of molecules.

The most direct evidence that negative catalysis sometimes works in this way in ordinary thermal reactions, and, therefore, incidentally that the chain mechanism can operate in such reactions, has been found by Bäckström.* In the photochemical oxidation of benzaldehyde, heptaldehyde, and of solutions of sodium sulphite, there are very large numbers of molecules transformed for each quantum of light absorbed, amounting respectively to 10,000, 15,000, and 50,000 for the three reactions. Such deviations from Einstein's law show that the light probably sets up chain reactions. These photochemical changes are markedly subject to the action of inhibitors, which presumably cut short the chains. Bäckström establishes the important

* *J. Amer. Chem. Soc.*, 1927, **49**, 1460; *Medd. K. Vetenskapsakad. Nobel-Inst.* 1927, **6**, Numbers 15 and 16; *Trans. Faraday Soc.*, 1928, **24**, 601.

fact that the corresponding reactions which take place in the dark are subject to the influence of the same inhibitors in an almost exactly parallel way. Thus it would appear that chain processes occur in the ordinary thermal reactions, and that the inhibitors act in the manner supposed by Christiansen's theory.

The results obtained for the oxidation of sodium sulphite solutions containing various alcohols as inhibitors are particularly instructive. The rate of reaction depends upon the concentration of the inhibitor, C, in the following way.

$$\text{Rate of dark reaction} = \frac{k_1}{k\mathrm{C}+k_2}; \qquad \text{Rate of photochemical reaction} = \frac{k_3 k_1}{k\mathrm{C}+k_2},$$

k_1, k_2, k_3, and k being constants, the latter depending on the nature of the alcohol.

The alcohols themselves are gradually oxidized; thus the mechanism of the inhibition seems to be that at some link of the sulphite oxidation chain an alcohol molecule is oxidized instead of a sulphite ion, and the chain is thereby interrupted. The exact mechanism of the normal uninterrupted chain is not exactly known: nor is it relevant to the discussion. By measurements of the rate of oxidation of the inhibitor the chain length can be found: the calculation is based upon the following considerations. Chains are broken in two ways, by the alcohol, and in some way which prevents them from reaching an infinite length when there is no alcohol present. This is represented by the two terms $k\mathrm{C}$ and k_2 in the above equations. When the inhibition is considerable it may be taken that all the chains are broken by alcohol molecules: this stage is marked by the fact that $k\mathrm{C}$ is large compared with k_2 and thus the rate is inversely proportional to the concentration of the inhibitor. Thus measurement of the number of alcohol molecules oxidized gives the number of chains broken in unit time: this must equal the number started. Dividing the total number of molecules of sulphite

oxidized by the number of chains gives the number of links in each chain. Another way of finding the chain length is by measurement of the quantum efficiency of the photochemical reaction under the same conditions of concentration: for, although the light increases the number of chains starting it does not alter their length provided the alcohol concentration is in the region where all the chains are broken by the inhibitor molecules. Bäckström finds striking agreement between the chain lengths determined in these two ways.

Although the reactions just described are not gaseous reactions they have been dealt with in some detail because the processes which they illustrate play an important part in gas reactions also. The action of 'antiknocks' may be interpreted as a phenomenon of negative catalysis of a chain reaction. There is evidence to show that in the combustion of hydrocarbons bodies of a peroxide character are formed and that these act as centres from which chains are propagated.* Metallic antiknocks, such as lead tetra-ethyl, are supposed to give rise to peroxides themselves, which react with and destroy the fuel peroxides and thus interrupt the chains. Further examples of this kind of action will arise in a later section dealing with the union of hydrogen and oxygen.

Quantitative treatment of reaction chains.

To write down the differential equation for the rate of a chain reaction we employ the law of mass action, but the simple application of this involves the concentration of the transitorily formed activated molecules which propagate the chain, and as this concentration is unknown the equation written down would be useless unless some other relations are established by means of which the unknown quantities can be eliminated. These relations are provided by the condition that the chains shall be stable, or the

* Egerton and Gates, *J. Inst. Petroleum Tech.*, 1927, **13**, 281.

condition of the system 'stationary'. This means that the number of chains starting in unit time must be equal to the number finishing, as long as the concentrations of the reacting substances are thought of as constant. If we imagine a system at the very instant when a chain reaction starts in it, it is evident that for a fraction of a second the reaction velocity will increase as the chains develop, but in an extremely short space of time will reach a 'stationary' value where the number of new active molecules formed in time dt is equal to the number disappearing. This 'stationary' value only remains constant, of course, so long as the concentrations of the reacting substances do not change appreciably—a condition which is, however, automatically provided for when we establish a differential equation only for the reaction velocity. Some examples follow.

(*a*) The best example to consider first is that treated by Christiansen and Kramers.* Here we have a single reacting gas, undergoing, for example, thermal decomposition. The molecules are activated by collision in the first instance, but the product of reaction is able to activate fresh molecules of the initial substance in giving up its excess energy ; moreover each molecule of the product is supposed to activate, on the average, α molecules in the process of relapsing to the normal condition. (If, for example, it activated one reactant molecule once in ten times, and nine times out of ten lost its energy without handing it on, α would be 0·1.)

Let n be the concentration of normal, unactivated molecules of the reacting gas, a that of activated molecules of the reacting gas, and a' that of activated molecules of the product. The condition for a stable chain is that

$$\frac{da}{dt} = 0 \text{ and } \frac{da'}{dt} = 0.$$

* *Z. physikal. Chem.*, 1923, **104**, 451.

Thus we have

$$\frac{da'}{dt} = A \,.\, a - Z_1 n a' = 0$$

Rate of spontaneous change of activated reactant into activated product. A is a constant.

Loss of activated product molecules by collision with normal molecules, which *may* be activated themselves in the process. Z_1 is a constant.

(1) (2)

$$\frac{da}{dt} = K \,.\, n^2 + \alpha Z_1 n a' - Aa - Z_2 n a = 0$$

Production of activated molecules of reactant by collision among themselves, i.e. independently of the chain process.

Corresponding to process (2) of the above equation.

Corresponding to process (1) above.

Rate of deactivation of active molecules of reactant by collisions with normal molecules. Z_2 is a constant.

The first and last terms of the second equation would naturally balance for thermodynamic reasons if no chemical reaction were going on. Z_1 and Z_2 depend upon the molecular speeds and diameters.

From the first equation

$$a' = \frac{A \,.\, a}{Z_1 n},$$

substituting in the second

$$K n^2 + \alpha Aa - Aa - Z_2 n a = 0,$$

whence

$$a = \frac{K n^2}{Z_2 n + A(1 - \alpha)}.$$

$$\text{Rate of reaction} = Aa = \frac{AK n^2}{Z_2 n + A(1 - \alpha)}.$$

If every activated molecule of product activates just one molecule of reactant, then $\alpha = 1$ and the rate reduces to $\frac{AK}{Z_2} n$.

Under these conditions the rate varies as the first power of n, although the reaction really depends upon collisions, a result which we have already derived from a more general argument in dealing with unimolecular reactions.

(*b*) It will be noticed that in the above example it was assumed that the activated molecules of the product lost their energy in no other way than in collisions with molecules of the reacting gas. They might also be supposed to lose it by collision with molecules of some foreign gas or with the walls of the containing vessel. To take these factors into account it is only necessary to add two terms to the equation for $\frac{da'}{dt}$ above. The equations then become

$$\frac{da'}{dt} = A \,.\, a - Z_1 n a' - f_s \,.\, a' - f_c \,.\, a' = 0$$

$$\frac{da}{dt} = Kn^2 + \alpha Z_1 n a' - Aa - Z_2 n a = 0$$

where f_s and f_c are factors which multiply a' to give the rate of deactivation by the surface and by foreign gases respectively.

Solving these equations as before we find

$$\text{Rate of reaction} = Aa = \frac{AKn^2}{Z_2 n + A\left(1 - \frac{\alpha Z_1 n}{Z_1 n + f_s + f_c}\right)}.$$

(*c*) For a reaction between two different kinds of molecule the equations may be written down in an analogous way.

To simplify matters let it be supposed that the chain is propagated by the handing on of the energy of the reaction products to molecules of one of the reacting gases only. Let a be the concentration of active molecules of this gas, and let a' be the concentration of active molecules of the reaction product at a given instant.

$$\frac{da'}{dt} = f_0(c) - f_1(c)a' + \alpha f_2(c)a - f_s a' - f_c a' = 0$$

(1) Production by 'spontaneous' reaction.	(2) Loss by deactivation of product by reactant, which takes the energy.	(3) Production from activated molecules of reactant by chemical transformation.	(4) Deactivation at surface.	(5) Deactivation in gas.

$$\frac{da}{dt} = f_1(c)a' - f_2(c)a = 0$$

Production from activated product—process (2).

Chemical transformation of activated reactant molecules (producing α active molecules of product in (3)).

$f_0(c)$, $f_1(c)$, $f_2(c)$, f_c are functions of concentration, determined essentially by mass action considerations, and f_s is a function of surface and possibly also concentration. The meaning of α here is very slightly different from the α of the reactions dealing with one reacting gas: there it represented the average number of reactant molecules produced from one active molecule of product; here it has been taken as the average number of active product molecules from one molecule of activated reactant. Moreover, in writing down the two equations, deactivation by processes (4) and (5) is assumed to happen only to product molecules, not to reactant molecules: this assumption simplifies the equation without introducing any real restriction, the breaking of the chain being postponed by one link only.

From the two equations we find

$$\text{Rate of reaction} = f_2(c)a = \frac{f_0(c)f_1(c)}{f_s + f_c + (1-\alpha)f_1(c)}.$$

Stationary and Non-stationary Processes.

The last equation is of the form

$$\text{Rate of reaction} = \frac{\text{Function of concentrations}}{\begin{array}{l}\text{Factor determining breaking of chains by surface} \\ + \text{Factor determining breaking of chains by collisions} \\ + A(1-\alpha)\end{array}}$$

$$= \frac{F(c)}{f_s + f_c + A(1-\alpha)}$$

where A is a constant or a function of concentration

according to circumstances, and α is the number of active molecules of product formed from one active molecule of the reactant chiefly involved in the propagation of the chain.

With $F(c)$ we are not at the moment much concerned; it depends upon the nature of the chemical act by which the chains are initiated.

f_s and f_c represent the two ways in which chains can be terminated—namely (a) by deactivation at the surface of the containing vessel of one of the molecules which would otherwise have continued the chain, and (b) by deactivation of such a molecule in a collision in the gas phase, without the handing on of the energy.

If α is not greater than unity, the velocity of reaction can only attain a considerable value if f_s and f_c are small, that is, if the chains are not broken very often.

When, however, α is greater than unity, phenomena of a most interesting kind become possible.* This condition that $\alpha > 1$ may be fulfilled in a sufficiently exothermic reaction, and especially one where $X \rightarrow 2Y$, or $X_1 + X_2 = 2Y$, each of the Y molecules possessing enough energy to be the potential origin of a new chain. It will be evident that under these circumstances the term $A(1-\alpha)$ in the above equation is negative. If the negative value is large enough it may equal $f_s + f_c$; the rate of reaction will then be infinite. The meaning of this is that, on account of the branching of the chains which occurs when $\alpha > 1$, the number of fresh chains which start in any element of time is greater than the number terminated: thus no stationary condition is possible. There can be no stable reaction velocity, but only one which increases with time till it reaches an infinite value. In other words an explosion occurs.

A distinction must be drawn between this kind of explosion and a thermal explosion which occurs when the rate of liberation of heat in a system exceeds the rate at

* Semenoff, *Z. Physik.*, 1927, **46**, 109; ibid., 1928, **48**, 571.

which it can be conducted away, so that the temperature rises and the reaction proceeds at an ever increasing rate until ignition results.

Critical Pressure Limits.

The relative magnitudes of the expressions $A(1-\alpha)$ and of f_c+f_s naturally vary with the concentration of the reacting gases and of any foreign gases present. Thus the denominator of the expression for the rate of reaction may be positive for certain concentrations and negative for others. At any concentration where $f_s+f_c+A(1-\alpha)$ just becomes zero there is a critical limit. On one side of the limit a stable velocity is possible, on the other side the number of chains starting is greater than the number terminated, so that the reaction almost instantaneously accelerates to explosion.

The limit may appear to be extraordinarily sharp. The stable velocity on one side of the critical limit may be quite small: at the limit a stationary condition ceases to be possible and the reaction must accelerate; thus, however small the velocity at a point just on one side of the limit, explosion takes place on the other side. The acceleration to the explosive point takes place in a time of the order of that required for chains to develop in the gas; which may be an immeasurably small fraction of a second. Thus we have the remarkable phenomenon of a critical concentration limit, on passing which a very slow reaction suddenly changes into explosion.

The critical limit may be an upper limit or a lower limit. This comes about in the following way. Chains are interrupted either by deactivation at the wall or in the gas phase. The greater the concentration of the gases, the smaller relatively is the influence of the wall factor. When this is the chief means by which the chains are broken there may be a transition from slow reaction to explosion as the pressure increases. When, on the other hand,

deactivation in the gas phase is the principal factor in controlling the length of the chains the transition from a stationary to an explosive process may occur as the pressure decreases.

When both factors operate simultaneously there may be both an upper and a lower limit of concentration, above and below which slow reaction occurs but between which lies a region of non-stationary, explosive processes.

Experimental evidence relating to stationary and non-stationary chain mechanisms in gas reactions.

(*a*) *The oxidation of phosphorus.* It has long been known that phosphorus will only glow if the pressure of oxygen is below a certain limit. But it would hardly have been justified, on the basis of the existing observations, to interpret this as a critical pressure in the sense of the last paragraph, in view of Rayleigh's demonstration that the glow of phosphorus is under some conditions a phenomenon depending on heterogeneous catalysis by nuclei of an oxidation product; these nuclei might be poisoned by an excess of oxygen, as well as by the various vapours which are known to inhibit the glow.

Chariton and Walta,* and more conclusively Semenoff,† have found, however, that there is also a lower critical pressure below which the gaseous reaction between phosphorus vapour and oxygen at ordinary temperatures hardly takes place at all, and above which it leads to the production of an explosive ignition. The critical oxygen pressure, p_k, is quite small, a fraction of a millimetre of mercury, and can be measured by allowing oxygen to enter through a capillary tube into a vessel containing phosphorus vapour and noting the point at which ignition occurs. Measurements on the change of pressure with time, by means of a McLeod gauge, show that the reaction at pressures below the critical is very slow. p_k is decreased if the

* *Z. Physik.*, 1926, **39**, 547. † Ibid., 1927, **46**, 109.

pressure of the phosphorus vapour, p_{P_4}, is increased, and is also decreased if the size of the vessel is increased. This is because the reaction is a chain reaction and the active molecules lose their activity when they collide with the walls of the vessel. This happens relatively less frequently in large vessels; hence the explosive region is reached more easily. The presence of argon lowers the critical pressure, because the foreign gas makes diffusion of the active molecules to the wall more difficult.

Semenoff's experimental results are summarized in the formula

$$p_{O_2}\sqrt{p_{P_4}}\left(1+\frac{p_{ar}}{p_{O_2}+p_{ar}}\right)d^{3/2}=\text{constant},$$

d being the diameter of the vessel, and all pressures referring to the critical limit. The critical oxygen pressure is independent of temperature.

Data are not available about the rate of reaction in the non-explosive region.

(*b*) *The oxidation of sulphur vapour at low pressures.* This has been investigated by Semenoff and Rjabinin.* The ordinary reaction between oxygen and sulphur, investigated by Norrish and Rideal (Chapter II), is negligibly slow below about 200° C., but at lower temperatures, 80° to 120° C., ignition of sulphur vapour mixed with oxygen at a rather low pressure can be effected if an electrodeless discharge is allowed to pass through the gas for a second or two. The discharge apparently creates active centres of some kind, possibly ozone molecules or oxygen atoms, from which reaction chains are propagated. This process is only possible between two quite definite limits of oxygen pressure, which evidently represent the upper and lower limits of the non-stationary chains.

(*c*) *The union of hydrogen and oxygen.*† This was the

* *Z. physikal. Chem.*, 1928, B, **1**, 192.

† Hinshelwood and Thompson, *Proc. Roy. Soc.*, 1928, A, **118**, 170; Gibson and Hinshelwood, ibid., 1928, A, **119**, 591; Thompson and Hinshelwood, ibid., 1929, A, **122**, 610.

first gaseous reaction to be studied where chains with a stable and measurable velocity are propagated. In certain regions of concentration explosive chains are also established. The principal facts about this remarkable reaction are as follows:

(1) Below 500° C. the combination takes place only on the walls of the vessel: the rate of reaction is not very markedly influenced by the pressure, and has a low temperature coefficient.

