HOMOGENEOUS REACTIONS

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THE FUNDAMENTAL QUESTION

We observe chemical changes of all kinds to go on and to lead to states of equilibrium. The study of these states of equilibrium is, roughly speaking, the affair of thermodynamics. But the rate at which equilibrium is attained varies to an unlimited extent. The object in studying what we call chemical kinetics is to arrive at an understanding of why molecules undergo chemical change, and to be able to predict the rate at which a given chemical reaction will take place under definite conditions. To realize that rate of chemical change is a significant matter it is only necessary on the one hand to consider the vast industrial processes depending on the catalysis of gas reactions, or on the other hand to reflect on the instability of all living matter, which makes large provinces of biochemistry an affair of reaction velocity. But before it is possible to predict rates of reaction for the benefit of these applied sciences, or indeed before we can say whether the problems they put are soluble at all, we have first to investigate the purely theoretical question of what actually happens in the act of chemical transformation. For this purpose, the study of simple reactions in the gaseous state offers most hope of success, because all the resources of the kinetic theory of gases can be drawn upon in aid of the enquiry.

Now in a survey of all the simple gaseous reactions which have been examined experimentally, we find that they fall into two fundamentally distinct classes, namely homogeneous reactions and heterogeneous reactions. In homogeneous reactions the chemical change takes place among molecules flying about freely in the gas phase; in heterogeneous reactions the chemical change takes place in contact with the wall of the vessel in which the gas is contained, or at the surface of some solid substance added to the system. The criterion of a homogeneous reaction is that its rate is independent of the extent of the solid surface exposed to the gas, while in a heterogeneous reaction the rate is directly proportional to the surface area.

Homogeneous gaseous reactions fall further into classes according to their "*order*," that is to say, according to the number of molecules participating in each individual act of chemical transformation. The order of a reaction is easily found by examining the effect of change of pressure on the velocity. Since, for example, the velocity of decomposition of ozone is proportional to the square of the partial pressure of the ozone, it follows from elementary considerations of probability that two molecules must come together before chemical change can occur. The process involved is thus $2O_3 = 3O_2$ and not $O_3 = O_2 + O$ which might have been the primary reaction, and have been followed by a rapid combination of the odd oxygen atoms. Unimolecular, bimolecular and termolecular gaseous reactions are known, but none of higher order.

A similar classification could be made of heterogeneous reactions. When for example nitrous oxide decomposes at the surface of platinum or gold the primary process is $N_2O = N_2 + O$ and not $2N_2O = 2N_2 + O_2$, which is the reaction taking place in the gas phase. But the real order of a heterogeneous reaction cannot be inferred from the effect of pressure on the velocity unless certain special conditions are fulfilled which require fuller consideration.[1]

ACTIVATION

In general, the act of chemical transformation of molecules depends upon a process known as "*activation.*" This involves the acquirement by the molecule or molecules of an amount of energy considerably above the average. The exact nature of this molecular energy—whether kinetic energy or internal energy of some kind—it is not necessary in the first instance to specify. Nor is the means by which the energy is acquired relevant immediately.

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[1] For a discussion of this see The Kinetics of Chemical Change in Gaseous Systems, Hinshelwood, Clarendon Press, Oxford, 1926, p. 155.

Under different circumstances and in different types of reaction the energy of activation may be of different kinds; it may sometimes be communicated to the molecule by a collision with another molecule or be received as a result of the absorption of some kind of radiant energy. Activation is an absolutely general process and is necessary both in homogeneous and in heterogeneous reactions. It forms the basis of the whole kinetic theory of reaction velocity. We may say that it is a necessary condition for chemical change that the molecule or molecules participating in the transformation should possess energy in excess of a certain minimum known as the *energy of activation.* The evidence upon which this statement is based is as follows.

1. In a chemical reaction which proceeds with measurable velocity only exceptional molecules are at any moment in a position to undergo transformation. This applies to reactions of the most diverse kinds. In a homogeneous unimolecular reaction, such as the decomposition of nitrogen pentoxide, it is obvious, since otherwise the molecules would all react at once. In a bimolecular change, such as the combination of hydrogen and iodine, it is easy to calculate the number of collisions taking place at a given temperature and pressure between molecules of hydrogen and molecules of iodine, and to show that only one of these in many millions leads to interaction. Again when oxygen at low pressure acts upon a hot tungsten wire, a very small fraction only of the molecules which strike the wire are able to react with it.[2]

2. Further the attainment of this exceptional reactive state is very markedly favoured by increase of temperature. The velocity constant of a reaction varies with temperature according to the Arrhenius equation[3] $d \log k/dT = E/RT^2$. This represents a very much more rapid increase than could be accounted for by such factors as increased collision frequency. Arrhenius himself suggested the existence of "inactive" and "active" molecules in equilibrium, the active molecules being formed endothermically from the inactive molecules. The increase of reaction velocity with temperature he attributed to the normal shift in

[2] Langmuir, J. Amer. Chem. Soc., **35**, 105, 931 (1913); **41**, 167 (1919).

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

the position of the equilibrium between active and passive molecules in accordance with the second law of thermodynamics. The quantity E of the equation would thus represent the heat of formation of the active molecules. The essential points of this theory are now generally accepted but expressed in rather a different way. We do not think of the active molecule as a sort of tautomeric form of the normal molecule, but merely as a normal molecule of exceptionally high energy content. In terms of the Bohr theory it can sometimes be regarded as a molecule in one of its higher quantum states, although it is not necessary in the first instance to formulate any precise views about this. The objection to thinking about the active molecule as a definite tautomeric form is that it would be very difficult to imagine what the tautomeric form could be in such simple reactions as the decomposition of ozone or of hydrogen iodide. That tautomeric change sometimes intervenes as one of the stages in more complex reactions, such as those of organic chemistry, is quite irrelevant. There is no reason why it should not. But it is not a fundamental characteristic of chemical change. An active molecule of hydrogen iodide has a structure no different from that of an ordinary one.[4]

The characteristic form of the relation between reaction velocity and temperature now follows at once from the equations of the kinetic theory, which express the distribution of energy among the molecules of a gas. At a given temperature the molecules have a certain average kinetic energy, a certain average rotational energy and so on. Some have much more than the average amount of a given kind, some much less. The exact form of the "distribution law" varies according to the kind of energy under consideration, but the following law is approximately true of all forms. If N be the total number of molecules, then the number N′ for which the energy of one particular kind, for example rotational, exceeds an amount ϵ is given by $N' = N e^{-\epsilon/kT}$ where k is the gas constant, R, divided by Avogadro's number. If instead

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[4] Compare Rice, Fryling and Weselowski, J. Amer. Chem. Soc., **46**, 2405 (1924). According to the present writer such views can only be applicable to quite special cases. See 1, p. 90.

of ϵ, the energy per molecule we write E, the energy per *gram* molecule, this becomes $N' = Ne^{-E/RT}$. The factor $e^{-E/RT}$ thus represents the probability that a molecule possesses energy of some given kind in amount greater than E, E being reckoned per gram molecule. Since the velocity of reaction is proportional to the number of activated molecules we have for the velocity constant

$$k = \chi e^{-E/RT}$$

The factor χ differs in form according to the nature of the reaction. In a bimolecular reaction, for example, it must involve the number of collisions between molecules of the right kind; in unimolecular reactions, on the other hand, it may be independent of the collision number, and may possibly involve the rate at which radiant energy can be transferred. To a first approximation it is independent of temperature—or at any rate its variation is negligible in comparison with the very rapid rate of change of the exponential factor $e^{-E/RT}$. Treating it therefore as constant and differentiating logarithmically with respect to T, we obtain the Arrhenius equation. Precisely analogous considerations, although slightly more complicated, apply to heterogeneous reactions.[5]

WHAT CONSTITUTES A SOLUTION OF THE FUNDAMENTAL PROBLEM OF CHEMICAL KINETICS?

In the light of what has just been said let us return for a moment to the question of the possibility of calculating reaction rates absolutely. We have seen that reactive molecules are represented by a fraction approximately equal to $e^{-E/RT}$ of the total number. E can be found from the temperature coefficient of the reaction velocity by application of the Arrhenius equation. The question arises whether we can hope to calculate it *a priori*, and the answer must be that the attempt is definitely outside the domain of chemical kinetics. Since it represents the energy which must be communicated to a molecule in order to render the parts capable of re-arrangement, its absolute calculation is obviously

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[5] Loc. cit., 1, p. 172 et seq.

a problem of molecular structure. A thermodynamic analogy may help at this point. The laws of thermodynamics enable us to predict with accuracy the shift of chemical equilibria with temperature, and even the absolute position of these equilibria, provided that we know the heat of reaction and certain other thermal properties of the system under consideration. But they do not under any circumstances relieve us from the necessity of finding out by quite independent means what the heat of reaction is in a given instance. To calculate heats of reaction would be a very difficult problem in molecular mechanics, which at the present time we should hardly think of attempting. In the study of kinetics the heat of activation, E, plays a part analogous to heat of reaction in the study of equilibria. It is a specific molecular property which must be determined for each reaction we study before further progress can be made. The legitimate scope of enquiry is then: given the heat of activation what is the absolute reaction velocity? This question we may hope to answer, and indeed a good deal of progress has already been made. In the equation.

$$\text{Rate of reaction} = \chi\, e^{-E/RT}$$

we must realize that E is the fundamental datum, determinable from the temperature coefficient, but the theoretical calculation of which belongs to the larger province of the relation between structure and physical constants. Our problem is to investigate the nature of χ in reactions of various types.

We will now review the various kinds of homogeneous reaction in order.

BIMOLECULAR REACTIONS

It is most convenient to start with the consideration of bimolecular reactions, because the theory of these has been more fully worked out than that of unimolecular and termolecular reactions. The following homogeneous bimolecular reactions are known: The decomposition of hydrogen iodide,[6] $2HI = H_2 + I_2$; the

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[6] Bodenstein, Z. physik. Chem., **29**, 295 (1899). In connection with some criticisms of H. A. Taylor, J. Amer. Chem. Soc., **28**, 984 (1924), see ref. 1, p. 49.

union of hydrogen and iodine,[7] $H_2 + I_2 = 2\,HI$; the decomposition of nitrous oxide,[8] $2N_2O = 2N_2 + O_2$; of ozone,[9] $2O_3 = 3O_2$; and of acetaldehyde in the gaseous state,[10] $2CH_3CHO = 2CO + 2CH_4$; the decomposition of chlorine monoxide,[11] $2Cl_2O = 2Cl_2 + O_2$ (ultimately), although attended with certain complications is also an essentially bimolecular change. All these have been fairly thoroughly investigated. The union of nitrogen and oxygen to nitric oxide,[12] and the decomposition of nitric oxide[13] have been stated to be bimolecular, but the experimental results, obtained by the rather unsatisfactory streaming method, are not quite unambiguous and are unsuitable for calculations, there being some doubt as to the homogeneous or heterogeneous nature of the reactions under the conditions of the investigations.

Bimolecular reactions depend upon collisions between two molecules. The number of collisions taking place in 1 cc. in unit time between like molecules can be calculated from the kinetic theory by the equation

$$\text{Number of collisions} = Z = \sqrt{2}\,\pi\,\sigma^2\,n^2\,\bar{u}$$

where σ = molecular diameter

$\bar{u}$ = root mean square velocity of the molecules

n = number of molecules in 1 cc. at the given temperature and pressure.