(2) Between 540° and 590° C. a reaction comes into prominence, which is undoubtedly a gas reaction; it is of very high order, and has a high temperature coefficient. At 560° the rate is roughly proportional to $[H_2]^3[O_2]^{3/2}$.

(3) This reaction, unlike the surface reaction, is not accelerated by increase in the surface of the walls of the vessel, but actually retarded, and to a marked degree. This fact suggests that it is a chain reaction, and that certain molecules are deactivated or destroyed at the walls, whereby the chains are shortened.

(4) Inert gases, including steam, have the most pronounced accelerating effect on the combination. Evidently they do not deactivate the active molecules which propagate the chain. In other words the collisions between active molecules and inert gas molecules are elastic. The inert gases, on the other hand, increase the length of the path which the chains must traverse before reaching the wall where they are broken. Hence the acceleration of the reaction. The order of the accelerating influence is $H_2O > A > N_2 > He$.

Excess of hydrogen or oxygen exerts an influence analogous to that of an inert gas, and this effect must be estimated and deducted from the total effect before the 'mass action' of the hydrogen and oxygen can be found.

(5) At lower pressures, between two sharply defined limits, the reaction becomes explosive. Thus the com-

plete relation between reaction velocity and pressure is shown in fig. 5.

It is remarkable that in the neighbourhood just to the right of C we have a state of affairs where the rate of reaction decreases with decreasing pressure, and yet if the pressure be reduced a point will be reached at which the mixture explodes; this illustrates the difference between the explosive chain and the 'thermal' explosion, which at some high enough pressure terminates the curve $C D$.

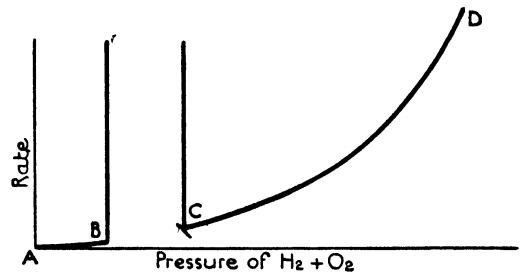


FIG. 5.

The limit at C is almost independent of the surface of the vessel: thus in accordance with the considerations of the earlier section on critical limits, it represents the point at which some deactivation process in the gas phase becomes marked enough to prevent branching chains from developing explosively. It is suggested that the deactivation process in question is the mutual destruction of H_2O_2 molecules, which between B and C are the centres from which explosive chains develop, e.g.

$$H_2 + O_2 = H_2O_2$$
$$H_2O_2 + H_2 = 2\,H_2O^*$$
$$H_2O^* + O_2 = O_2^* + H_2O$$
$$O_2^* + H_2 = H_2O_2, \text{ \&c.}$$

The lower limit at B would be the point at which the deactivating influence of the walls of the vessel is just great enough to keep the chains from developing explosively.

* Signifies an activated molecule.

(6) There is also some evidence that the principal process initiating the stable chains in the region *CD* is the direct termolecular reaction

$$2\,H_2 + O_2 = 2\,H_2O.$$

(*d*) *The influence of nitrogen peroxide on the union of hydrogen and oxygen.** H. B. Dixon observed that a trace of nitrogen peroxide lowers the temperature of ignition of hydrogen in oxygen by as much as 200°. Quantitative investigation of the influence of nitrogen peroxide on the rate of combination of hydrogen and oxygen in the region of 400° C., where the normal reaction is quite negligibly slow, revealed the existence of another remarkable 'critical limit' phenomenon. A sufficiently small trace of nitrogen peroxide produces no observable effect; as the amount is increased, a sharply defined limit is reached beyond which almost immediate explosion of the gases occurs when they are admitted to the reaction vessel. With still greater amounts of nitrogen peroxide a second limit is reached, as sharply defined as the first, beyond which explosion no longer occurs, but only a very slow combination.

The action of the nitrogen peroxide can be interpreted by the theory that it acts both as a centre from which chains are set up, e.g. by an exothermic reaction with hydrogen, and also as an 'antiknock', reacting with and destroying the hydrogen peroxide formed in the chains of the hydrogen-oxygen combination. When the first mode of action comes into play strongly enough the lower limit is passed; when the second breaks the chains often enough the upper limit is reached.

(*e*) *The reaction between nitrogen pentoxide and ozone.*† According to Schumacher and Sprenger the reaction between N_2O_5 and O_3 is a bimolecular reaction, which

* Gibson and Hinshelwood, *Trans. Faraday Soc.*, 1928, **24**, 559; Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, A, **124**, 219.

† *Z. physikal. Chem.*, 1928, **136**, 77; 1928, B, **2**, 267.

proceeds by a chain mechanism involving the intermediate production of a new oxide of nitrogen, NO_3 or N_2O_6. Spectroscopic observations confirm the supposition that a hitherto unknown oxide is formed.

The velocity of reaction is given by

$$\frac{dC}{dt} = 8{\cdot}7 \times 10^{15} \,.\, e^{-\frac{22000}{RT}} \,.\, C_{N_2O_5} \,.\, C_{O_3}.$$

According to considerations of the kind discussed in Chapters II and III the rate of an ordinary bimolecular reaction with this heat of activation would be about

$$10^{11} \,.\, e^{-\frac{22000}{RT}} \,.\, C_{N_2O_5} \,.\, C_{O_3}.$$

The much greater observed rate might indicate a chain reaction: but it may also be connected with the many degrees of freedom possessed by the complex $N_2O_5 \,.\, O_3$, so that the argument is not a conclusive one, although the facts upon which it rests are very interesting.

(*f*) *Decomposition of Nitrogen Pentoxide.** The principal facts about this reaction have already been stated. The observation of Sprenger that below a certain pressure the reaction ceases entirely indicates a chain mechanism, but its nature is not clear.

Phenomena of 'Intensive Drying'.

Some of the reactions described in this chapter constitute what is virtually a separate and distinct type of chemical change, namely one where there is no region of transition between very slow reaction and explosively rapid reaction. Such changes, which must be exothermic, depend upon branching reaction chains which 'get out of hand' when a certain critical concentration is exceeded.

Now of reactions which are inhibited by intensive drying the majority, as we have seen, are between substances in

* *Z. physikal. Chem.*, 1928, **136**, 49.

two phases, or are heterogeneous reactions, where the action of the small traces of water can easily be interpreted in terms of the theory of surface films. Of the small residuum of reactions, all, except one doubtful case and the union of hydrogen and chlorine, are changes the speed of which cannot be measured. They proceed instantaneously or not at all. It has never been possible to dry ammonium chloride to a state where it dissociates with measurable speed. Thus it would appear to be probable that the water in these reactions, and it must be repeated that their number is small, provides centres from which branching chains proceed. If the concentration is great enough, the reaction is almost instantaneous; if not, the change is negligibly slow. This would explain why the trace of water is effective, and larger quantities without further effect. It also becomes clear that to extend conclusions drawn from observations on this kind of reaction to reactions which have a stable measurable velocity is illogical.

Specific nature of energy transfers in chain reactions.

In the Nernst chain, atoms of hydrogen and chlorine are the active agents in the propagation. In other chain reactions the active agents are not special atomic or molecular species, but simply ordinary molecules possessing a considerable excess of energy. It might be supposed therefore that inert gases would have a retarding influence on such reactions, depriving the activated molecules of their energy and breaking the chains. We have seen that in the gaseous reaction between hydrogen and oxygen foreign gases do not exert this retarding effect, but rather an accelerating effect due to the increase in the chain length caused by elastic collisions between the activated molecules and those of the inert gas.

Energy transfers between molecules are indeed very specific: in fact the transfer of internal energy in a so-called 'collision of the second kind' is something rather

analogous to a chemical act. In the photochemical decomposition of ozone sensitized by chlorine, each quantum of light originally absorbed by the chlorine causes the decomposition of an ozone molecule, whatever the relative concentrations of ozone and chlorine may be. Thus the activated chlorine must survive a great many collisions without losing its energy, until it finds an appropriate ozone molecule. The specific action of hydrogen on quasi-unimolecular reactions is another example.

This specificity being recognized, the fact that foreign gases do not retard the decomposition of nitrogen pentoxide no longer speaks against the possibility of a chain mechanism for this reaction.

It may also be mentioned here that in specific molecular actions a particularly marked influence of like molecules upon one another is often to be observed. This is encountered in various ways in spectroscopy, in the extinction of the polarization of mercury resonance radiation with increasing vapour pressure,* in the damping of fluorescence in concentrated solutions,† and in various chemical reactions. As an example of the latter the decomposition of acetaldehyde (p. 70) may be quoted, where collisions between two molecules of the aldehyde are much more effective than collisions of aldehyde molecules with those of other gases.

* V. von Keussler, *Ann. Phys.*, 1927, [IV], **82**, 793.

† Perrin, *Compt. Rend.*, 1927, **184**, 1097.

VII

THE KINETICS OF HETEROGENEOUS REACTIONS

So long as we have confined our attention to homogeneous reactions it has been possible to take into consideration the majority of the known examples, but when we turn to heterogeneous reactions we find the number to be almost unlimited. It will therefore be expedient to illustrate, by such examples as may appear most typical, the different kinds of heterogeneous reaction which can take place, rather than to attempt an exhaustive description of individual reactions. It is difficult, moreover, among the mass of investigations to trace the origin of even the most important theoretical ideas, which are often contained implicitly in quite early work, and may have been in current use for the interpretation of experimental observations long before any explicit statement of them is made.

It is becoming recognized that something fundamental underlies the almost universal tendency of gaseous changes to take place in contact with a solid surface more readily than in the gas phase, and that the 'wall-effect' is not to be dismissed as merely a 'disturbing factor'. But before this difficult question can be approached some preliminary matters relating to the mode of action of the solid surface must be considered.

The Adsorption Theory.

The molecules of a gas are not, except perhaps in very special instances, brought into a chemically active condition by mere mechanical impact with the solid surface. The highly specific action of different surfaces, illustrated for example by the hundreds of examples quoted in Sabatier's work *La Catalyse en Chimie Organique*,* at once rules out so simple an hypothesis.

* Second Edition. Paris and Liège, 1920.

Intermediate compound formation between the molecules of the gas and those of the catalysing surface is not usually a helpful hypothesis. The assumptions which have to be made about the existence of compounds nearly always do violence to the principles of general inorganic chemistry. It is undesirable to postulate for *ad hoc* purposes the formation of compounds the separate existence of which is known to be unlikely or impossible.

All the advantages of the intermediate compound theory without most of the disadvantages are possessed by what may be called the chemical adsorption theory.

Faraday went to the root of the matter and stated at the outset that the films of gas known to be adsorbed by surfaces were the seat of the chemical changes. This idea has long been used in the interpretation of catalytic phenomena,* and, without further specific assumptions about the nature of the films, has been accepted for many years.

The simplest supposition to make is that the increased concentration in the condensed film brings about increased velocity of reaction in virtue of a purely mass action effect. This theory, however, has been shown in many ways to be untenable. The clearest proof of its inadequacy is afforded by the study of those reactions in which the same substance can undergo transformation in alternative ways. Thus alcohol vapour can suffer decomposition into ethylene and water or into aldehyde and hydrogen according to the equations†

$$C_2H_5OH \begin{cases} \nearrow C_2H_4 + H_2O & \text{(i)} \\ \searrow CH_3CHO + H_2 & \text{(ii)} \end{cases}.$$

Different surfaces accelerate the alternative reactions to quite different degrees. For example, copper at 300° C. causes the decomposition of alcohol into aldehyde and hydrogen almost exclusively, while alumina at the same temperature favours the rival reaction almost entirely.

* Compare Bone and Wheeler, *Phil. Trans. Roy. Soc.*, 1906, A, **206**, 1.

† Sabatier, loc. cit.

Although different increases in the concentration of the alcohol vapour are doubtless produced at the different surfaces, these increases, in so far as they have a simple mass action effect, should operate to exactly the same extent in respect of the alternative reactions, because the rate of each is directly proportional to the concentration of alcohol. Different catalysts would be expected to produce different changes in the total rate of transformation of the reactant, but to be without effect on the relative amounts of the products.

Additional examples of such alternative reactions where the relative rates are influenced by the nature of the surface are the following:

$$\mathrm{H.COOH} \begin{cases} \nearrow \mathrm{H_2O + CO} \\ \searrow \mathrm{H_2 + CO_2} \end{cases} *$$

and

$$2\,\mathrm{CH_3COOC_2H_5} \begin{cases} \nearrow \mathrm{(CH_3)_2CO + 2\,C_2H_4 + CO_2 + H_2O} \\ \searrow \mathrm{(CH_3)_2CO + C_2H_4 + C_2H_5OH + CO_2} \end{cases} .\dagger$$

Surfaces must therefore be supposed to have some specific influence on the stability of molecules adsorbed upon them. That these specific influences, of the kind usually called 'chemical', play an all-important part has long been recognized, and is often expressed by the assumption of 'complex' formation.‡

Langmuir § put forward an extremely definite form of this idea. The adsorbed molecules are supposed to be held to the surface by ordinary 'valency forces', either 'primary valencies' or 'secondary valencies'. In the light of recent developments in the theory of atomic structure it would probably be sufficient to say that the adsorbed molecules are attached to the molecules constituting the surface by non-polar linkages. Thus the kind of union between tungsten and oxygen adsorbed on its surface, to

* Sabatier and Mailhe, *Compt. rend.*, 1911, **152**, 1212.

† Sabatier, loc. cit., *supra*.

‡ Compare Armstrong and Hilditch, *Proc. Roy. Soc.*, 1922, A, **100** 240.

§ *J. Amer. Chem. Soc.*, 1916, **38**, 2221.

take one of Langmuir's examples, differs in no essential way from that which exists in tungsten oxide. The only difference between adsorption and oxide formation is that in adsorption the atoms of the metal, though attached to oxygen, remain also firmly held to their neighbours, whilst in oxide formation these linkages between the tungsten atoms themselves are completely dissolved.

The 'nickel-hydrogen complexes' responsible for catalytic hydrogenation differ only from nickel hydrides in that the affinity of the hydrogen for the nickel is not sufficient to overcome the forces holding the nickel atoms in the space lattice of the solid. Carbon monoxide being able, on the other hand, to detach the nickel atoms from their places, a definite carbonyl results. With platinum neither hydrogen nor carbon monoxide can loosen the atoms from their lattice, but the films which are formed are nevertheless held by the linkages characteristic of hydrides and carbonyls respectively. When other examples are reviewed, such as the adsorption of ammonia by silica, or carbon monoxide by the silicates in glass, less conviction may be felt about the correctness of this point of view, but the vast literature relating to coordination compounds shows how varied the possible types of linkage are.

If adsorption really takes place in this way, the surface must become saturated as soon as it is covered with a single layer of molecules of the adsorbed gas; only in exceptional instances will the formation of a second layer be possible.

The unimolecular nature of the adsorbed layer was emphasized by Langmuir, and has been regarded as an essential part of the theory. The alternative view is that the adsorption film is 'atmospheric' in character with a high density of gas in immediate contact with the surface, thinning continuously with increasing distance until the normal density of the gas phase is reached.*

* For detailed discussion of adsorption theories see E. Hückel, *Adsorption und Kapillarkondensation*, Leipzig, 1928.

The whole trend of modern researches into the chemistry of interfaces has been in the direction of showing that molecules at the boundary of two phases have a definite orientation. Thin layers of the higher fatty acids upon water, for example, turn their carboxyl groups into the water and stand erect with methyl groups directed outwards. The orientation and properties of such boundary layers is largely governed by the presence of 'polar' groups, or groups which are the seat of a certain chemical unsaturation. Groups such as the hydroxyl or carbonyl radical are typical polar groups.

Molecules in adsorbed layers have also a definite orientation. If a complete layer is formed over a surface, with those groups possessing the greatest attraction for the surface turned inward, we have virtually a new surface with properties determined by the nature of the groups which are directed outwards. There seems to be no very good reason why this, in certain cases, should not adsorb a second layer of molecules. Indeed, the assumption that this double-layer adsorption occurs has occasionally been found helpful. But there is a large difference between this extension of the single-layer theory and the 'atmospheric' theory.

The theory of the unimolecular layer has two supports. First, it is a natural consequence of the view that definite chemical linkages unite adsorbed molecules to surfaces, for then saturation is obviously reached when the single layer is complete. Secondly, a certain amount of direct experimental evidence has been brought forward in its favour. The general theoretical argument must be acknowledged to be strong, and the result not only to be free from the vagueness of the alternative suppositions but also to be an excellent compromise between the intermediate compound theory and the theory of a purely 'physical' adsorption.