σ is calculated from viscosity data, and since viscosity is a phenomenon directly concerned with the mean free path and therefore with the collision number, any arbitrariness in our definition of the diameter of a molecule does not in the least affect the validity of the formula. Thus we can calculate the number of collisions with great certainty as to the order of magni-

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[7] Bodenstein, loc. cit., 6.

[8] Hunter, Z. physik. Chem., **53**, 441 (1905). Hinshelwood and Burk, Proc. Roy. Soc., A, **106**, 284 (1924).

[9] Chapman and Jones, J. Chem. Soc., **97**, 2463 (1910).

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

[11] Hinshelwood and Prichard, J. Chem. Soc., **123**, 2730 (1923). Hinshelwood and Hughes, J. Chem. Soc., **125**, 1841 (1924). The results were confirmed in Bodenstein's laboratory. Z. physik. Chem., **116**, 372 (1925).

[12] Nernst, Z. anorg. Chem., **49**, 213 (1906).

[13] Jellinek, Z. anorg. Chem., **49**, 229 (1906).

tude, although not with minute accuracy. It is to be noted that all molecular diameters are of the order 10^{-8} cm.

As we have said, the number of collisions turns out to be many millions of times greater than the number of molecules which react. This was one of the reasons for supposing activation to be necessary. Suppose one of the colliding molecules requires energy greater than E_1* and the other energy greater than E_2. The fractions of the total number having energies respectively greater than these amounts are $e^{-E_1/RT}$ and $e^{-E_2/RT}$ approximately. Thus of all the collisions, the fraction in which the two molecules satisfy the postulated condition is $e^{-E_1/RT} \times e^{-E_2/RT}$ or $e^{-(E_1+E_2)/RT}$. If we write $E = E_1 + E_2$ this means that a fraction $e^{-E/RT}$ of the collisions is between active molecules. The rate of reaction should be proportional to the total number of collisions multiplied by this factor. Thus number of molecules reacting $= A.\ Z.\ e^{-E/RT}$.

We know nothing about A except that it is independent of temperature. The internal economy of molecules, for all we know to the contrary, might be such that only one collision in many millions could be effective even when the condition of sufficient energy is satisfied. If, to take a rough and ready analogy, we liken the energy of activation to the effort necessary to drag open the heavy door of a safe, then the factor A represents the chance of finding the right combination for first opening the lock, a process which involves no expenditure of energy, but without which no expenditure of energy produces any effect. We shall see, however, that in bimolecular reactions the combination of the molecular locks is of an extremely primitive kind, and that the energy condition is the only important one.

Without knowing anything about A we can find E for, since Z is proportional to $T^{\frac{1}{2}}$, we have

$$k = \text{constant} \cdot \sqrt{T} \cdot e^{-E/RT}$$

whence, taking logarithms and differentiating, we have

$$d \log k/dt = E/RT^2 + 1/2T$$

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* E_1 and E_2 are calculated per *gram* molecule.

E can thus be found from the ratio of the velocities at two temperatures, and we can then substitute in the former equation and find A. Experiments show that in all known instances of bimolecular reactions the expression—number of collisions × $e^{-E/RT}$—comes out *nearly* equal to the actual number of molecules observed to react.[14] Thus no other *important* factor beyond the possession of the energy is necessary as a condition for reaction.

The consequence of this striking result is very clearly shown by comparing the different bimolecular reactions among themselves. Since all molecular diameters are of about the same magnitude, the collision number does not greatly vary between one gas and another. Moreover, if no important condition except the energy condition has to be satisfied, then the rate of a bimolecular reaction can be seen from the equation to be determined mainly by the value of the exponential factor $e^{-E/RT}$. Different bimolecular reactions have very different values of E. The greater the value of E the smaller the factor $e^{-E/RT}$, and therefore the smaller the reaction rate, or, looked at in another way the higher the temperature at which the rate of reaction will attain any given value. This expectation is confirmed in a very striking way.[15] For example, the energy of activation in the chlorine monoxide decomposition is 21,000 calories; that in the decomposition of hydrogen iodide is 44,000 calories. The latter reaction should therefore go much more slowly, as indeed it does. The two rates should be approximately equal at temperatures such that E/RT is the same for each. It is in fact found that the decomposition of hydrogen iodide proceeds at the same rate at 760° abs. as that of chlorine monoxide at 384° abs. Thus the absolute temperatures are almost exactly in the ratio of the heats of activation. Again, hydrogen iodide and acetaldehyde decompose at approximately the same rate at the same temperature. In accordance with this we find that their heats of activation are nearly identical, that of acetaldehyde being 45,500 calories. If

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[14] W. C. McC. Lewis, J. Chem. Soc., **113**, 471 (1918). Dushman, J. Amer. Chem. Soc., **43**, 397 (1921).

[15] Hinshelwood and Hughes, J. Chem. Soc., **125**, 1841 (1924). Hinshelwood and Thornton, Phil. Mag., **50**, 1135 (1925).

specific factors of the kind indicated by the analogy of the combination lock played any important part, there is no reason why these two reactions should not have equal heats of activation, but rates thousands of times different at the same temperature. There is then no doubt whatever, when it is found that all the known bimolecular reactions fit in in the same way, that the acquisition of the energy of activation is the all-important factor. The theory of the effect of temperature on reaction velocity shows the possession of this energy to be *necessary*, the kind of calculation which we have just been considering indicates that it may also be a *sufficient* condition for reaction.