Definite agreement, however, about the validity of the direct experimental evidence is hardly reached.

Langmuir* made measurements on the amounts of gas adsorbed at very low pressures by means of direct readings with a McLeod gauge, and came to the conclusion that saturation was reached with the completion of a unimolecular layer.

Carver † measured the amount of toluene vapour adsorbed by glass and arrived at the same conclusion.

Other observers have found results in disagreement with the theory. An example is to be found in the work of Evans and George ‡ on adsorption by glass wool.

The measurements are, however, always difficult to interpret with certainty, since the true area of the adsorbing surface, which determines the number of molecules of the adsorbent actually exposed to the gas, is represented at best roughly by the apparent area, and often bears no relation to it. This is especially marked in the case of non-crystalline materials such as glass.

Perhaps the most convincing series of measurements are those of Paneth and Vorwerk,§ made, however, with solutions. The true molecular surface of a specimen of lead sulphate powder was determined by the radio-active indicator method, and this powder was then used as an adsorbent for dye-stuffs. The amount of dye removed from solution by the powder was determined colorimetrically. The results obtained by this method supported the theory of the single layer very well.

Although this theory must contain a great deal of truth, it is probably to be regarded as an ideal limiting case. The possibility of the following complications must always be borne in mind.

(i) Actual solution of the gas in the solid undoubtedly occurs in some cases.

This process may be a slow one compared with the

* *J. Amer. Chem. Soc.*, 1918, **40**, 1361. † Ibid., 1923, **45**, 63.
‡ *Proc. Roy. Soc.*, 1923, A, **103**, 190.
§ *Z. physikal. Chem.*, 1922, **101**, 445, 480.

simple surface adsorption,* but, even where solution equilibrium takes years to reach, there is always the possibility that solution to the depth of a few molecular layers of the solid takes place within quite a short time. Palladium, platinum, iron, and silica all become definitely permeable to hydrogen at high temperatures.

(ii) The adsorbing surface may not be homogeneous.

In non-crystalline substances like glass or vitreous silica the greatest variety of surface configuration is possible, including sponge-like structures with pores of different magnitudes. But even with metals and other crystalline solids the surface may be very far from possessing the uniform 'chequer-board'-like structure, to use Langmuir's phrase, of the ideal solid. The researches of Beilby, described in his book, *The Aggregation and Flow of Solids*,† have shown that the greatest complexities of surface structure may arise in metals. Surface films of a granular nature are often formed, and this irregularity may well descend to units of molecular magnitude.

H. S. Taylor‡ has laid great stress on this inhomogeneity of catalytic surfaces. He suggests that the atoms constituting a metallic surface can exist in different degrees of saturation, varying from that which would be characteristic of a perfect plane crystal face down to that of a single atom attached at one point only. This would lead one to suppose that adsorption occurs not uniformly over the surface but predominantly on certain 'active points' of the surface. We shall have evidence in favour of this view in a later section.

(iii) Different kinds of adsorption have sometimes been distinguished.§

The distinction is not very sharp, but is made on the following grounds. Adsorption of gases by inert materials

* Cf. Bangham and Burt, *Proc. Roy. Soc.*, 1924, A, **105**, 481.

† Macmillan, 1921. ‡ *Proc. Roy. Soc.*, 1925, A, **108**, 105.

§ Cf. Benton, *J. Amer. Chem. Soc.*, 1923, **45**, 887.

such as charcoal seems to be roughly proportional to the ease with which the gas can be liquefied. This suggests a condensation of a physical kind on the adsorbent, possibly by liquefaction in its pores. On the other hand, the adsorption of gases by metals such as platinum, nickel, and iron is highly specific. Not even approximate parallelism with condensibility is to be observed. If this distinction between the two kinds of adsorption is justified, which seems a little doubtful, it is the second kind—the so-called primary adsorption—which is evidently responsible for catalytic phenomena.

Our immediate object, however, is to discuss the kinetics of catalytic reactions, and for this purpose an exact knowledge of the mechanism of adsorption is not absolutely essential. All that is required is a knowledge of the relation between the amount of gas adsorbed on the solid and the pressure of the gas in the homogeneous phase. To obtain the equation expressing this relationship it is not necessary to make hypotheses concerning the nature of the forces acting, nor is it essential to have pronounced definitely upon the question of unimolecular or multimolecular layers, nor, for many purposes, to have decided whether the surface of the catalyst displays a homogeneous array of atoms or the highly complex structure with active points which Taylor believes to be probable.

It is, on the other hand, necessary to adopt one or other of the really fundamental alternatives, namely, whether there is a definite saturation limit to adsorption, or whether the adsorption goes on increasing indefinitely with increasing concentration in the gaseous phase. The simplest form of the first alternative is the unimolecular layer theory, the simplest form of the second the atmospheric theory. It might be thought that an experimental decision between these two possibilities could be made quite easily. The matter is, however, not quite simple, since slow solution effects and other complications are often superposed on

the true adsorption when the concentrations in the gas phase are high, and these make it very difficult to decide quite certainly whether or not a true saturation limit exists. On the whole, however, it seems to be clear that, apart from complicating factors, there is a real and definite limit, as the unimolecular layer theory would lead one to expect.

The theoretical treatment of the 'atmospheric' theory is very difficult, and an empirical equation has to be used for the relation between the amount of gas adsorbed and the pressure.

If x be the amount of gas adsorbed on the surface of the solid when the pressure is p, then

$$x = a \,.\, p^n,$$

where n is a fraction always less than unity and a is a constant.

This is the well-known Freundlich 'adsorption-isotherm '.* Both a and n are functions of temperature.

The value of n is frequently sufficiently small to make the curve bend round sharply from linearity. Both a and n must be found empirically from the experimental observations.

The figure shows the sort of curve which represents the usual adsorption isotherm.

Curve 1 is represented by $x = a \,.\, p^n$, where n is less than 1. There is no definite limit to the value of x, but the curve may be made to bend round as sharply as desired by taking sufficiently small values of n.

Curve 2 reaches a definite saturation limit. A simple equation representing this type of curve is derived in the next section.

If the range of experimental observation is confined to the region to the left of the line AB, almost any set of values, to whichever type of curve they really belong, can

* See Freundlich, *Kapillarchemie*, 2nd edition, Leipzig, 1922.

be expressed by the Freundlich equation, when an appropriate choice of the constants is made, and, even in the region to the right of AB, the complications to which reference has already been made make a choice between the two types of curve rather difficult. If the surface is not strictly uniform but possesses regions with varying adsorptive capacity—as may often be found when material of a granular nature is used—the determination of whether

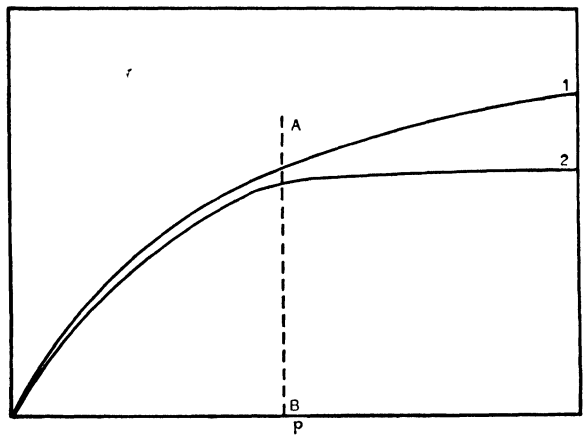


FIG. 6.

or not a definite saturation limit exists becomes specially difficult. The superposition of two curves, such as (*a*) and (*b*) below, each of which may tend to a definite limit, gives rise to (*c*) which apparently does not. (Fig. 7.)

Numerous examples of adsorption isotherms are to be found in Freundlich's *Kapillarchemie.*

Until it leads to definite inconsistency with facts, which does not seem likely, we shall therefore do well to adopt the theory of the definite saturation limit. We may also accept, with reservations, the view that it represents a unimolecular layer covering the active points of the catalyst. This theory has the following advantages : it is inherently probable, it leads to a simple relation between the amount adsorbed and the pressure, and the equation

expressing this relationship hardly differs in the numerical results it gives from the empirical equation of the alternative theory. We will now proceed to find this relation.

The equilibrium between the gas phase and the adsorbed layer according to the theory of the definite saturation limit.

The theory of this was worked out in a simple manner by Langmuir.*

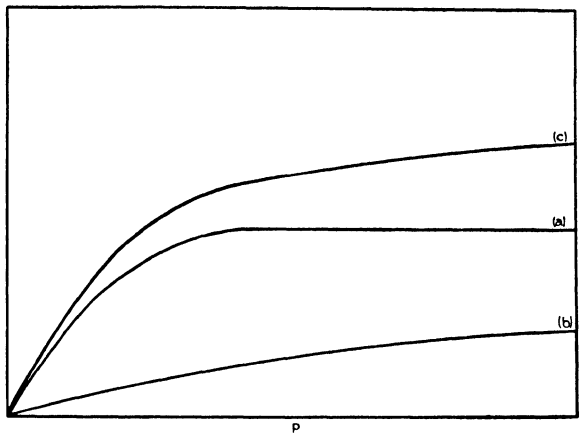


FIG. 7.

Let gas at pressure p be in equilibrium with unit area of the surface of a solid.

Let σ be the fraction of the surface covered with adsorbed gas. Then $(1 - \sigma)$ is the fraction left uncovered. In view of the possibility that the surface is not homogeneous and that adsorption only occurs on active centres, 'fraction of surface covered' must be understood to mean the fraction of the available surface which is actually covered. Thus, from the point of view of adsorption, the surface might be 'covered' when certain patches only were completely occupied by adsorbed molecules, and the rest of the surface might be incapable of taking up gas at any pressure.

Equilibrium is established when the rate of condensa-

* *J. Amer. Chem. Soc.*, 1916, **38**, 2221.

tion of gas on to the surface is equal to the rate of evaporation from the surface.

At constant temperature we have

$$\text{rate of condensation} = k_1 \cdot p(1-\sigma),$$

where k_1 is a constant, since the absolute rate of condensation is proportional to the number of impacts per second on the uncovered part of the available surface, and this number is proportional to the pressure of the gas and to $(1-\sigma)$.

For the opposing process we have

$$\text{rate of evaporation} = k_2 \cdot \sigma,$$

where k_2 is constant, since the rate of evaporation depends only on the amount of gas on the surface.

For equilibrium, therefore,

$$k_1 \cdot p(1-\sigma) = k_2 \cdot \sigma,$$

$$\sigma = \frac{k_1 \cdot p}{k_2 + k_1 p}.$$

This expression involves two constants which must be determined from experimental data.

Two important special cases.

In two limiting cases, which occur frequently in practice, this equation reduces to a simple form involving one constant only.

(1) *Surface only sparsely covered with adsorbed molecules.*

When the adsorption is slight the equation

$$k_1 p(1-\sigma) = k_2 \cdot \sigma$$

reduces to

$$k_1 p = k_2 \cdot \sigma,$$

since, when σ is very small, $(1-\sigma)$ is approximately equal to 1.

Thus

$$\sigma = \frac{k_1}{k_2} \cdot p.$$

When, therefore, the adsorption is small the amount of gas adsorbed is directly proportional to the pressure.

(2) *Surface nearly saturated.*

The equation $k_1 p(1-\sigma) = k_2 . \sigma$

now reduces to $k_1 p(1-\sigma) = k_2$,

since when σ is nearly equal to unity the variations in σ itself are negligible compared with the corresponding variations in $(1-\sigma)$.

Thus $$(1-\sigma) = \frac{k_2}{k_1} \times \frac{1}{p}.$$

When, therefore, the adsorption is large and the surface is nearly saturated we have the important result that the amount of free surface remaining is inversely proportional to the pressure of the gas.

These two propositions will find frequent application when we come to the discussion of the kinetics of catalytic reactions.

The simple formulae we have just derived, although sufficiently accurate for most practical purposes, sometimes fail to represent the facts completely. Examples are known where the adsorption isotherm is linear over a considerable range of concentration in the continuous phase and then bends sharply round at the saturation value. In general, however, the simple formulae are applicable.

KINETICS OF HETEROGENEOUS REACTIONS

A. One Reacting Gas: the reaction is unretarded by the products.

It has to be realized that the seat of the reaction is the adsorbed layer and that, except in so far as its acts as a reservoir which regulates the concentration of the molecules in this layer, the gas phase is completely outside the reaction.

The law of mass action holds in its ordinary form for heterogeneous reactions, but the 'active mass' is no longer the simple concentration of the gas in the homo-

geneous phase. The amount of gas adsorbed, and therefore in a position to react, is the real active mass.

Kinetically the reaction equations assume the simplest form in the extreme cases of very small adsorption on the one hand and almost complete saturation on the other.

When the adsorption is small the amount of gas adsorbed is directly proportional to the pressure. If the change taking place in contact with the surface involves one molecule only of the gas, that is if it is a truly unimolecular change, we have simply that the rate of change is directly proportional to the number of adsorbed molecules and, therefore, directly proportional to the pressure of the reacting gas. If, then, p is the pressure at time t of the gas undergoing chemical transformation, the reaction proceeds in accordance with the equation

$$-dp/dt = k \,.\, p.$$

The ordinary unimolecular law is thus obeyed.

Many examples of this type of reaction are known ; the decomposition of arsine;* the decomposition of phosphine on surfaces of glass,† porcelain,‡ silica;§ the decomposition of formic acid vapour on a variety of different surfaces—glass, platinum, rhodium, titanium oxide, and others;‖ the decomposition of nitrous oxide on the surface of gold;¶ the decomposition of sulphuryl chloride on the surface of glass;** the decomposition of hydrogen iodide on the surface of platinum;†† the decomposition of hydrogen selenide on the surface of selenium.‡‡ A general discussion

* van't Hoff, *Études de Dynamique chimique*, p. 83.
† van't Hoff and Kooij, *Z. physikal. Chem.*, 1893, **12**, 155.
‡ Trautz and Bhandarkar, *Z. Anorg. Chem.*, 1919, **106**, 95.
§ Hinshelwood and Topley, *J. Chem. Soc.*, 1924, **125**, 393.
‖ Ibid., 1923, **123**, 1014.
¶ Hinshelwood and Prichard, *Proc. Roy. Soc.*, 1925, A, **108**, 211.
** The same, *J. Chem. Soc.*, 1923, **123**, 2725.
†† Hinshelwood and Burk, *J. Chem. Soc.*, 1925, **127**, 2896.
‡‡ Bodenstein, *Z. physikal. Chem.*, 1899, **29**, 429.

of reactions of this type is given by Bodenstein and Fink.* All those which have just been enumerated proceed in accordance with the unimolecular law.

As an example we may quote some figures relating to the decomposition of nitrous oxide on gold at 900° C.

Time in minutes	Per cent. decomposed	$1/t \cdot \log \frac{100}{(100-x)}$
t	x	(t in seconds)
15	16·5	0·000201
30	32	0·000215
53	50	0·000218
65	57	0·000217
80	65	0·000219
100	73	0·000218
120	78	0·000210

In the experiment from which these figures are taken the time required for the decomposition of half the nitrous oxide was 53 minutes, the initial pressure being 200 mm. When the initial pressure was 400 mm. the time of half-change at the same temperature was found to be 52 minutes, showing in another and more conclusive way the unimolecular character of the reaction equation.

If the adsorption is small, and the reaction depends upon an essentially bimolecular process among the adsorbed molecules, for example $2A \rightarrow A_2$ or $2A \rightarrow B + C$, then, since the chance that two molecules occupy adjacent positions on the surface depends upon the square of the surface concentration, the rate of reaction is proportional to the square of the gas pressure, and the reaction is kinetically bimolecular.

Examples of this particular case are uncommon. As we have already seen, the decomposition of nitrous oxide, which is bimolecular in the homogeneous phase, becomes unimolecular on the surface of gold—and also of platinum. Langmuir,† however, finds that the combination of hydro-

* *Z. physikal. Chem.*, 1907, **60**, 46.

† *J. Amer. Chem. Soc.*, 1916, **38**, 1145.

gen atoms to the molecular form is probably a bimolecular reaction at the surface of tungsten. The decomposition of nitric oxide at the surface of platinum* and that of acetaldehyde † at various metal surfaces probably involve two molecules of the reacting gases; but kinetically the reactions are not simple changes of the second order.