When we attempt to go into the finer details of the reaction mechanism we can speak with less certainty. From the expression: *number of molecules entering into collision* $\times$ $e^{-E/RT}$ we can calculate the absolute rate of reaction within a factor of two or three times. This is remarkable enough having regard to the fact that it is an *absolute* calculation, and that an essentially wrong theory would throw us out by many *powers of ten.* We can thus regard the χ of the previous section as adequately explained in terms of collisions. But to be able to answer the question as to whether literally *every* collision is effective, we should need experimental data much more accurate than we possess or are ever likely to possess. Some of the active molecules may rebound without suffering chemical change. We only know that this number is not large enough to interfere with the general concordance of the results with the theory we have been considering. The factors which limit the precision of our knowledge are (*a*) the approximate nature of the distribution law which gives rise to the simple exponential factor in the equation for the reaction rate (*b*) the approximate nature of our values for σ (*c*) the experimental difficulty of determining E with very great precision. E can usually be found to within 3 to 5 per cent; this leaves us in doubt about the value of $Z.e^{-E/RT}$ to the extent of a factor of two or three when the number of molecules reacting is of the order $10.^{16}$ A certain amount of not very profitable discussion has arisen on this point, i.e., whether "every" activated molecule reacts. It is not probable that we shall ever know.

We can say, however, that we understand the nature of the factor χ in the case of bimolecular reactions.

TERMOLECULAR REACTIONS

Four termolecular gaseous reactions are known, all of which involve the participation of two molecules of nitric oxide. They are:

$$2\,NO + O_2 = 2\,NO_2 \qquad (^{16})$$
$$2\,NO + Cl_2 = 2\,NOCl \qquad (^{17})$$
$$2\,NO + Br_2 = 2\,NOBr \qquad (^{18})$$
$$2\,NO + 2H_2 = N_2 + 2H_2O \qquad (^{19})$$

This last reaction takes place in stages thus

$$2\,NO + H_2 = N_2O + H_2O \quad \text{or} \quad N_2 + H_2O_2$$

followed by the rapid decomposition of the nitrous oxide or hydrogen peroxide first produced. It is thus kinetically termolecular.

These reactions proceed in accordance with equations such as the following

$$\frac{-\,d[NO]}{dt} = k[NO]^2\,[O_2] \quad \text{or} \quad \frac{-\,d[NO]}{dt} = k[NO]^2\,[H_2]$$

The most natural supposition is that they depend upon a simultaneous collision between three molecules. It is however possible to assume that two molecules of nitric oxide first unite to form N_2O_2 and that there follows a bimolecular reaction between N_2O_2 and chlorine, bromine, oxygen or hydrogen as the case may be. If equilibrium between N_2O_2 and 2NO is established rapidly the concentration of N_2O_2 will always be proportional to $[NO]^2$, and since the rate of the bimolecular reaction will be proportional to $[N_2O_2]\,[O_2]$ for example, it will be proportional in turn to $[NO]^2\,[O_2]$ and thus kinetically termolecular. This seems to be a rather artificial assumption; it is not really

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[16] Bodenstein (and Fr. Lindner), Z. physik. Chem., **100**, 68 (1922).

[17] Trautz, Z. anorg. Chem., **88**, 285 (1914).

[18] Trautz and Dalal, Z. anorg. Chem., **102**, 149 (1918).

[19] Hinshelwood and Green, J. Chem. Soc., **129**, 730 (1926).

a necessary one, as we may see if we reflect on the peculiar nature of a ternary collision. In a binary collision there is a finite time during which two molecules are within a small enough distance of each other for a ternary collision to result should a third molecule arrive on the scene. This may be called the "duration of a collision." Now there is not a very great deal of difference from the kinetic point of view between two molecules of nitric oxide in a collision of finite duration, and the transitory formation of a molecule of N_2O_2, or a so-called "complex" of two molecules of NO. There are, however, positive objections to the hypothesis of N_2O_2 formation which we shall be in a position to understand when we have considered the question of the temperature coefficient of termolecular reactions.