When the adsorption is great, and the surface is satu-

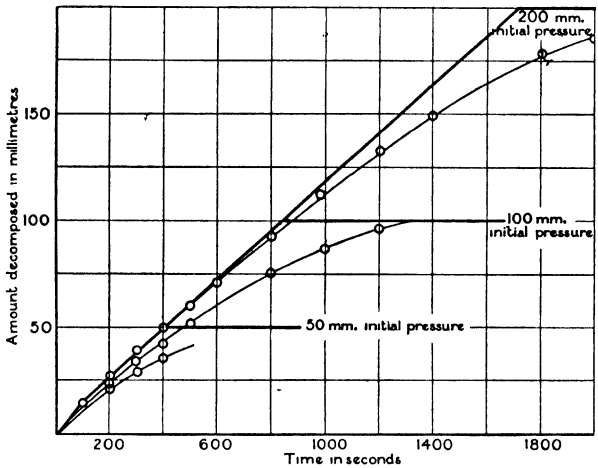


FIG. 8.—Rate of decomposition of ammonia on a tungsten wire at 856°, showing approach to theoretical behaviour of a reaction of zero order. The lines on which no experimental points are marked represent the ideal zero-order change. The 'half-life' periods at 50, 100, and 200 mm. initial pressure are in the ratio 1 : 1·92 : 3·52. In the ideal case this would be 1 : 2·0 : 4·0. In a unimolecular change all would be equal.

rated or nearly saturated, considerable amounts of gas may be removed by chemical change without the amount in the adsorbed layer suffering appreciable diminution, since that which reacts and leaves the surface is at once replaced from the gas phase. Thus there is a constant rate of reaction in spite of diminishing concentration in the gas phase, and the reaction appears to be of 'zero order'. When the pressure is sufficiently reduced, however, a point must come when the surface is no longer saturated, and the

* Bachmann and G. B. Taylor, *J. physical Chem.*, 1929, **33**, 447.

† *Proc. Roy. Soc.*, 1928, A, **121**, 141.

zero-order reaction passes into one of the unimolecular type.

In solutions this type of reaction is common with enzymes ; it is also frequently found in the catalytic hydrogenation of liquids. An example of a nearly zero-order gas reaction is to be found in the catalytic decomposition of ammonia on the surface of tungsten,* and also on the surface of molybdenum.† Thus at 856° C., with 200 mm. of ammonia in contact with a heated tungsten wire, 59 mm. were decomposed in 500 seconds, while in 1,000 seconds 112 mm. were decomposed. The falling off from linearity is but slight. This is illustrated by the accompanying figure, where the thicker lines represent the theoretical curves for a reaction of zero-order.

Another example of a reaction nearly independent of pressure in this way is the catalytic decomposition of hydrogen iodide on the surface of a heated gold wire.‡ The initial pressure of the gas can be varied from 100 mm. to 400 mm. with a resulting change in the absolute rate of reaction which amounts to about 45 % only instead of 400 %.

Intermediate cases are found where the main part of the reaction takes place while the adsorption varies along the portion XY of the adsorption isotherm (Fig. 9).

Two arbitrary constants are now needed. The rate of reaction varies in proportion to the fraction of surface covered, and therefore to $\frac{k_1 p}{k_2 + k_1 p}$. We have, therefore,

$$-dp/dt = k \,.\, p/(1 + bp).$$

According to this the rate increases less rapidly than in direct proportion to the pressure, and therefore it is possible to use as an approximation the equation

$$-\frac{dp}{dt} = kp^n,$$

* Hinshelwood and Burk, *J. Chem. Soc.*, 1925, **127**, 1116.

† Burk, *Proc. Nat. Acad. Sci.*, 1927, **13**, 67; Kunsman, *J. Amer. Chem. Soc.*, 1928, **50**, 2100.

‡ *J. Chem. Soc.*, 1925, **127**, 1552.

n being an appropriately chosen fractional number. Each of the equations has two disposable constants, and therefore they may be almost indistinguishable within the limits of experimental error.

The second is the form of equation which Stock and Bodenstein* found to express the rate of decomposition of antimony hydride at 25° C. The value used for n was 0·6.

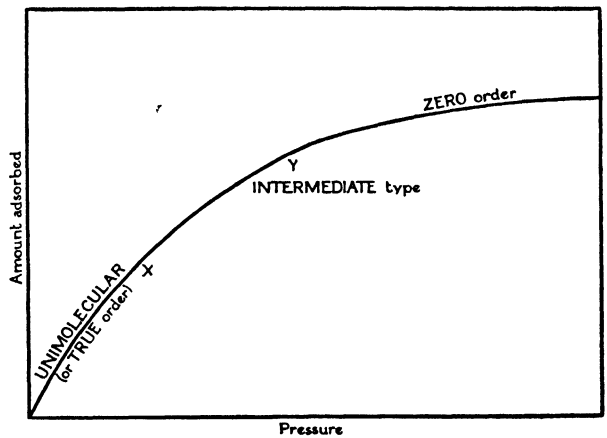


FIG. 9.

The reaction took place on an extended surface of metallic antimony. The following results are taken from the paper:

Time in minutes	p	k
0	1·000	
1	0·940	0·062
2	0·884	0·059
3	0·830	0·060
4	0·779	0·058
5	0·731	0·057
6	0·683	0·059
7	0·637	0·059
8	0·592	0·060
9	0·549	0·061
10	0·509	0·058
11	0·467	0·065
12	0·428	0·062
13	0·392	0·062

* *Ber.*, 1907, **40**, 570.

Time in minutes	p	k
14	0·359	0·064
15	0·327	0·057
16	0·295	0·060
17	0·266	0·062
18	0·238	0·064
19	0·212	0·064
20	0·189	0·060
21	0·166	0·065
22	0·144	0·067
23	0·123	0·069
24	0·108	0·056
25	0·093	0·059
26	0·080	0·057

The pressures are expressed as fractions of the initial pressure.

Integrating the equation $-dp/dt = kp^n$ we obtain the result

$$k = \frac{1}{(1-n)(t_2 - t_1)} \cdot \{p_1^{1-n} - p_2^{1-n}\}.$$

The values of k are calculated from each value of p and the one following.

The hydrides of phosphorus, arsenic, and antimony thus form an interesting transition series. On similar sorts of surface antimony hydride is the least stable, decomposing with measurable speed at ordinary temperatures, and phosphine is the most stable, not decomposing at an appreciable rate below a red heat. Arsine occupies an intermediate position. At low temperatures the adsorption is considerable, and, as a result, the stibine decomposition requires the p^n equation, while the more stable hydrides, which only decompose rapidly at higher temperatures where the adsorption is smaller, obey the unimolecular law. It is interesting, moreover, that with stibine itself the exponent n increases towards unity as the temperature at which the reaction takes place is raised.

When the surface is almost completely covered there is no distinction kinetically between processes which involve

one molecule only of the reacting gas and those which involve two. Thus the changes $A \rightarrow B + C$, and $2A \rightarrow B + C$ would both be of zero order and indistinguishable.

Retardation of the Reaction by its Products.

If any of the products of the reaction are themselves adsorbed strongly enough to occupy an appreciable fraction of the surface, less space becomes available for the reacting molecules, and the rate of transformation is proportionately diminished. There is now a competition, for places on the surface of the solid, between the molecules of the reactant and those of the product. In the general case this leads to a rather complicated equation for the progress of the reaction.

Let σ be the fraction of the active surface which is covered with molecules of the reactant when the pressure of this is p, and let σ' be the fraction covered with molecules of the adsorbed product when the pressure of this is p'.

Then, for the fraction of surface left free from adsorbed molecules we have $(1 - \sigma - \sigma')$, and, equating for each gas the rate of condensation on the uncovered surface and the rate of evaporation from that part of the surface which it occupies, we have for the adsorption equilibria

$$k_1 p\,(1 - \sigma - \sigma') = k_2 \sigma \text{ and } k_1' p'\,(1 - \sigma - \sigma') = k_2' \sigma'.$$

The rate of reaction is proportional to the number of molecules of reactant on the surface and therefore to σ, but to express σ in terms of the pressures four arbitrary constants are needed.

We shall therefore consider in detail the simpler case where the adsorption of the reacting gas itself is small, that is to say, when it has very little influence on the adsorption of the product, and its molecules only occupy a small fraction even of such space as the molecules of the product leave for it.

Under these conditions

$$\sigma' = \frac{k_1' p'}{k_2' + k_1' p'}$$

and therefore $$1 - \sigma' = \frac{k_2'}{k_2' + k_1' p'}.$$

The rate of reaction is then given by the product of this free surface and the specific reaction rate per unit free surface, which is proportional to the pressure of the reactant.

Thus $$-\frac{dp}{dt} = k(1 - \sigma')p.$$

Therefore $$-\frac{dp}{dt} = \frac{k \cdot k_2' \cdot p}{k_2' + k_1' p'}.$$

If a is the original amount of the reactant and x the amount transformed at time t, then p is proportional to $(a - x)$ and p' is proportional to x.

The equation for the rate of reaction then becomes

$$\frac{dx}{dt} = \frac{k(a - x)}{1 + bx},$$

where k and b are new constants.

An example of a change satisfying this equation very closely is to be found in the catalytic decomposition of nitrous oxide on the surface of platinum.* This reaction is retarded by the oxygen produced in the change itself, and its rate is expressed by the equation

$$-\frac{d[N_2O]}{dt} = \frac{k[N_2O]}{1 + b[O_2]}$$

where $$[N_2O] = a - x, \ [O_2] = x.$$

The integrated form of this is

$$k = \frac{1 + ab}{t} \cdot \log \frac{a}{a - x} - \frac{bx}{t}.$$

The applicability of this expression may be tested as follows. If we write $1/t \log \frac{a}{a - x} = k_m$ and $x/t = v$, then it

* *J. Chem. Soc.*, 1925, **127**, 327.

will be seen that k_m should be a linear function of v, and the linearity of this relation is a characteristic test of the form of the equation not influenced by the choice of the actual value of the constants, which only determines the slope of the line and its intercepts on the axes. Since

$$v = (a + 1/b)\, k_m - k/b$$

the slope of the line will be $a + 1/b$ and the intercept on the v axis will be $-k/b$. The following experiment is an illustration of the use of the method :

Temperature 741° C. $a = 95$

x	t	v	k_m	$v + 0{\cdot}0135$	$(v + 0{\cdot}0135)/k_m = a + 1/b$
10	315	0·0318	0·000353	0·0453	129·8
20	750	0·0267	0·000315	0·0402	127·8
30	1400	0·0214	0·000271	0·0349	128·6
40	2250	0·0178	0·000243	0·0313	128·8
50	3450	0·0145	0·000216	0·0280	129·5
60	5150	0·0116	0·000194	0·0251	128·9

0·0135 is the intercept on the line $k_m = 0$.

The linearity of the relation between k_m and v is shown by the constancy of the slope as recorded in the last column.

When the adsorption of the retarding gas is so strong that the limiting law holds, namely the free space is inversely proportional to the pressure, the reaction velocity equation assumes a still simpler form. The rate of change is now directly proportional to the pressure of the reactant and inversely proportional to that of the product.

Thus $$\frac{dx}{dt} = \frac{k(a-x)}{x}.$$

This limiting case is almost realized in the decomposition of ammonia on the surface of a heated platinum wire,* in the region of 1,000° C. In the first few instants the reaction velocity appears to be extremely high, but falls off as soon as the smallest traces of hydrogen make their appearance ;

* *J. Chem. Soc.*, 1925, **127**, 1114.

the surface seems to become almost saturated with hydrogen at quite low pressures. Thereafter the reaction proceeds at a rate which is inversely proportional to the pressure of hydrogen. The following figures taken from the results of experiments in which varying amounts of hydrogen were added initially to the ammonia illustrate this inverse relationship.

Temperature 1,138° C. Initial pressure of ammonia 100 mm. of mercury

Amount of ammonia decomposed in 120 seconds	Pressure of hydrogen added initially
33	50
27	75
16	100
10	150

The equation expressing the retarding action of the products is not always of such a simple form. While the decomposition of ammonia on platinum is well enough represented by the simple equation

$$-\frac{d[NH_3]}{dt} = \frac{k[NH_3]}{[H_2]},$$

Bodenstein and Kranendieck* found that the decomposition on the surface of quartz glass was retarded by hydrogen according to a much more complicated law.

In the equation

$$\frac{dx}{dt} = \frac{k(a-x)}{1+bx}$$

the factor $1/(1+bx)$, which represents the retarding effect, reduces as we have seen to $1/bx$ for large values of b and becomes equal to unity naturally when b vanishes. For intermediate conditions it may be represented approximately by an inverse fractional power of x. This is the origin of the relation sometimes found empirically that the retarding effect of a gas on a reaction is proportional to the square root of its pressure. No significance is to be

* *Nernst-Festschrift*, 1912, p. 99.

attached to the square root. It means simply a fractional power in the neighbourhood of 0·5.

The complexity of the catalytic surface sometimes reveals itself in experiments on the retarding action of gases. Burk,* for example, finds that the rate of decomposition of ammonia on molybdenum, although strongly retarded by nitrogen, does not approach zero as the surface becomes saturated with nitrogen. This shows that there must be certain parts of the active surface which the nitrogen cannot poison, or else that the nitrogen film itself has a certain catalytic activity. Schwab † finds the rate of decomposition of ammonia on platinum, at lower pressures, to be retarded by nitrogen as well as by hydrogen, while, at higher pressures, Hinshelwood and Burk found no retardation. It is evidently unwise therefore to extrapolate measurements much beyond the range of pressure in which the observations are made. At low pressures the most active centres of the surface may be those principally concerned ; at higher pressures quite other centres may be the most important, the more active ones being already poisoned, while the less active ones have resisted poisoning.

The 'Order' of Heterogeneous Reactions.

A gaseous reaction of zero order is one in which the absolute rate of change is independent of the pressure of the reacting gas. A reaction of the first order is one in which the rate is proportional to the pressure, or in which the *fraction* of the total which is transformed in a given time is independent of the concentration.

The time required for the transformation of half the total amount of substance is one of the most useful criteria. In reactions of zero order it is directly proportional to the initial pressure, in reactions of the first order

* *Proc. Nat. Acad. Sci.*, 1927, **13**, 67.
† *Z. physikal. Chem.*, 1927, **128**, 161.

independent of the initial pressure, and in reactions of the nth order inversely proportional to the $(n-1)^{th}$ power of it.

We adopt this kinetic definition of reaction order without reference to the actual number of molecules involved in each act of chemical transformation. In homogeneous reactions the kinetically determined order is equal to the number of molecules participating in the actual change of which the rate is being measured. In heterogeneous reactions this equality is not necessarily preserved. It will be convenient to call the order inferred from the effect of pressure on the time of half-change the *apparent order*, and to refer to the number of molecules involved as the *true order* of the reaction. We have now to consider the relation of the true and the apparent order in various cases.*

First, when the reaction is unretarded by the products there are two extreme cases. If the adsorption is small the true and apparent orders are equal. We consider still the case of one reacting gas.

The chance that n molecules shall occupy positions on the surface sufficiently close to render interaction possible depends on the nth power of the surface concentration, and this in its turn depends on the nth power of the pressure.

If, on the other hand, the surface is completely covered, the apparent order is zero, whatever the true order may be, since the number of groups of n molecules cannot change with pressure so long as the surface remains covered.

In intermediate cases the apparent order is between zero and the true order, but this value itself varies with the pressure. Moreover, it should change considerably with temperature. If, therefore, a value for the reaction order is found which does not decrease towards zero as the pressure increases, and which, moreover, does not vary with temperature, it may be taken as the true order.

* For a recent and very full summary of the possible cases, see Schwab and Pietsch, *Z. physikal. Chem.*, 1928, B, **1**, 385.

Secondly, with retarded reactions further complications arise. We will consider the case where the products of reaction are so strongly adsorbed that the free surface is inversely proportional to their pressure.

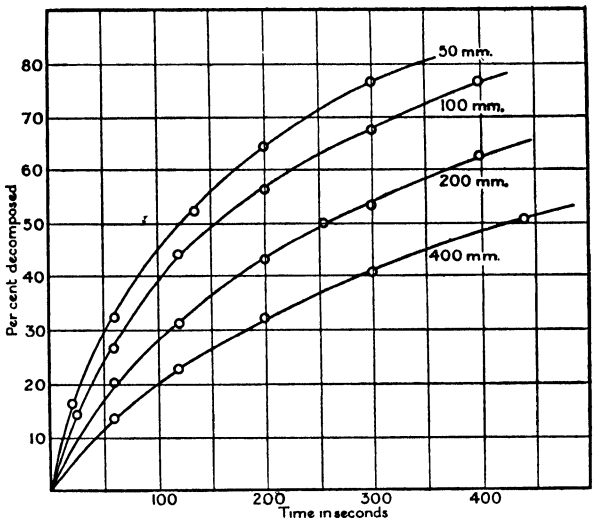


FIG. 10.—Influence of initial pressure on catalytic decomposition of nitrous oxide.

Let the true order of the reaction be the first. Then the velocity equation assumes the form

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

Integrating

$$kt = a \log a - a \log (a-x) - x.$$

If τ is the time of half-change, we find by putting $x = 1/2a$,

$$\tau = \frac{1}{k}(a \log 2 - a/2).$$

This shows that the half-life increases in direct proportion to the initial pressure. This would indicate an apparent reaction order of zero. Expressed loosely, the reaction appears to be faster at low pressures than at high pressures. This is illustrated by the curves in Fig. 10.

Again, if the true order of reaction is the second,

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

whence it is easily found that

$$\tau = \frac{1}{k}(1 - \log 2).$$

Thus the half-life is independent of the initial pressure. The apparent order is thus the first.

In general, then, the effect of a strong retarding action by the products of reaction is to reduce the apparent order of the reaction to one below the true order.

From the foregoing discussion it will be seen that some circumspection is necessary in inferring the true order of a heterogeneous reaction from the influence of pressure, but that when all the circumstances are taken into account this order can usually be found. There is no evidence that reaction products can ever exert a retarding action proportional to a higher power of their pressure than the first, nor is there any theoretical ground why they should possibly be able to do so. Hence, when we find a reaction, such as the decomposition of nitrous oxide, proceeding relatively faster at lower pressures, it is quite certain that the true order cannot be higher than the first.

The decomposition of nitric oxide at the surface of a hot platinum wire was found by Hinshelwood and Green* to be apparently of the first order, from experiments on variation of the initial pressure. Retardation by oxygen was observed, but was not at first considered marked enough to have reduced the order from two to one. Further investigation by Bachmann and Taylor† shows that the oxygen retardation is very considerable; and that therefore we have here an example of the reduction of the true order two to an apparent order of one.

* *J. Chem. Soc.*, 1926, 1709.

† *J. Physical Chem.*, 1929, **33**, 447.

The now discarded diffusion theory o heterogeneous reactions leads to slightly different results respecting the relation of the true order and the apparent order. These will be indicated in a later section.

B. Two Reacting Gases.

Reactions which are unretarded by the products will first be considered. When the adsorption of all the reacting gases is small, the numbers of molecules of each which are present on the surface of the catalyst at any moment are proportional to the respective pressures. The reaction occurring on the surface will therefore follow the same kinetic equation as that which would be followed if the identical reaction took place homogeneously.

As an example of this we may take a heterogeneous reaction between two molecules of A and one of B. The surface being but sparsely covered with A and B the chance that two molecules of A and one of B occupy positions sufficiently near together for them to be able to interact depends upon the square of the number of A molecules and upon the number of B molecules. Since these in turn depend upon the pressures we have

$$\frac{dx}{dt} = k[A]^2[B].$$

Similarly the catalytic combination of ethylene and hydrogen in the presence of metallic copper is approximately bimolecular between 150° and 250° C.*

As soon, however, as one or other of the reacting gases is rather strongly adsorbed, the reaction kinetics become much more complicated. In the combination of ethylene and hydrogen on copper Pease† found that at 0° and 20° C. the simple bimolecular course is no longer followed. The

* Grassi, *Nuovo Cimento*, 1916, [6], **11**, 147. Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 2235.

† Pease, *J. Amer. Chem. Soc.*, 1923, **45**, 1196.

velocity still increases more or less in proportion to the hydrogen concentration, but actually decreases with increase in the concentration of ethylene. This means that the ethylene, at these lower temperatures, nearly saturates the surface, so that further increase in its pressure cannot appreciably augment the number of molecules adsorbed, but may, and does, lead to an actual displacement of the less strongly adsorbed hydrogen.

Langmuir's investigation of the interaction of hydrogen and oxygen on the surface of heated platinum wires* may be taken as a further example. Over a certain range of temperature the velocity of reaction on the platinum surface is proportional to the pressure of oxygen but inversely proportional to the pressure of hydrogen. This proves that the hydrogen is preferentially adsorbed, and may displace the oxygen.

These principles will now be exemplified by the discussion of some typical reactions.

(*a*) *The interaction of carbon monoxide and oxygen.*

The progress of this reaction on the surface of quartz was studied by Bodenstein and Ohlmer.† The velocity was found to vary in direct proportion to the pressure of oxygen, and in inverse proportion to the pressure of the carbon monoxide itself.

The interpretation of this result seems to be as follows. Carbon monoxide is strongly adsorbed. Therefore the amount of space left uncovered on the catalyst is inversely proportional to its pressure.

Oxygen is but slightly adsorbed. Therefore the rate of reaction is proportional to the pressure of oxygen. It is further evident that for interaction to occur it is not sufficient for an oxygen molecule merely to strike an adsorbed molecule of the monoxide, for this would simply make the

* *Trans. Faraday Soc.*, 1922, **17**, 621.

† *Z. physikal. Chem.*, 1905, **53**, 166.

rate of reaction independent of the carbon monoxide concentration, but it must itself become adsorbed on that part of the surface which is free. This assumption makes the rate proportional to the extent of the free surface as well as to the oxygen pressure. The supply of carbon monoxide molecules on the surface is so large that nearly all the oxygen molecules which take up their abode on the catalyst find a molecule of carbon monoxide adjacent to them. The only effect of the pressure of the monoxide is therefore in determining the free space. The rate of reaction is thus proportional to $[O_2]/[CO]$.

These inverse proportionality relationships, which are quite common, are very important in showing that, in some instances at least, adsorption of both reacting substances on the surface of the catalyst itself is necessary. *A* must not merely strike adsorbed *B*, but must be adsorbed adjacent to it. Otherwise excess of *B* could not actually retard the combination.

With a different quartz glass Benton and Williams * have found a different law, namely that the rate varies as $[O_2][CO]^{1/2}$. This illustrates the varying adsorptive properties of various kinds of quartz.

Langmuir † made experiments at low pressures on the combination of carbon monoxide and oxygen on the surface of platinum. Up to 700° abs. the rate of reaction was found to be directly proportional to the pressure of oxygen and inversely proportional to that of the carbon monoxide, just as in the experiments of Bodenstein and Ohlmer.

At temperatures between 750° and 1,050° abs., however, the adsorption of carbon monoxide being evidently much less, a simpler reaction took place. This proceeded with a velocity proportional to the pressure of oxygen when the carbon monoxide was in excess, and to the pressure of the carbon monoxide when the oxygen was in excess. At

* *J. Physical Chem.*, 1926, **30**, 1487.

† loc. cit.

these temperatures the two gases appear to compete for the surface of the platinum on more or less equal terms.

In the low temperature region interesting curves are obtained when the pressure of the reacting gases is plotted against time, the rate of diminution of pressure of course measuring the rate of reaction. They have the form shown in the figure.

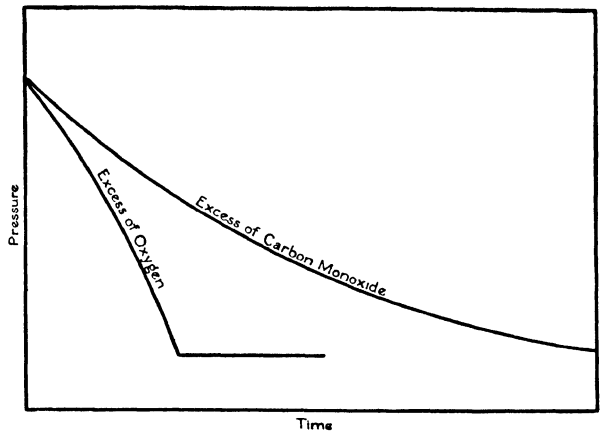


FIG. 11.

When oxygen is in excess the curve has a form indicating that the rate of reaction increases as the carbon monoxide is used up. The film of carbon monoxide remains practically complete until nearly all the supply in the gas phase is exhausted, and then the reaction comes to an abrupt end.

When carbon monoxide is in excess the film is never completely burnt off the platinum, and the rate of reaction falls off gradually as the oxygen is used up.

When more or less equivalent proportions are used the increase in rate due to the increasing number of gaps in the carbon monoxide film is almost exactly counterbalanced by the falling off in rate due to the diminishing pressure of oxygen, and nearly straight lines are found.

(*b*) *The interaction of hydrogen and oxygen.*

Langmuir,* investigating the interaction on the surface of platinum, found once more that the character of the reaction changed with temperature. Both in the low temperature region and in the high temperature region the results were analogous to those which he had found with carbon monoxide and oxygen. The hydrogen now plays a role analogous to that of the monoxide in the other reaction.

In contact with silver Benton and Elgin† find the rate to be proportional to the pressure of the hydrogen, and independent of that of the oxygen: it is reduced by the presence of steam. In contact with gold‡ the rate is directly proportional to the square of the hydrogen pressure and the first power of the oxygen pressure, and inversely proportional to the pressure of water vapour.

(*c*) *The interaction of nitrous oxide and hydrogen.*

On a platinum surface the hydrogen forms apparently an almost complete film, in the gaps of which the nitrous oxide reacts.§ The reaction, $N_2O + H_2 = N_2 + H_2O$, follows a course almost exactly analogous to that of the oxidation of carbon monoxide at low temperatures. Curves almost exactly similar to those already described in connexion with that reaction are obtained, the change coming to an abrupt end when the nitrous oxide is in excess, and reaching its end asymptotically when the hydrogen is in excess.

(*d*) *The combination of ethylene and hydrogen.*

Besides the investigations of Grassi and of Pease,|| with which we have already dealt, there are available some observations of Rideal,¶ who employed nickel as a catalyst. He found the rate of reaction

$$C_2H_4 + H_2 = C_2H_6$$

* loc. cit.

† *J. Amer. Chem. Soc.*, 1926, **48**, 3027. ‡ Ibid., 1927, **49**, 2426.

§ Hinshelwood, *Proc. Roy. Soc.*, 1924, A, **106**, 292.

|| loc. cit. ¶ *J. Chem. Soc.*, 1922, **121**, 309.

to vary in direct proportion to the pressure of hydrogen when ethylene was in excess, and in direct proportion to the pressure of ethylene when the hydrogen was in excess. Ethane had no influence on the rate of combination.

(*e*) *The interaction of hydrogen and carbon dioxide.*

The progress of the reaction

$$CO_2 + H_2 = CO + H_2O$$

on the surface of a heated platinum wire has been studied

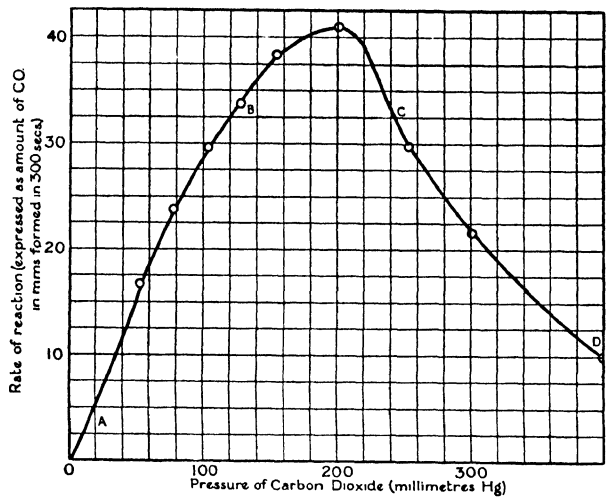


FIG. 12.—Influence of carbon dioxide pressure on the rate of the reaction $CO_2+H_2 \rightarrow CO+H_2O$ at 1,000° C. Pressure of hydrogen 100 mm.

by Hinshelwood and Prichard.* The measurements were made in the region of 1,000° C. The reaction was made irreversible by the continuous removal of the water formed. The rate of reaction was proportional to the pressure of hydrogen at least up to 300 mm. of mercury. It was proportional to the pressure of carbon dioxide for small pressures, and more or less inversely proportional to the pressure of the carbon dioxide at high pressures of this gas. This relationship is shown in the figure.

* *J. Chem. Soc.*, 1925, **127**, 806.

The low pressure part, *AB*, of the carbon dioxide curve corresponds to Rideal's observation of the influence of ethylene pressure on the rate of interaction of ethylene and hydrogen in presence of nickel, while the high pressure part, *CD*, corresponds to the results of Pease for the influence of the ethylene pressure on the combination in presence of copper. We have the initial increase due simply to the increasing number of molecules of carbon dioxide on the surface, followed by the passage through a maximum and subsequent decrease as the carbon dioxide displaces the hydrogen more and more.

The examples we have quoted illustrate nearly all the possible kinds of behaviour.

Reference should once more be made to the combination of ethylene and bromine on ordinary glass surfaces, where the rate of reaction was found by Stewart and Edlund * to be proportional to the concentration of the bromine vapour and of the ethylene. This would mean small adsorption of each gas.

It is hardly necessary to point out that all these various types of behaviour would be shown successively in the same reaction if the pressure of each of the reacting gases were varied from the highest to the lowest value. Every experimental study made under conditions circumscribed by the limitations of practical technique reveals only a fragment of the complete picture.

Retarded Reactions. The interaction of sulphur dioxide and oxygen.

As an example of a retarded reaction we may take the classical investigation of Bodenstein and Fink † on the reaction

$$2\,SO_2 + O_2 = 2\,SO_3.$$

* *J. Amer. Chem. Soc.*, 1923, **45**, 1014.

† *Z. physikal. Chem.*, 1907, **60**, 1.

When it takes place in contact with platinum this reaction is retarded by the sulphur trioxide which is formed.

The rate of reaction is proportional to the quantity (amount of SO_2 adsorbed) × (amount of O_2 adsorbed).

The exact equation expressing this as a function of the various concentrations is very complicated, since the sulphur trioxide displaces both of the other gases to a greater or smaller extent.

In practice the rate of reaction is found to be sufficiently well represented by the equations

$$\frac{d[SO_3]}{dt} = \frac{k[O_2]}{[SO_3]^{1/2}}$$

when sulphur dioxide is in excess, and

$$\frac{d[SO_3]}{dt} = \frac{k[SO_2]}{[SO_3]^{1/2}}$$

when oxygen is in excess.

The term $\frac{1}{[SO_3]^{1/2}}$ is an empirical expression proportional to the amount of surface left free when the concentration of the sulphur trioxide in the gas phase is $[SO_3]$.

The Diffusion Theory of Heterogeneous Reactions.

One of the most striking features about heterogeneous reactions is the frequency with which the change is retarded either by the products of the reaction or by one of the reacting substances when it is present in excess. Before the development of the current method of regarding these phenomena, an interpretation of a rather different kind was placed upon them.

It was supposed that the actual rate of reaction at the surface of the catalyst was great compared with the rate at which the reacting substances could diffuse through a continuous layer of the retarding gas.

This theory was a development of Nernst's diffusion theory of reactions taking place between substances in different phases, but it is by no means inseparably connected with this. It was employed and developed by Bodenstein, and can usually be made to account more or less satisfactorily for the influence of the various concentrations on the rate of reaction.

One illustration will suffice. The equation

$$\frac{d[SO_3]}{dt} = \frac{k[SO_2]}{[SO_3]^{1/2}},$$

representing the reaction between sulphur dioxide and excess of oxygen on the surface of platinum, can be derived by assuming the platinum to be covered with a continuous layer of sulphur trioxide, the thickness being proportional to the square root of the pressure. Through this layer the molecules of sulphur dioxide and of oxygen must thread their way up to the surface of the catalyst. When oxygen is in excess in the gas phase, there will always be a plentiful supply of it in contact with the platinum, and every molecule of sulphur dioxide which arrives there will be able to react at once. The observed rate of reaction is therefore determined simply by the rate at which molecules of sulphur dioxide diffuse through the sulphur trioxide film. In accordance with the well-known law of diffusion, this rate is proportional to the concentration gradient in the film, which is expressed by

$$\frac{\text{concentration in the gas phase} - \text{concentration at the surface}}{\text{thickness of film}}.$$

Since the reaction at the surface is assumed to be very rapid, the concentration here is maintained at zero. The rate of combination is thus proportional to

$$\frac{k[SO_2]}{[SO_3]^{1/2}}.$$

In those reactions where the rate is inversely propor-

tional to some function of the pressure of one of the reacting substances it becomes necessary to assume that a film of this substance covers the surface, and that the other reactants have to diffuse through it. The interaction must be supposed only to accomplish itself at the actual surface of the catalyst.

Explanations may be devised with the aid of this theory almost as well as with the aid of the rival theory. Simple unretarded reactions demand, it is true, rather forced hypotheses about diffusion into the catalyst, or about the existence of permanent skins of foreign gas on the surface, but the real evidence against the diffusion theory is of a more general character.