Bodenstein made the remarkable observation[16] that the reaction $2NO + O_2 = 2\ NO_2$ has a very small but quite definitely negative temperature coefficient. Expressed in the usual way as the ratio of the velocity at $(t + 10)°$ to the velocity at $t°$ the coefficient changes from 0.912 in the neighborhood of 0° to 0.997 in the neighborhood of 350°. We should expect the temperature coefficient of a termolecular reaction to be much smaller than that of a bimolecular reaction for the following reason. A collision between three molecules is an event of great rarity compared with a binary collision. Hence if equal degrees of activation were required in two reactions, one termolecular and one bimolecular, the termolecular reaction would have to take place very much more slowly. Conversely, if the two reactions did in fact take place with the same speed at the same temperature, this would be because the termolecular reaction was associated with a much smaller energy of activation. Therefore, other things being equal, it would have a much smaller temperature coefficient. We can easily make a rough quantitative estimate of the difference to be expected. Bodenstein takes the ratio of the number of ternary collisions in a gas to the number of binary collisions as roughly equal to the ratio of the molecular diameter to the mean free path. This makes ternary collisions about 10^3 times less frequent at atmospheric pressure. The precise geometrical disposition of the molecules at the moment of impact is probably more important in a reaction like $2NO + O_2 = 2NO_2$ than in a simple bimolecular reaction like $2HI = H_2 + I_2$, so that the chance of a suitable termolecular encounter is probably about 10^4 times smaller than that of a suitable bimolecular encounter. Thus if a termolecular reaction is to attain the same rate as a bimolecular reaction at the same temperature, the energy of activation associated with it must be smaller by an amount ΔE such that $e^{-E/RT} \div e^{-(E+\Delta E)/RT} = 10^4$. At ordinary temperatures this means that the heat of activation would be about 6000 calories smaller, and at 1000° abs. about 15,000 to 20,000 calories smaller. It was pointed out in the last section that for bimolecular reactions the relation between heat of activation and absolute speed is fairly definitely known. A bimolecular reaction which could take place with measurable speed at the ordinary temperature would have a heat of activation of about 14,000 calories. Thus the heat of activation of a termolecular reaction which could occur rapidly enough to be measured at the ordinary temperature would not have to exceed about 8000 calories. The corresponding temperature coefficient would be quite small. The general discussion showed that the velocity constant of any reaction is a product of an exponential factor and another, being of the form $\chi\ e^{-E/RT}$. In bimolecular reactions χ involves the collision frequency, and thus increases in proportion to the square root of the absolute temperature. In termolecular reactions the term $e^{-E/RT}$ is such that a small positive temperature coefficient is to be expected. Thus the term χ, which depends on the frequency of ternary collisions must *diminish with temperature,* so that the velocity may in certain cases have a negative temperature coefficient, as for example in the reaction under discussion. Bodenstein suggests that this decrease is accounted for by the diminished "duration of collisions" at higher temperatures. The molecules move faster the higher the temperature; hence the smaller is the chance that two molecules shall remain close together long enough to be caught by a third molecule. The inversion of the temperature coefficient of the reaction velocity will of course only occur when the heat of activation is a small one, so that the "normal" temperature effect, represented by the exponential factor, is easily masked. In the combination of nitric oxide with chlorine and bromine respectively the temperature coefficient has actually a small positive value but very little above unity. In a reaction which does not take place with appreciable speed except at quite high temperatures the effect of the diminishing collision frequency should no longer be noticeable, because the heat of activation should be quite large. The reaction between nitric oxide and hydrogen[19] takes place in the neighborhood of 1100° abs. at a speed comparable with that of the reaction between nitric oxide and oxygen at the ordinary temperature. The heat of activation is 44,000 calories. A bimolecular reaction taking place with this same speed in the same region of temperature would be found to have a heat of activation of about 60,000 calories. It is obvious therefore that the relation between the two heats of activation is just about what would be expected from the relative chances of ternary and binary collisions. But quite precise calculations about termolecular collisions are difficult to make, so that it is not possible to analyze the matter in any more detail.

The discussion of these reactions becomes formally somewhat different if the view is adopted that they are really bimolecular reactions between N_2O_2 and a molecule of one of the other gases. The hypothetical bimolecular reactions must be assumed to have the normal temperature coefficients, but these are reduced or even inverted because the N_2O_2 is more and more dissociated at higher temperatures. It is very easy to show that the apparent heat of activation of the whole reaction is then equal to the difference between the heat of activation of the bimolecular reaction and the heat of dissociation of the double molecules of nitric oxide into single molecules. While formally this is quite satisfactory, Bodenstein points out that it necessitates the assumption of a quite considerable heat of formation of N_2O_2, which therefore, in accordance with Nernst's theorem, should be fairly stable at low temperatures. Since no trace of N_2O_2 formation has ever been observed the objection is a serious one. It will be seen that a general understanding of the mechanism of termolecular reactions is possible, although numerical calculations must at present deal with orders of magnitude rather than exact values. Still, within these limits the matter is quite clear. A very different state of affairs is found in dealing with unimolecular reactions.

UNIMOLECULAR REACTIONS

The thermal decomposition of nitrogen pentoxide,[20] and the thermal decomposition of gaseous acetone[21] are homogeneous unimolecular reactions. The decomposition of sulphuryl chloride,[22] although it takes place mainly on the walls in vessels of soda-glass, seems to be much less influenced by the walls in the case of vessels of Pyrex glass. The decomposition of phosphine,[23] at one time thought to be a homogeneous reaction, is mainly heterogeneous under the conditions where it can be measured. The claims that the transformation of cyclo-propane into propylene[24] becomes homogeneous at higher temperatures seem to rest upon a quite inadequate basis.

We shall confine our attention therefore to the decomposition of nitrogen pentoxide and to that of acetone. In the first reaction the nitrogen pentoxide decomposes into oxygen, nitrogen dioxide and tetroxide; in the second the acetone gives primarily carbon monoxide and ethane which suffers further decompositions. Nitrogen pentoxide decomposes at the ordinary temperature, acetone at a dull red heat.

The present position of the theory of unimolecular reactions may be outlined as follows:

1. Perrin[25] suggested that, since the rate of a unimolecular reaction is independent of the pressure of the gas, and it is thus possible to expand to an infinite volume without changing the probability that a molecule should be transformed, the process of chemical change cannot be determined in any way by molecular

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[20] Daniels and Johnston, J. Amer. Chem. Soc., **43**, 53 (1921).

[21] Hinshelwood and Hutchison, Proc. Roy. Soc., A, **111**, 245 (1926).

[22] D. F. Smith, J. Amer. Chem. Soc., **47**, 1862 (1925).

[23] Trautz and Bhandarkar, Z. anorg. Chem., **106**, 95 (1919). Hinshelwood and Topley, J. Chem. Soc., **125**, 393 (1924).

[24] Trautz and Winkler, J. pr. Chem., **104**, 53 (1922).

[25] Perrin, Ann. de Phys., [ix], **11**, 1 (1919).

collisions. This was the main support to the well-known "radiation theory" developed by W. C. McC. Lewis and by Perrin himself.