One of the most important of the arguments against it is a quantitative one.* To account for the extreme slowness of some reactions it would be necessary to suppose the existence of retarding layers of such thickness that they would be of visible dimensions.

Between the highest and the lowest temperatures at which measurement is practicable the variation of reaction rate is many thousandfold. If the diffusion theory is applicable at all, the layer through which the reacting molecules have to pass cannot very well be less than a single molecule in thickness, even at the highest temperature, for a very simple calculation shows that the rate at which molecules of the reactant could come into contact with the bare surface is many times greater in most instances than the fastest measurable rate of reaction. At the lowest temperatures, then, the diffusion layer would have to be many thousands of molecules in thickness. This is easily shown to be a quite inadmissible supposition. No such difficulty is encountered when the variation in the observed reaction rate is attributed to the specific effect of temperature on the actual chemical transformation at the surface of the catalyst, to the uncovered portions of

* Cf. Langmuir, loc. cit., *supra*.

which the molecules of reactant are supposed to have free access.

Rate of diffusion varies as the square root of the absolute temperature. Heterogeneous reactions have the high temperature coefficients characteristic of all chemical changes. If, therefore, the simple diffusion theory is adopted, there is no alternative but to suppose that the thickness of the retarding layer changes rapidly with temperature. The objections to such a supposition have been indicated. To meet these it might be suggested that only those molecules can reach the surface of the catalyst and react, the kinetic energy of which is sufficient to enable them to penetrate a permanent adsorbed layer of some kind, this process being rather different from ordinary diffusion, where all the molecules thread their way through the obstacle. This hypothesis, even if there were anything to be said for it on general grounds, which is open to question, would be ruled out by observations on the temperature coefficients of those reactions where a single molecule undergoes alternative transformations. According to the hypothesis the total reaction velocity should vary with temperature in accordance with the Arrhenius equation, whereas experiment shows that the velocities of the separate transformations vary independently, and each according to an equation of the Arrhenius form. The temperature coefficient of the total reaction velocity is thus a composite one. This is inconsistent with the assumption that the variation in rate is governed by a process common to both of the alternative reactions, namely the penetration of an impeding film by the molecule of the reactant.

It should perhaps be pointed out that if the diffusion theory were true, our previous conclusions about the relation between the true and apparent order of the reaction would have to be modified. In general the reaction rate would depend upon the first power of the concentration of

that reactant which happened to be in defect, or to have the lowest diffusion coefficient.

*The adsorption of mixtures of gases.**

This problem is obviously relevant to the subject, but not very much satisfactory information is available about it. It must therefore suffice here to indicate a matter of some theoretical importance.

If we assume a uniform homogeneous adsorbing surface, then, by writing down the equations for the rate of condensation and rate of evaporation of two gases which are simultaneously adsorbed, it may be shown that the relative amounts of each taken up by the adsorbent should be independent of the absolute pressure of the gases, and dependent only on the relative pressures of the two. Indications that this condition is not always fulfilled have been interpreted by assuming:

(1) that multimolecular layers are formed, in which a unimolecular film of one gas may itself hold molecules of a second gas;†

(2) that the surface of the adsorbent is not homogeneous. Further reference to this assumption will be necessary in the next chapter.

Reference should be made here to the work of Palmer,‡ who used the method of measuring the 'cohering' voltage between metallic filaments for investigating the nature of the gas films adsorbed by metals. The interpretation of the results depends upon certain assumptions, the validity of which is a little difficult to estimate, but the phenomena observed are of much interest. In particular, it is found that when a mixture of gases is admitted to the metal the initially formed film appears to differ somewhat in com-

* Cf. Hückel, *Adsorption*, p. 217.

† Cf. Hurst and Rideal, *J. Chem. Soc.*, 1924, **125**, 694.

‡ *Proc. Roy. Soc.*, 1924, A, **106**, 55; 1926, A, **110**, 133; 1929, A, **122**, 487.

position from that existing when equilibrium is established. The explanation is probably as follows: the gases first condense on the surface in proportion to the numbers of molecules of each striking it, i. e. in direct proportion to the partial pressures and the molecular velocities. The final equilibrium depends also on the rates of evaporation. If the gases are both strongly adsorbed, so that their rates of evaporation are small, the equilibrium may take a measurable time to be established.

It may be a similar phenomenon which is encountered when a gaseous reaction product formed *in situ* on a surface retards the reaction, while the same gas added from without has no retarding influence.

The Influence of Heterogeneous Catalysts on the Equilibrium Point in Reversible Reactions.

In heterogeneous reactions we frequently find relations between rate of reaction and concentration quite different from those which the law of mass action would indicate to be valid for a homogeneous system. It is a little difficult, at first sight, to see how, by equating the rates of the forward and reverse reactions, we are still to arrive at the correct equilibrium relations. The general problem is very complex, but one simple example may be given to illustrate the manner in which conflict with the second law of thermodynamics is avoided.

Let the reaction $AB \rightleftarrows A + B$ take place in contact with a heterogeneous catalyst.

Suppose AB is only slightly adsorbed, B very strongly adsorbed, and A slightly adsorbed.

Then we might have for the rate of the direct reaction

$$\frac{-d[AB]}{dt} = \frac{k_1[AB]}{[B]}.$$

But just because B is strongly adsorbed, the rate of the

reverse reaction might become independent of B and we should have

$$\frac{d[AB]}{dt} = k_2[A].$$

By equating these rates we arrive at the normal expression for the equilibrium constant

$$\frac{[AB]}{[A][B]}.$$

VIII

ACTIVATION IN HETEROGENEOUS REACTIONS

In order to take part in a heterogeneous reaction molecules must be adsorbed by a catalyst. But attachment to the surface is not by itself sufficient to cause their transformation. They require activation just as in homogeneous reactions.

A systematic attempt to correlate the catalytic effect of different surfaces with their adsorptive capacity was made by Taylor and his collaborators. Taylor and Burns,* for example, investigated the adsorption of hydrogen, carbon dioxide, and ethylene by the six metals nickel, cobalt, palladium, platinum, iron, and copper. All these metals are able to catalyse the hydrogenation of ethylene to ethane, while nickel, cobalt, and palladium also catalyse the reduction of carbon monoxide and of carbon dioxide to methane.

There is a general correlation between adsorptive capacity and catalytic effect to the extent that all the metals show some capacity for adsorbing those gases the interaction of which they are able to promote. Beyond this the correlation does not extend.

There is no quantitative proportionality between degree of adsorption and rate of reaction. Nor is any such close relation to be expected. Indeed, at temperatures where reaction attains a measurable speed adsorption is often quite small. Thus, although the adsorption of ethylene by certain kinds of copper catalyst can be demonstrated at lower temperatures, the velocity of interaction of ethylene and hydrogen only attains an appreciable speed at temperatures where the adsorption becomes almost too small to measure.

* *J. Amer. Chem. Soc.*, 1921, **43**, 1273.

It is clear, therefore, that thermal activation plays a part in surface reactions as important as that which we have seen it to play in homogeneous changes.

In general, the influence of temperature on the rate of heterogeneous reactions is very great. At one time a view was current that heterogeneous reactions as a whole had temperature coefficients of a much smaller order than homogeneous reactions. This must have been to some extent a preconceived idea based upon the diffusion theory, because there is no experimental ground for such a belief.

Heterogeneous reaction velocities nearly always satisfy the Arrhenius equation $d \log k/dT = E/RT^2$, and the values of the constant E are not of a different order of magnitude from those belonging to purely gaseous reactions. In a great many instances the value of E is in the neighbourhood of 30,000 calories.

Until more definite information is forthcoming about its real meaning we may call E the *apparent heat of activation.*

As we have seen, there is abundant evidence that the heat of activation in homogeneous reactions represents the thermal energy with which the molecules must be supplied, by collision or otherwise, before they can enter into reaction. There is every reason to believe that, in heterogeneous reactions, adsorbed molecules must be supplied with energy in an analogous way.

This is evident when the mechanism of a heterogeneous reaction is considered in more detail. Molecules from the gas phase strike the surface. They may rebound or they may become attached to the surface and sojourn there for a period.

One of two things may then happen. After a time they may re-evaporate. This depends upon their acquiring sufficient kinetic energy to carry them beyond the range of attraction of the surface forces. Escape may be rendered easier at certain times if the attractive force passes periodically through a minimum value as a result of

internal changes both in the adsorbed molecules and in the molecules of the surface.

On the other hand, during their sojourn on the surface the adsorbed molecules may undergo chemical change, consisting either in simple rearrangement or decomposition, or in interaction with adjacent molecules.

In whichever of these ways the chemical transformation comes about, all the information about the nature of chemical change which has been derived from the study of reactions in the gaseous phase justifies the conclusion that the molecules must be activated by the acquisition of thermal energy considerably above the mean. This energy we may call the *true heat of activation.*

The actual processes of molecular transformation in surface reactions cannot be fundamentally different from those in homogeneous reactions. Gas molecules come almost at once into thermal equilibrium with the surface on which they are adsorbed. Among them there is a distribution of internal energy, determined by the temperature of the surface. Although their internal configuration, and consequently their stability, is modified profoundly by the forces acting between them and the molecules constituting the surface, the adsorbed molecules form a system possessing a certain uniformity within its own bounds. A heterogeneous reaction may indeed be regarded as a homogeneous reaction in two dimensions instead of three.

In considering the molecular statistics of homogeneous reactions, we sought for, and found, a correlation between the velocity constant and the number of molecules possessing the energy of activation. It remains to be seen what results are yielded by similar attempts to interpret the molecular statistics of heterogeneous changes. At the outset it is better to state that the problem now becomes much more complex and that its solution is at the present moment only partially achieved.

Serious confusion arises unless one thing is taken carefully into account. Only those molecules which are actually adsorbed are in a position to participate in the reaction. Velocity constants, however, are always calculated in terms of the total amount of gas in the reaction vessel. If we have to deal with a unimolecular reaction in a single phase, the velocity constant is equal to the fraction of the total number of molecules which reacts in unit time. Since all the molecules have an equal chance of being in the activated state, direct correlation between the velocity constant and the heat of activation may reasonably be sought. In a heterogeneous reaction, all the molecules have not an equal chance of being in the activated state. Only those which are adsorbed have this chance.

Thus the only correlation which may reasonably be sought is one between the heat of activation and the velocity constant expressed, not as a fraction of the total number of molecules, but as a fraction of the number actually adsorbed at any moment. If $k_{\text{obs.}}$ is the observed velocity constant, calculated in terms of the total gas, and α is the fraction of the total gas which is actually adsorbed, then the 'true' velocity constant would be $k_{\text{obs.}}$ divided by α. This we may represent by the letter χ.

We are now in a position to see the difference between the true and apparent heats of activation. The true heat of activation, Q, is given by

$$\frac{d \log \chi}{dT} = \frac{Q}{RT^2},$$

while the apparent heat of activation is given by

$$\frac{d \log k_{\text{obs.}}}{dT} = \frac{E}{RT^2}.$$

Since the adsorption varies with temperature, α is not independent of T. E and Q are therefore not necessarily equal.

Relation between the true and apparent heats of activation.

For simplicity we will assume that only one gas takes part in the chemical change. Unretarded reactions, and reactions retarded by the presence of their products, must be considered separately, because there are important differences between the results for these two classes.

In dealing with the unretarded reactions it will be best to restrict ourselves to those in which the adsorption of the reacting gas is small, so that the amount adsorbed is proportional to the pressure. Further, in dealing with retarded reactions we shall assume that the adsorption of the retarding gas is sufficiently great for the free surface to be inversely proportional to its pressure. Such loss of generality as this method involves is not very serious, because, in the first place, very many reactions are found in practice to conform to the conditions we are supposing, and, in the second place, a more complete investigation of the most general case leads to results which are too complicated to apply to actual experimental data.

1. *Unretarded reactions.*

Let σ be the fraction of the active surface which is covered with adsorbed molecules of the reactant when the pressure in the gas phase is unity.

The establishment of the adsorption equilibrium is rapid in comparison with any disturbance of it due to the removal of the molecules in chemical change. Equating therefore, the rate of evaporation and the rate of condensation we find an expression for σ.

Rate of condensation on to the surface $= a(1 - \sigma)$, where a is constant at constant temperature, but varies slightly with temperature.

Rate of evaporation from surface $= x\sigma$, where x is the rate of evaporation, at temperature T, for unit area of covered surface.

Since evaporation can only take place when the adsorbed molecules acquire a definite amount of kinetic energy, directed away from the surface, we may express the variation of x with temperature in the form

$$x = be^{-\lambda/RT},$$

where b is constant, and λ may formally be called the 'energy of desorption'.

Thus for equilibrium we have

$$a(1-\sigma) = be^{-\lambda/RT}.\sigma.$$

Since σ is small compared with unity, $(1-\sigma)$ is nearly equal to 1; hence $\sigma = Ce^{\lambda/RT}$, where C is a new constant equal to a/b.

If χ is the true velocity constant of the reaction, per unit area of the catalyst actually covered, then the observed velocity constant, $k_{\text{obs.}}$, is proportional to $\chi\sigma$.

Therefore

$$k_{\text{obs.}} = \text{constant} \,.\, \chi\sigma = \text{constant} \,.\, \chi Ce^{-\lambda/RT},$$

but

$$\chi = \text{constant} \,.\, e^{-Q/RT},$$

where Q is the true heat of activation.

Therefore

$$k_{\text{obs.}} = \text{constant} \,.\, e^{-(Q-\lambda)/RT}.$$

The constant varies but slightly with temperature—approximately as the square root of the absolute temperature.

Thus

$$\frac{d \log k_{\text{obs.}}}{dT} = \frac{[Q-\lambda]}{RT^2}.$$

The apparent heat of activation is given by

$$\frac{d \log k_{\text{obs.}}}{dT} = \frac{E}{RT^2}.$$

Therefore

$$E = Q - \lambda.$$

2. *Retarded reactions.*

Let σ' be the fraction of the active surface covered with the retarding gas at unit pressure. Then the fraction left free is $(1-\sigma')$, and of this let a fraction σ be occupied by

the reactant when its concentration in the gas phase is unity.

The adsorption equilibrium of the retarding gas is expressed as follows:

$$\text{rate of condensation} = a'(1-\sigma'),$$

σ being small compared with unity.

$$\text{Rate of evaporation} = x'\sigma',$$

where x' is the rate of evaporation at temperature T for unit area covered.

By the same argument as before

$$x' = b'e^{-\lambda'/RT},$$

where λ' is the 'energy of desorption' of the gas.

Equating the two rates we obtain

$$a'(1-\sigma') = b'\sigma'e^{-\lambda'/RT},$$

but now σ' is nearly equal to unity; therefore

$$(1-\sigma') = \text{constant} \,.\, e^{-\lambda'/RT}.$$

Further, for the reactant we have as before

$$\sigma = \text{constant} \,.\, e^{+\lambda/RT}.$$

Now the observed velocity constant, $k_{\text{obs.}}$, is proportional to the true velocity constant multiplied by $\sigma(1-\sigma')$, since $(1-\sigma')$ is the fraction of the total active surface which is available for molecules of the reactant, and σ is the fraction of this fraction which is actually occupied.

Thus

$$\begin{aligned} k_{\text{obs.}} &= \text{constant} \,.\, \chi \,.\, e^{-\lambda'/RT} \,.\, e^{+\lambda/RT} \\ &= \text{constant} \,.\, e^{-Q/RT} \,.\, e^{-\lambda'RT} \,.\, e^{+\lambda/RT} \\ &= \text{constant} \,.\, e^{-(Q+\lambda'-\lambda)/RT}. \end{aligned}$$

Therefore

$$\frac{d \log k_{\text{obs.}}}{dT} = \frac{[Q+\lambda'-\lambda]}{RT^2}.$$

Comparing this with the equation

$$\frac{d \log k_{\text{obs.}}}{dT} = \frac{E}{RT^2},$$

it follows that

$$E = [Q+\lambda'-\lambda].$$

General discussion of temperature coefficients of heterogeneous reactions.

When the products of reaction exert no retarding influence, the apparent heat of activation is less than the true value by an amount λ, which determines the variation with temperature of the adsorption.

The existence of a marked retarding influence of the products has, on the other hand, the effect of increasing the apparent heat of activation.

There is one important special case in which the apparent heat of activation becomes equal to the true value. This is when the surface is completely covered with the reactant over the whole range of temperature, and there is no retardation due to the presence of the products of reaction. σ has the constant value unity, and the variation of the observed reaction velocity is due entirely to the changing rate of the actual chemical transformation.

In general, since the adsorption is often too small to be measured directly, it is rather difficult to estimate the magnitude of the correction which should be applied to the apparent heat of activation. It may sometimes be very great. When the adsorption is quite small, for example when there is a simple first order decomposition, it is possible that the energy changes accompanying adsorption are also small. The temperature coefficient of the number of molecules adsorbed would then be small compared with that of the actual chemical change. In some experiments of Taylor and Burns, for example, the amounts of various gases adsorbed on metals varied quite appreciably with temperature, but, on the whole, to an extent small in comparison with the usual variation of chemical reaction rates.

Direct measurement of heats of adsorption, however, reveals relationships of some complexity.* The integral

* Beebe and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 43; Fryling, *J. Physical Chem.*, 1926, **30**, 818; Kistiakowsky, Flosdorf, and Taylor, *J. Amer. Chem. Soc.*, 1927, **49**, 2200; Burk, *J. Physical Chem.*, 1928, **32**, 1601.

heat of adsorption of gases like hydrogen on metals such as nickel may amount to 10,000 or 20,000 calories. Moreover the differential heat of adsorption varies in a complicated manner, sometimes increasing at first with the amount of gas taken up, passing through a maximum and then decreasing. Since hydrogen itself is probably adsorbed, partly at least, in the atomic form, and the resolution is highly endothermic while the adsorption of the atoms is exothermic, and since different parts of the catalytic surface have different activity, the complexity of the thermal phenomena is understandable.

In the absence of more detailed information about the actual magnitude of the adsorption in specific instances, it is at least worth while to see what regularities, if any, reveal themselves when the apparent value of E is used as an approximation for the true value. Nevertheless it is most desirable that experimental investigation should be made of reaction rates in conjunction with actual adsorption measurements, in order to leave no uncertainty about this matter.

The natural line of inquiry is to study the progress of a given reaction on various catalytic surfaces, to determine the relative numbers of molecules adsorbed on each surface, and to seek a correlation between the heat of activation, using provisionally the apparent value as a sufficiently good approximation to the true value, and the velocity of change referred to equal numbers of adsorbed molecules. Unfortunately, no example has hitherto been found suitable for experimental investigation, in which both the adsorptions and the reaction velocities can be measured. Thus no really valid test can be made. The existence of centres of varying activity would still further complicate the interpretation even of direct measurements of adsorption.

A fortunate chance might, nevertheless, allow some regularity to reveal itself. This would come about under

the following conditions: it might so happen that the degree of adsorption of a gas on a number of different surfaces, which catalyse its chemical transformation, was of the same order of magnitude for each. There would then be, if not an exact, at least a general correlation between the reaction velocity and the heat of activation. High values of the heat of activation would in general be associated with low values of the reaction rate, and vice versa.

Such a correlation was sought for, using data relating to the decomposition of formic acid vapour. The reaction $H.COOH = CO_2 + H_2$ is catalysed by a number of different surfaces. The rate of reaction for unit area of total surface was determined in each instance, together with the apparent heat of activation. The logical position of such an investigation is this: a positive result in a sufficient number of instances would have shown both that there is a definite correlation between heat of activation and speed of reaction, and also that the simplifying assumption about more or less equal adsorptions was justified. A negative result, on the other hand, does not prove that there is no correlation: it merely leaves the matter where it was.

The results were, in fact, negative. In the following table E_{CO_2} represents the apparent heat of activation in the decomposition of formic acid vapour into carbon dioxide and hydrogen. The numbers in the last column represent the relative velocity of reaction at 200° C. for equal surfaces of the various catalysts, and are referred to platinum, which is taken as 100.

Surface	E_{CO_2}	Relative Velocity
Glass	24,500	0·05
Gold	23,500	2
Silver	31,000	2
Platinum	22,000	100
Rhodium	25,000	500

Thus glass and rhodium give approximately the same value for the heat of activation, yet the reaction proceeds

10,000 times as rapidly on the rhodium surface. The lack of correlation is sufficiently evident.

But it is not at all difficult to admit that the number of molecules adsorbed on parts of the glass surface possessing catalytic virtue may be ten thousand times smaller than the number which rhodium can accommodate. The matter is thus left open.

Nevertheless it seemed useful to record the actual results as examples of the kind of relationship which is found by experiment.

If sufficient confidence is felt, on general grounds, in the existence of an exact correlation of the kind we have been seeking, then these results could be used in a converse manner to calculate the relative numbers of formic acid molecules accommodated by various surfaces.

A similar lack of correlation between the observed rate of reaction and the value of E is found by Kunsman* for the decomposition of ammonia on various catalysts.

A second possibility of revealing a correlation presents itself in the study of alternative reactions.

Formic acid decomposes in the two ways:

$$\mathrm{H.COOH} \begin{cases} \nearrow \mathrm{H_2 + CO_2} & (1) \\ \searrow \mathrm{H_2O + CO} & (2) \end{cases}$$

Both of these reactions take place simultaneously on the surface of glass.

If molecules of formic acid can be adsorbed in two distinct ways on the surface of glass, and if reaction (1) and reaction (2) are respectively characteristic of the two modes of adsorption, then we are virtually dealing with two different catalysts, and the situation is not very different from the one which we have already discussed. But if, as we might perhaps expect, there is only one mode of adsorption, and decomposition of the formic acid molecules in one or other of the alternative ways is governed purely by

* *J. Amer. Chem. Soc.*, 1928, **50**, 2100.

some internal probability, then we should be justified in looking for some connexion between the heat of activation associated with a given mode of decomposition and the relative probability of its occurrence.

On the surface of glass, in the neighbourhood of 280° C., the two alternative reactions take place with nearly equal speeds, yet the heats of activation are very different.* E_{CO}, the heat of activation associated with the decomposition into carbon monoxide and water, is about 16,000 calories, while E_{CO_2} is about 28,000 calories. If the numbers of molecules which are activated for the two possible reactions are proportional respectively to $e^{-E_{CO}/RT}$ and $e^{-E_{CO_2}/RT}$, and if, moreover, there is any connexion between the chance of the molecules becoming activated and the occurrence of a given transformation, then the reaction yielding carbon monoxide should predominate over the competing reaction to an overwhelming extent. The ratio of the rates of the two reactions should be $e^{-28,000/RT}$ divided by $e^{-16,000/RT}$, so that about e^{10} molecules should split up into carbon monoxide and water for every one splitting up into carbon dioxide and hydrogen. But the numbers of molecules decomposing in the two ways are roughly equal.

This result would seem to indicate that the mere acquisition of the necessary energy of activation is not by itself sufficient to initiate the chemical transformation. It is necessary to suppose that the activated molecules decompose only when they pass through some unstable phase in their existence. The phase in which they are capable of breaking down into carbon monoxide and water is passed through much more rarely than that in which they are able to decompose into carbon dioxide and hydrogen. This neutralizes the effect of the lower heat of activation on the probability of the first mode of transformation.

* Hinshelwood, Hartley, and Topley, *Proc. Roy. Soc.*, 1922, A, **100**, 575.

It must be repeated that this argument depends upon the assumption that there is only one way in which the molecules of formic acid can be attached to the surface of the catalyst. There is, however, some evidence against this assumption. Constable* finds that the two simultaneous reactions undergone by allyl alcohol when passed over heated copper are differently influenced by the physical state of the catalyst. This points to the conclusion that there are two independent centres of activity on the catalyst surface with two different modes of adsorption, or, at any rate, centres where the energy of adsorption is so different that different reactions are facilitated. Hoover and Rideal† find that the two alternative decompositions of ethyl alcohol by thoria show a different behaviour towards poisons, which points to the same conclusion.

The heterogeneous decomposition of nitrous oxide in contact with a heated gold wire is interesting, though undoubtedly rather exceptional. The reaction is unimolecular with respect to nitrous oxide. The heat of activation, obtained from the temperature coefficient of the reaction velocity, is 29,000 calories.

If we assume the very simple decomposition mechanism that nearly all the molecules of nitrous oxide which strike the wire and acquire from it energy greater than E can decompose, then we have

$$\frac{\text{number of molecules reacting in unit time}}{\text{number of molecules striking the wire in unit time}} = e^{-E/RT}.$$

From this equation a value of E equal to 30,000 calories is found. This is in rather striking agreement with the value found from the temperature coefficient. It would appear that the course of the reaction could be explained by the supposition that every molecule striking the wire in an appropriate manner reacts forthwith. But this is only a possible explanation. It is by no means necessarily the

* *Proc. Roy. Soc.*, 1926, A, **113**, 254.

† *J. Amer. Chem. Soc.*, 1927, **49**, 104.

correct one, and it is certain that so simple a mechanism could not be made to explain all, or even many, other heterogeneous reactions. It seems clear that in general actual sojourn of the molecules on the surface is necessary, and this applies *a fortiori* when reaction depends upon the interaction of two or more species of molecules. Schwab and Pietsch * find that the thermal decomposition of methane at the surface of a hot wire is very much more rapid than could be accounted for by the number of methane molecules striking the wire with the appropriate kinetic energy of translation. This supports the conclusion that the methane molecules actually sojourn on the wire and derive energy from the atoms constituting the surface.

Having outlined these various principles and some attempts, only partially fruitful, at their application, we will now approach the problem from a different angle.

Comparison of Homogeneous and Catalysed Reactions. Influence of the Catalyst on the Heat of Activation.

A heterogeneous catalyst may influence a reaction in two ways. It may modify the mechanism of the reaction by allowing it to proceed along a path which would not be possible for the homogeneous change, and it may also facilitate the change by lowering the energy of activation. This second influence will only be detectable under such conditions that the true and apparent heats of activation are nearly equal. Reactions which are markedly retarded by their products are thus ruled out of consideration.

We will discuss the problem by reference to the three reactions :

$$2\,N_2O = 2\,N_2 + O_2,$$
$$2\,HI = H_2 + I_2,$$
$$2\,NH_3 = N_2 + 3\,H_2.$$

The first two reactions have been proved experimentally to be bimolecular. The homogeneous decomposition of

* *Z. physikal. Chem.*, 1926, **121**, 189.

ammonia has not been measured, but, from analogy with other known instances, it seems almost certain that it also would be a bimolecular change.

The modification of the reaction path is exemplified by the thermal decomposition of nitrous oxide, which on the surface of platinum or of gold takes place in a unimolecular manner. The decomposition of hydrogen iodide on the surface of platinum is likewise unimolecular.* The metal surfaces seem to render possible, in virtue of their affinity for free atoms, changes which in the gaseous phase would be impossible on account of the very great energy of activation required. The nitrous oxide decomposition appears, for example, to be resolved into the stages $N_2O = N_2 + O$; and $O + O = O_2$. The metal surface acts as a temporary abode for oxygen atoms until they encounter others of their kind and evaporate. The production

* It is perhaps necessary to mention a possible objection to the conclusion that the catalytic reactions are truly unimolecular. If there were a complete layer of, say, nitrous oxide molecules on a surface, and reaction were determined by the impact of a second nitrous oxide molecule on one of these then the reaction would appear to be unimolecular although essentially bimolecular. But there are certain strong objections to such an hypothesis.

First, it is frequently found that when two molecules of *different* kinds react under the influence of a surface catalyst, both must be actually adsorbed—it is not enough for one to be adsorbed and for the other to strike it. The evidence for this is that excess of one reactant can bring about an actual decrease in the reaction rate due to displacement of the other reactant.

Secondly, if the proposed mechanism were correct there is no reason why the reaction velocity should ever become independent of pressure at higher pressures as it does in certain examples.

Thirdly, if in all cases there is one complete layer it is rather surprising that the molecules do not interact among themselves in that layer rather than await the arrival of molecules from the gas phase. This last argument is not, however, conclusive, since an example, the catalytic decomposition of acetaldehyde, is known where the reaction does apparently depend on collision between a molecule from the gas phase and an adsorbed molecule. (*Proc. Roy. Soc.*, 1928, A, **121**, 141.) But the whole behaviour of this reaction is markedly different from that of the reactions such as the decomposition of nitrous oxide.

of free oxygen atoms in the gas phase would be so highly endothermic as to be practically impossible.

Since the reactions, which are bimolecular when homogeneous, appear to be resolved into unimolecular reactions followed by a rapid combination of the free atoms, a somewhat indirect answer has to be given to the principal question, namely, the effect which the catalyst has on the energy of activation.

The homogeneous decomposition of nitrous oxide depends upon the collision of two molecules with a combined energy of 58,500 calories. The heats of activation associated with the unimolecular transformations on the surface of platinum and of gold are 32,500 calories and 29,000 calories respectively. Thus the homogeneous reaction demands the simultaneous activation of two molecules to a total extent of 58,500 calories, while the heterogeneous transformations demand activation to the extent of about half this amount only. The catalysts may therefore be said to reduce the energy of activation, but they do this in the rather indirect way of changing the reaction mechanism from one which requires the simultaneous activation of two molecules to one which requires the activation of a single molecule only.

The values 32,500 and 29,000 for the heats of activation are uncorrected for the change with temperature of the number of molecules adsorbed, and this obviously detracts from the conclusiveness of the results. In the other two instances which we proposed to discuss this uncertainty can, fortunately, be eliminated, or at least considerably reduced.

As we found in an earlier section, there is one type of catalytic reaction in which the observed heat of activation does not require correction for the changing adsorption of the reactant, namely, reactions of zero order. In these the surface of the catalyst is completely covered with adsorbed molecules, and, so long as increase

of temperature does not cause the reaction order to change from zero, the number of molecules participating in the reaction may be regarded as constant. So long as this condition is fulfilled there seems no good reason for doubting that the observed heat of activation is a measure of the energy required to enable the adsorbed molecules to enter into reaction. It is a real measure of the molecular stability.

The decomposition of hydrogen iodide on the surface of gold, and the decomposition of ammonia on the surface of tungsten, nearly conform to the condition.

For the hydrogen iodide decomposition the heat of activation is 25,000 calories. This is very considerably lower than the value 44,000 calories associated with the homogeneous reaction.

It is instructive to compare with this the heat of activation which the hypothetical *unimolecular* homogeneous reaction would possess. From the known thermochemical data we have

$$2\,HI = H_2 + I_2 - 3{,}000 \text{ cals.},$$
$$H_2 = 2\,H - 96{,}000 \text{ cals.},$$
$$I_2 = 2\,I - 34{,}000 \text{ cals.},$$

whence

$$HI = H + I - 66{,}500 \text{ cals.}$$

Thus the *minimum* activation would be 66,500 calories.

It is probable that the actual mechanism of the decomposition is unimolecular, but, the observed order of the reaction being zero, we cannot tell whether the molecules decompose singly or by interaction with their neighbours. The catalytic decomposition of hydrogen iodide on the surface of platinum can actually be shown to be unimolecular. The heat of activation in this instance is even lower (14,000 cals.), but is again subject to the same uncertainty as the values for the unimolecular reactions of nitrous oxide.

The homogeneous decomposition of ammonia, being im-

measurably slow even at temperatures in the region of 1,000° C., must have a heat of activation greater than 70,000 or 80,000 calories (page 97). The heterogeneous decomposition on the surface of tungsten has a heat of activation of 39,000 calories.

We may conveniently summarize these various relationships in the form of a table.

Reaction Thermal decomposition of	Total activation required for the homogeneous change (bimolecular)	Total activation required for the heterogeneous change (probably, or certainly, unimolecular)
Hydrogen iodide	44,000	25,000 (gold)
Nitrous oxide	58,500	29,000 (gold)* 32,500 (platinum)*
Ammonia	probably $> 80{,}000$	39,000 (tungsten)

* Plus correction.

The surface reactions have heats of activation about half as great only as the bimolecular homogeneous changes. The function of the surfaces in these examples seems to be to permit the occurrence of a unimolecular process in place of a bimolecular process requiring an energy of activation about twice as great.

The quantitative results must be regarded as of an approximate character only, since it is far from certain that the true heat of activation is ever accurately extricable; but in a general way it seems clear that the main argument is supported by experiment.

Reactions in which the retarding effect of the products is marked.

The relation between the true and apparent heats of activation is given by the equation

$$E_{\text{app.}} = E_{\text{true}} + \lambda' - \lambda.$$

In considering the interaction of carbon monoxide and

oxygen on the surface of platinum, a reaction which takes place at a rate inversely proportional to the pressure of the carbon monoxide, Langmuir * assumed that the change with temperature of the reaction velocity was entirely due to the variation in the rate of evaporation of carbon monoxide molecules from the retarding film. This assumption was equivalent to equating $E_{\text{app.}}$ and λ'. He speaks, therefore, of the observed heat of activation, 31,800 calories, as the 'heat of evaporation of the adsorbed carbon monoxide'. This cannot be absolutely correct in principle, although in special instances λ' may be large compared with the other terms. In the example which Langmuir was studying the assumption is to some extent justified by the circumstance that at higher temperatures, when the platinum surface becomes almost denuded of adsorbed molecules of the monoxide, the rate of reaction is very great and practically determined by the rate at which the molecules can come into contact with the surface. Under these conditions, moreover, the rate of reaction becomes almost independent of temperature. This shows, probably, that E_{true} is small compared with λ'. In general, however, both terms will be of considerable importance. This means that retarded reactions will tend to have rather high temperature coefficients, the analysis of which will be difficult.