2. Two ways out of this situation have been proposed. Lindemann[26] pointed out that the ordinary experimental data relating to unimolecular reactions only proved that such reactions were independent of pressure over a certain range and did not necessarily justify extrapolation to infinite dilution. Independence of pressure over a wide, though not indefinitely extended range, can be accounted for without abandoning the hypothesis that activation is brought about by collision. It is only necessary to make the assumption that molecules gain and lose the energy of activation much more rapidly than they react. This could happen if the molecules had not only to receive the necessary energy but to be in a suitable internal phase before they could react, and if they got into this phase so rarely that they would probably lose the energy of activation they might gain in one collision by suffering another collision before reacting. By the distribution law there would be a constant fraction of the total number in possession of the energy of activation at any moment, whatever the pressure, and of these a constant fraction would react, this fraction being small enough to cause no appreciable change in the total concentration of active molecules. The reaction would thus be unimolecular over a considerable range of pressure. But at very low pressures the time between collisions would ultimately become so great that the loss of "active" molecules by chemical change could no longer be regarded as small in comparison with the rate of activation and de-activation. The supply could no longer be maintained, and the unimolecular velocity constant would decrease. The reaction would gradually assume the character of a bimolecular change. Christiansen and Kramers[27] propose what is known as the "chain mechanism." According to this the products of reaction, carrying away the original heat of activation plus any heat of reaction, are supposed to be able to activate by collision the next molecule of the

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[26] Lindemann, Trans. Faraday Soc., **17**, 598 (1922).

[27] Christiansen and Kramers, Z. physik. Chem., **104**, 451 (1923).

reacting substance which they encounter. This process goes on indefinitely. The normal proportion of molecules which gain the energy of activation by collision is thus kept constant whatever the pressure, or however fast active molecules are removed by chemical reaction, because every such removal is forthwith replaced by a fresh molecule activated by the "hot" reaction products. Thus the chemical change can take place in accordance with the unimolecular law, although in essence bimolecular. According to this theory a marked retarding influence should be exerted by inert gases such as the products of reaction themselves, since these would remove the energy from the "nascent" molecules of product before this energy could be given to fresh molecules of the reactant. Christiansen and Kramers are obliged to make the arbitrary assumption that the reaction products do not give up their energy except to the right kind of molecule. An assumption of this sort seems to demand experimental support before it can be accepted.

We have thus the following possibilities:

Activation by collision	Lindemann mechanism Christiansen-Kramers mechanism
Activation by absorption of radiation	Simple radiation theory[28] Extended radiation theory[29]

The simple radiation theory supposes that the molecule is activated by a quantum of monochromatic radiation, the frequency of which is given by E/Nh where E is the heat of activation, N is Avogadro's number and h is Planck's constant. A modification of the simple radiation theory supposes that several quanta are absorbed simultaneously or successively, while the extended radiation theory assumes that a whole continuous range of frequencies may be drawn upon for the supplying of the energy of activation.

These various possibilities will now be considered in relation to the experimental data for the decomposition of nitrogen pentoxide and of acetone.

[28] Perrin (25). W. C. McC. Lewis, J. Chem. Soc., **109**, 796 (1916); **111**, 457 (1917); **113**, 471 (1918).

[29] Cf. Tolman, J. Amer. Chem. Soc., 47, 1524 (1925).

The simple radiation theory breaks down at once. It predicts that the decomposition of nitrogen pentoxide should depend upon the absorption of radiation in the short infra-red. Radiation of the calculated frequency is now known to be without influence on the rate of reaction. The calculated frequency for the acetone decomposition lies in the visible region, where acetone does not absorb.

There is no obvious direct test of the extended radiation theory. It will, however, require further consideration when the collision mechanisms have been examined.

The chain mechanism is highly improbable. Hunt and Daniels[30] showed that the presence of a very large excess of nitrogen did not influence the rate of decomposition of nitrogen pentoxide, even when the pressure of the pentoxide was very small. Hirst[31] showed that argon had no effect on the rate of reaction. The rate of decomposition of acetone is not appreciably changed by the presence of nitrogen or of carbon monoxide, although experiments have not been made with very low pressures of the acetone.

Moreover it is not certain that the chain mechanism will work at all when the reaction is endothermic, as the unimolecular decomposition of N_2O_5 into N_2O_4 and O would be. It would however be unwise to reject the suggestion finally.

Lindemann's suggestion encounters still greater difficulties. In the first place, Hunt and Daniels found that the unimolecular character of the nitrogen pentoxide decomposition was preserved down to pressures of 0.01 mm. mercury, at least. Hirst and Rideal[32] have confirmed this, and shown that the velocity constant at very low pressures actually tends to increase somewhat rather than to decrease. This last fact is important in that it removes the objection that the experiments were not made at pressures sufficiently low for the expected decrease to reveal itself. The increase is supposed to be due to the circumstance that at high pressures some de-activation of molecules takes

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[30] Hunt and Daniels, J. Amer. Chem. Soc., **47**, 1602 (1925).

[31] Hirst, J. Chem. Soc., **127**, 657 (1925).

[32] Hirst and Rideal, Proc. Roy. Soc. A, **109**, 526 (1925).

place by collision with other molecules, and that this gets less at lower pressures.

A still more serious matter is that both in the decomposition of nitrogen pentoxide and in that of acetone the number of molecules which react is any way greater by very many times than the number which could be brought into the activated state by collision. The mechanism which is under discussion of course demands that the number of collisions should be not merely sufficient but much more than sufficient to keep up the supply of molecules with the necessary energy. In the case of the acetone decomposition the number of molecules reacting is about 10^5 times greater than the number which could be activated by collision.