The decomposition of ammonia on the surface of platinum takes place at a speed which is inversely proportional to the pressure of the hydrogen present. The combined influence of the two terms E and λ' produces an apparent heat of activation of more than 100,000 calories. This is in striking contrast with the value of E_{true}, 39,000 calories for the unretarded reaction on the surface of tungsten. The decomposition of ammonia on molybdenum is of zero order, but retarded by nitrogen ; the value of E according to Burk is 53,200 calories. Kunsman finds 32,000 calories

* *Trans. Faraday Soc.*, 1922, **17**, 621.

only. Here the effect of the retardation by nitrogen seems to be quite marked, and, moreover, variable.

The Nature of the Action of Surfaces.

We have hitherto given most of our attention to the adsorbed molecules of the reactant. We must now consider more closely the part played in catalytic phenomena by the nature of the surface itself. The question to be solved is, in its simplest terms, what the catalyst does to the adsorbed molecules to influence their stability.

The first step in the elucidation of this difficult problem is to ascertain whether the whole surface of the catalyst is uniformly active. We have already referred to the view expressed by Taylor * that only a small fraction of the total surface is necessarily active in catalysing a given reaction, and, moreover, that this fraction is a function, not merely of the surface itself but of the reaction catalysed. The centres which are active in respect of one reaction may be quite inactive in respect of another, although the surface, regarded as a whole, catalyses both equally well.

This theory is based upon evidence of several different kinds. First, the ease with which catalytic activity can sometimes be destroyed by heating is considered by Taylor himself to indicate that a very active surface is still far from possessing the completely regular arrangement of atoms which is characteristic of the true space lattice of the solid. He supposes that there exist, at the surface of the solid, groups of atoms in varying degrees of saturation. Some groups are part of the completed lattice, while others consist of small numbers of atoms rising in the form of peaks from the surface. In extreme cases there may be isolated atoms attached to the main groups by a single valency only. On these isolated peaks several molecules of a gas might be adsorbed, instead of the single molecule

* *Proc. Roy. Soc.*, 1925, A, **108**, 105.

which could be held by an atom in a normal space lattice. The effect of heat on a catalyst with this surface structure would be to bring about a more regular arrangement of the atoms and thereby destroy the active peaks.

Whether or not this picture of the surface is a legitimate one, it must be remarked that the destruction of catalytic activity by heat is only observed in the case of finely divided solids, and here it can be equally well explained by supposing that heating brings about a diminution of the total surface.

Other and more conclusive evidence about the existence of active centres, whatever their nature may be, is, however, available. Catalytic poisons sometimes destroy the activity of a surface towards a particular reaction without reducing the total adsorption of the reacting substances to anything like a proportionate extent. Taylor quotes some experiments of Pease, in which quantities of carbon monoxide quite insufficient to displace all the hydrogen or ethylene from a copper catalyst completely inhibited the reaction between these two gases.

An even more remarkable fact is that catalysts may be 'poisoned' with respect to one reaction while retaining their activity with respect to other reactions. Vavon and Huson* found that the hydrogenation of propyl ketone in presence of colloidal platinum was inhibited by amounts of carbon disulphide insufficient to prevent the hydrogenation of piperonal and nitrobenzene. Further amounts of carbon disulphide stopped the hydrogenation of piperonal but not that of nitrobenzene.

Another instance of the same curious phenomenon can be cited. Hydrogen has a most pronounced inhibiting effect on the thermal decomposition of ammonia at the surface of a heated platinum wire. On the other hand, it is found to be almost without influence on the decomposition of hydrogen iodide on the surface of the same wire,

* *Compt. Rend.*, 1922, **175**, 277.

and actually at a lower temperature. This cannot be explained by the assumption that the hydrogen iodide displaces the hydrogen while the ammonia is unable to do so, for the decomposition of hydrogen iodide is of the first order under these circumstances, and this indicates that its adsorption is but small. Similarly carbon dioxide has practically no effect on the rate of decomposition of nitrous oxide in contact with platinum, but can exert a very pronounced inhibiting action on the water-gas reaction.

The observation of Burk has already been mentioned, namely, that the rate of decomposition of ammonia on molybdenum, although reduced by the presence of nitrogen, does not approach zero as the surface becomes saturated with nitrogen. This is easily interpreted in terms of the theory of centres of different activity; but there is also the possibility that the nitrogen film itself has some catalytic activity. The possibility that unimolecular gas films on surfaces may themselves be the catalysts in certain reactions should not be ignored, and in many examples would provide an alternative to the hypothesis of non-uniformity of the surface. But the cumulative evidence for this latter assumption is very strong.

Turning now to evidence from a different field of observation, the heat of adsorption of oxygen by charcoal was found by Garner and Blench* to be as much as 220,000 calories for the first amounts of oxygen taken up, and less for subsequent amounts. The initial value is very much greater than the heat of combustion of solid carbon. Since solid carbon has a very great latent heat of vaporization, the heat of combustion of gaseous carbon is very great and is estimated at 380,000 calories. Thus those carbon atoms which adsorb the first traces of oxygen are apparently in a state half-way between that of solid carbon and that of vaporized carbon. This seems to agree with

* *J. Chem. Soc.*, 1924, **125**, 1288.

Taylor's picture of a surface with atoms in varying degrees of saturation.

In some reactions the relative degrees of adsorption of different gases which have to be postulated for the purpose of interpreting the kinetics of the reactions seem to bear no relation to the measured degrees of adsorption on the surface as a whole. For example, the centres on a platinum surface which are effective in catalysing the interaction of hydrogen and carbon dioxide appear to adsorb carbon dioxide more strongly than they adsorb hydrogen. This must be inferred from the fact that excess of carbon dioxide can almost completely inhibit the reaction, while hydrogen has no such effect. The total measurable adsorption of carbon dioxide on platinum at the temperature of the reaction is, however, negligible compared with that of hydrogen.

The idea that the surfaces of heterogeneous catalysts present regions of graded activity helps also in the interpretation of certain biochemical phenomena. Quastel and Wooldridge,* for example, find that a number of organic substances reduce methylene blue under the influence of Bacillus coli, and that when the bacillus is exposed to adverse conditions, it loses its activity not suddenly but step by step towards one after another of the substances.

These various observations, revealing the complexity of catalytic surfaces in general, do not render necessary any appreciable modification of what we have said about the actual kinetics of heterogeneous reactions. There is, moreover, no reason why sometimes the whole surface may not be uniformly active. In the general case, however, we must be prepared to recognize that, even in respect of one given reaction, a surface may present centres of various degrees of activeness. The kinetics of a reaction taking place on such a surface would be almost the same as on a surface of uniform structure, except that the quantitative

* *Biochem. J.*, 1927, **21**, 148, 1224.

relations between reaction rate and pressure would not be so clear-cut. Since, however, the simple formulae derived from theory seldom apply with complete numerical exactness, this does not really introduce anything new.

Beyond the point that we have now reached inquiry divides into many channels, among which it is not quite easy to discern the course of the main stream. We must therefore bring together a number of facts and theories, relating to the influence of surfaces on the stability of adsorbed molecules, which are not at the present time very definitely co-ordinated.

Several investigators have suggested that the actual spacing of the atoms in the solid catalyst has a very pronounced influence on the catalytic activity.* The evidence for this is of two kinds.

Adkins and Nissen,† for example, found that alumina prepared in different ways exhibited very varying catalytic activity towards the decomposition of formic acid. This could hardly be due simply to the different surface areas of the several preparations, since the variation was not confined to the total speed of reaction but affected also the relative speeds of the two alternative decompositions which formic acid undergoes. Moreover, the apparent heats of activation varied from one kind of alumina to another.‡

They found analogous results for the catalytic reactions of various alcohols and esters on surfaces of material prepared in different ways.§

* Langmuir, *Trans. Faraday Soc.*, 1922, **17**, 607. W. C. McC. Lewis, ibid., 661.

† *J. Amer. Chem. Soc.*, 1923, **45**, 809.

‡ Adkins and Nissen appear to think that because the heat of activation is dependent upon the method of preparation of the catalyst it can have no connexion with the stability of the molecule (this is quite apart from any distinction between true and apparent heat of activation). This is of course a complete misunderstanding, for the stability of the molecule is also a function of the nature of the surface upon which it is adsorbed. Otherwise catalysis would not exist.

§ *J. Amer. Chem. Soc.*, 1924, **46**, 130.

Palmer and Constable * found that the catalytic activity of copper towards the dehydrogenation of alcohols depended upon the temperature at which the copper had been reduced from its oxide in preparation, and that the heat of activation likewise depended on the method of reduction of the copper.

The activity of many catalysts increases with the number of times that they have been used to bring about a given reaction. There is no absolutely conclusive proof that this is not due to an actual increase in the total surface, but in certain instances it is so pronounced and happens so quickly that it seems more easily attributable to a change in the configuration of the surface.

Rather closely connected with this question of surface configuration is that of the so-called 'promoter action'.† The essential fact about this phenomenon is that a composite surface may possess catalytic properties of which the constituents are quite devoid. If a metal M forms a solid solution with another metal N, then at the interface M/N the forces exerted on an adsorbed molecule will be quite different from those which are exerted on a molecule adsorbed on either M or N separately.

It is rather desirable that investigations should be made of promoter action in reactions which only involve the decomposition or transformation of a single substance. When two substances interact, it is always possible that one component of the surface adsorbs one reactant and the other component adsorbs the other reactant. From what has been said about the localization of catalytic activity in special regions of the surface it will be seen that measurements of the total adsorption of the reactants by the separate constituents of the composite catalyst would throw no light on whether or not this actually occurred.

* *Proc. Roy. Soc.*, 1924, A, **106**, 250.

† Compare Taylor, *J. physical Chem.*, 1924, **28**, 915 (other references there). Hurst and Rideal, *J. Chem. Soc.*, 1924, **125**, 685.

Thus far attention has been given to the nature and spacing of the points on the surface to which the molecules of the adsorbed substance attach themselves. We will now regard the matter in the light of a principle of great importance, namely, the orientation of molecules in surface layers.

The effect of orientation is illustrated in an interesting manner by some experiments of Palmer and Constable* on the rate of dehydrogenation of alcohols in presence of metallic copper. Primary alcohols appear to be adsorbed with the $-CH_2OH$ group attached to the catalyst. The hydrogen is lost from this group in the chemical change, so that it appears reasonable to suppose that this is the portion of the molecule which must be activated. The hydrocarbon chain, therefore, would not be expected to have much influence on the process, and it was indeed found by experiment that the rates of reaction of five primary alcohols are equal. Moreover, the temperature coefficients of the reaction velocity are also equal.

Burk † has laid much stress on the possibility that a molecule might be attached to a surface at more than one point, whereby a distortion, or partial separation of its atoms, is produced. Ammonia, for example, might be held to the surface of a metal by a hydrogen atom and a nitrogen atom simultaneously. Such a distortion is thought of as lowering the heat of activation and facilitating decomposition.

The orientation of molecules at interfaces is closely connected with the phenomenon of boundary potential differences. To quote from Hardy,‡ the interfacial region 'has a configuration or structure which is intrinsically unstable at the given temperature and pressure, and acquires stability only by the intervention of the forces at the interface.

* *Proc. Roy. Soc.*, 1925, A, **107**, 255.

† Burk and Gillespie, *Proc. Nat. Acad. Sci.*, 1928, **14**, 470.

‡ 'Chemistry at Interfaces', *J. Chem. Soc.*, 1925, **127**, 1207.

Moreover, the (boundary) phase is the seat of an electric field of prodigious intensity.' This is a principle which cannot be ignored in relation to chemical transformations at catalytically active surfaces.

It is connected, on the one hand, with the view that adsorption is governed to a great extent by the 'dipole' character of the adsorbed substance, and, on the other hand, with the theory that there is a close relationship between chemical change and ionization. For the first there is much to be said, for the second, on the whole, much less. Finch and Stimson,* following up some earlier work of H. Hartley,† have shown that gases such as oxygen, hydrogen, carbon monoxide, carbon dioxide, and steam impart electrical charges to hot metal surfaces. But whether or not the charged molecules adsorbed on the surface have any connexion with chemically active molecules, or whether the thermionic phenomena are quite independent, is hard to say. The answer given to this question would probably depend upon the attitude adopted to the more general question of the relation between ionization and chemical reaction. The view suggested earlier in this book is that the connexion is an inessential one.

Norrish‡ has sought to connect the catalytic activity of surfaces with their polar nature. By polar nature is meant a certain chemical unsaturation, usually associated with the presence of oxygen in the molecule. His work on the combination of ethylene and bromine has already been mentioned. The combination hardly takes place at all in vessels coated with paraffin wax, but is promoted by surfaces of such oxygen-containing substances as cetyl alcohol and stearic acid. To be quite conclusive such observations would have to be combined with others showing that the actual adsorption on paraffin wax is not very

* *Proc. Roy. Soc.*, 1927, A, **116**, 379.

† Ibid., 1914, A, **90**, 61.

‡ *J. Chem. Soc.*, 1923, **123**, 3006.

markedly less than on the 'polar' substances, or, better, that the heat of activation is really reduced when the molecules are adsorbed on the polar surface.

It must not be forgotten that a purely 'chemical' view of surface action has its adherents. If we regard molecules of hydrogen, adsorbed on the surface of an active nickel catalyst, as held by single valency bonds to the atoms of nickel we are already taking a very definitely chemical view of the matter. The system we are considering differs from a hydride of nickel only in that the nickel remains attached to the surface instead of being carried away in the gas phase. Under these circumstances we can only expect catalytic phenomena to be of an extremely specific nature.

On the other hand, since it seems that homogeneous reactions usually take place much less readily than surface reactions, the question obtrudes itself, again and again, whether the operation of some general cause is not superimposed on the various specific influences.

When two or more molecules must interact, their encounter is obviously facilitated by a more or less prolonged sojourn of one of them on a surface. It is not difficult to believe that adsorption in adjacent positions on a surface comes about more often than an appropriate encounter of the molecules moving at random in the free state.

But this factor is inoperative in the case of the many unimolecular transformations which take place in contact with solid surfaces.

Langmuir has pointed out that the adsorption of such gases as oxygen and hydrogen is probably accompanied by the resolution of the molecules into atoms. This production of free atoms naturally has the effect, on the one hand, of enhancing the reactiveness of the gases, and, on the other, of rendering possible the occurrence of such reactions as $N_2O = N_2 + O$. This permits the simple

unimolecular change to supersede a more complex bimolecular change involving the simultaneous activation of two molecules.

The experiments of Gauger,* Wolfenden,† and Kistiakowsky ‡ on the critical potentials of adsorbed hydrogen and nitrogen seem to provide direct evidence that these gases are taken up by metal surfaces in the form of free atoms, thus confirming Langmuir's view.

Another mechanism is perhaps worth considering. We may suppose a molecule to be composed of two parts, A and B, the separation of which constitutes the chemical decomposition of the molecule. Let B receive an impact from another molecule which imparts to it momentum directed away from A. The small inertia of A enables it to follow B without the development of much strain between the two. If, however, A were firmly enough held to a surface its inertia might be so great that the accelerating force, instead of drawing A after B, would cause the disruption of the 'bond' between them. The reluctance of homogeneous changes to proceed would thus be due to the small inertia of different parts of the molecules, which renders disruption by collision difficult. This, however, is but one of many mechanical pictures which speculation could draw.

There remains the possibility that the appearance of a general reduction of molecular stability accompanying adsorption on surfaces is illusory, and that the stability of molecules is increased as often as it is diminished. When the stability happens to be increased, naturally no effect is observed. It was the extremely widespread occurrence of catalytic reactions, and the rarity of homogeneous changes, which suggested the alternative view that there is some general influence superimposed on all the specific in-

* *J. Amer. Chem. Soc.*, 1924, **46**, 674.
† *Proc. Roy. Soc.*, 1926, A, **110**, 464.
‡ *J. Physical Chem.*, 1926, **30**, 1356.

fluences. If these specific influences alone are operative, further progress must await the solution of the wider problem of the general relation between mode of chemical union and properties. In the meantime, by empirical means, a special inorganic chemistry of interfaces is being built up.

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