It might be suggested that the calculations about the rate of activation by collision are founded upon false assumptions, and are quantitatively quite wrong. But the fact that analogous calculations yield such a coherent and satisfactory interpretation of bimolecular reactions makes this criticism seem rather improbable. A particularly striking contrast is found between the decomposition of gaseous acetone and that of acetaldehyde.[10] Although these two reactions are chemically similar, and take place in the same region of temperature, the first is unimolecular and the second bimolecular, as shown by the influence of pressure. This means that the second definitely depends upon collisions. If the calculation of the maximum rate of activation by collision is wrong as applied to acetone, there is no particular reason why it should not give equally discordant results when applied to the bimolecular reaction of the aldehyde. Yet in this instance the maximum number of molecules which can be activated by collision comes out, as usual, to be almost equal to the number which do actually react.

On the whole, therefore, there seems to be no good ground at present for denying that unimolecular reactions are what they seem to be, namely changes in isolated molecules, not determined by collisions with other molecules. It must be admitted that views about this matter have veered round rather rapidly during the last few years and are still far from fixed.

As far as we can see at the moment it looks as if some generalized form of radiation theory is not excluded. Perhaps the view that the molecules interchange energy by any kind of thermal radiation which they are capable of absorbing or emitting is the most satisfactory. The whole range of isothermal radiation, with which any gas at constant temperature is in equilibrium, can then be invoked. This might quite possibly have been accepted without much discussion as a reasonable and innocuous suggestion if the controversies over the obviously inadequate special radiation theory had never been raised. The special radiation theory is destroyed by the criticism that exposure of the gas to a source of intense radiation of the appropriate wave length should cause an enormous acceleration of the reaction, which is not in fact observed. The view here suggested as possible, though by no means proven, is at least not open to this objection. The radiation is not supposed to be necessary in itself; it merely provides the means by which the Maxwell distribution of internal energy among the molecules is maintained in spite of the loss of activated molecules in reaction, and despite the inadequacy of collisions as a means of maintaining this distribution. It is essentially the isothermal radiation which is involved. This, from the very nature of the fact that it is in equilibrium with the gas, is presumably convertible into all the other forms of molecular energy. Thus we cannot attempt to increase the rate of reaction by irradiation from an external source, since in the attempt we should increase simultaneously all the different kinds of molecular energy, and thus raise the temperature of the whole gas. Acceleration of a reaction by increase of temperature is, of course, not a phenomenon which need cause us worry. Since the radiation need not be assumed to be more than an internal carrier of energy, the distribution law to be used in the equation for the velocity of reaction is that referring to the internal energy of the molecules, and is not governed directly by the nature of the radiation.

Another point is whether interchange of energy among molecules by radiation can occur at a sufficiently rapid rate. This has been discussed by several writers but the question cannot at the moment be said to have received any definite answer.

The whole matter must be regarded as open.

In the case of bimolecular reactions, the factor E/RT has approximately the same value for different systems at temperatures of equal reaction velocity. There are also strong indications of a similar proportionality of E and T in termolecular reactions. It is interesting to find that the same is true of unimolecular reactions. The heat of activation in the decomposition of nitrogen pentoxide is 24,700 calories. The velocity constant at 55° is 0.00150. The velocity constant of the acetone decomposition does not reach this value until 562° is reached, that is, an absolute temperature 2.55 times as great. We find, in keeping with this, that the heat of activation of the acetone is also much greater, namely 68,500 calories. The respective values of E/RT are 38.0 for nitrogen pentoxide and 41.4 for acetone. It is clear, therefore, that, in this example also, the heat of activation plays the principal rôle in determining the absolute rate of reaction; other factors must play a comparatively minor part.

A GENERAL RULE

On the basis of what has been said, an attempt may be made to formulate a general rule which has never before been expressly stated. It appears to be of fundamental importance, although of an approximate character. The velocity constant of a reaction can be expressed in the form $\chi\ e^{-E/RT}$. The rule is that among reactions of a given type the variations in χ are small compared with the variations in the exponential term, and that, therefore, the gaining of the energy of activation is the principal determining factor in reactions. There is an analogy to this in the process of vaporisation, where the chance of a molecule gaining enough energy to evaporate is $e^{-\lambda/RT}$, λ being the latent heat. The rate of evaporation at a given temperature is then $A.e^{-\lambda/RT}$. Trouton's rule, which is roughly true, shows that for a given rate of evaporation λ/T is the same for most substances. Thus, variations in A from one substance to another are small compared with those of the exponential term. This again indicates that the acquirement of the energy is not only necessary, but sufficient, for evaporation to occur.

The rule about chemical reactions, which we have just discussed, is an approximation to the statement that the gaining of the energy of activation is not merely a necessary, but also a sufficient, condition for reaction to occur. This state of affairs is not exactly realized, but there is evidently an approach to it.

THE KIND OF ENERGY CONCERNED IN ACTIVATION

We have already discussed the question whether in unimolecular reactions the molecules are activated by collision or by radiation. The experimental evidence seems to show that they cannot be activated rapidly enough by collision. In polymolecular reactions collisions are necessary anyhow, whether they are directly concerned in the process of activation or not. Since the distribution law for all kinds of energy is approximately of the form $e^{-E/RT}$ it is easy to see that the number of collisions between molecules possessing already some kind of energy in excess of E is nearly equal to the number of collisions in which the kinetic energy of translation exceeds this same amount. It is thus quite possible, or even probable, that the energy of activation in polymolecular reactions is, in the first instance, ordinary translational energy, which is converted into internal energy of the right kind at the moment of impact. But there is no reason why all forms of energy should not be operative at once, since there is a continual interchange between all the possible forms of thermal energy. For fuller discussion reference may be made to a paper of Tolman.[29]

THE INFLUENCE OF INERT GASES AND OF MOISTURE ON THE RATE OF GASEOUS REACTIONS

In general this is small or negligible. Foreign gases, such as nitrogen, carbon dioxide or oxygen, do not accelerate or retard the simple bimolecular reactions such as the decomposition of nitrous oxide. Nor is the decomposition of nitrogen pentoxide affected by the presence of a large excess of foreign gases. Griffith and McKeown[33] came to the conclusion that the decomposi-

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[33] Griffith and McKeown, J. Chem. Soc., **127**, 2086 (1925).

tion of ozone was somewhat retarded by oxygen and slightly accelerated by argon, nitrogen and helium. Unfortunately under the conditions of their experiments the reaction was partly homogeneous and partly heterogeneous, which makes the results a little inconclusive. (It is possible with suitable vessels to investigate the purely homogeneous reaction as Chapman and Clarke have shown.) But, from the fact that the velocity constants drift less when the reaction is accelerated by an inert gas than in the absence of the inert gas, the conclusion was drawn that the homogeneous change was the one accelerated. Griffith and McKeown suggest that the activated ozone molecules remain associated for a finite time during which they may collide with a molecule of the inert gas. Collision with oxygen favors the resolution of the complex into molecules of ozone once more, while collision with argon favors the resolution into the products of reaction. The magnitude of these effects is not great, but it is desirable that the matter should be investigated further.

Knowledge of the influence of inert gases is of particular interest in the case of reactions where two molecules unite to form a single one, or where two atoms unite to form a molecule, e.g., $Br + Br = Br_2$. Herzfeld[34] points out that when two atoms collide and form a molecule by an exothermic reaction, then the "nascent" molecule contains not only the original energy of the two atoms but also any heat liberated in the reaction. It should therefore, according to him, be incapable of continued existence unless it can give up this excess energy in a collision with some other molecule. Thus for the reaction $A + B = AB$ to complete itself there is needed not merely a binary collision of A and B but a ternary collision of A, B and a third molecule C. This argument does not apply to bimolecular reactions of the type $A + B = C + D$, because C and D fly apart after the collision in which they are formed, carrying with them the excess energy in the form of kinetic energy.[35] No reaction so far mentioned in this discussion is of the kind to which Herzfeld's theory is applicable. Nor are examples easy to find: reactions such as the union

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[34] Herzfeld, Z. Physik, **8**, 132 (1922).

[35] Born and Franck, Ann. Phys., [iv], **76**, 225 (1925).

of ethylene with chlorine[36] and with bromine[37] are surface reactions. The same is probably true of the union of hydrogen chloride and ammonia.[38] In these, therefore, there is naturally no difficulty about removing the heat of reaction from the "hot" newly formed molecules. The combination of phosphorus trichloride with chlorine[39] to form the pentachloride is, it is true, a homogeneous reaction, but its rate is much too great to be measured.

Indeed, the only reaction which is suitable for the testing of Herzfeld's theory is the combination of bromine atoms to form molecules. The rate of this was determined by an indirect method by Bodenstein and Lütkemeyer[40] and by Bodenstein and Müller.[41] It was not influenced by inert gases in the sense to be expected; the fraction of the total number of collisions between bromine atoms which leads to combination was found to be rather a small one, but it was independent of the total pressure of the gases present in the system.

It is, of course, now recognized that, since molecules possess more than a single degree of freedom, it is quite possible for them to contain energy considerably in excess of the energy of decomposition into their atoms. If, therefore, the heat of reaction were shared among several degrees of freedom there is no reason why the molecule should be incapable of continuing to exist when once formed. Since, however, the vibrational and rotational energy are quantised, it is improbable that the amount of energy to be shared out will be an exact number of quanta. Hence the sharing will be impossible unless the difference between the total energy and some exact number of quanta can be disposed of. In reactions where two or more molecules of product are formed the translational energy of the rebounding molecules provides a means of adjustment. When one molecule only is formed the

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[36] Norrish and Jones, J. Chem. Soc., **129**, 55 (1926).

[37] Stewart and Edlund, J. Amer. Chem. Soc., **45**, 1014 (1923).

[38] Unpublished observations of R. E. Burk in Oxford.

[39] H. A. Taylor, J. Physical Chem., **28**, 510 (1924).

[40] Bodenstein and Lütkemeyer, Z. physik. Chem., **114**, 208 (1924).

[41] Bodenstein and Müller, Z. Elektrochem., **30**, 416 (1924).

excess would have to be radiated away. The radiation need only be a small quantum of some appropriate quite low infra-red frequency, which would not be noticed in an ordinary experiment. But little is known about this.

Of the chemical changes which have been investigated, homogeneous gas reactions do not constitute a very large fraction. Hence it is not always safe to apply to them conclusions which have been reached in quite different fields. The question has sometimes been raised whether it is profitable to attempt the interpretation, in terms of the kinetic theory, of reactions which, it is alleged, would not go at all if the gases were completely dried. This question is based upon a misconception. Most of the reactions investigated by Baker and others, and which have been found to be inhibited by intensive drying are either reactions between substances in different phases, e.g., the action of sulphur trioxide on barium oxide, or are surface reactions—the combination of ammonia and hydrogen chloride is probably an example of this kind. The photochemical union of hydrogen and chlorine is inhibited by drying,[42] but this is a special case of a very peculiar kind, which presents abnormal features in nearly every possible respect. In none of the simple homogeneous gas reactions of definite order, of which the molecular statistics have been worked out, has the inhibition by drying been demonstrated, or even claimed. Nor would such an effect be intelligible. A typical instance of the behaviour of a system where reaction is stopped by drying is provided by the union of ammonia and hydrogen chloride. Unless quite exceptional precautions are taken to dry the containing vessels, the reaction takes place with immeasurable rapidity. If the walls are completely dried, the reaction does not take place at all. There is no regular proportionality between water content and reaction velocity, as there would be if a definite ternary interaction between NH_3, H_2O and HCl occurred. On the other hand, in a heterogeneous reaction this behavior is quite understandable;[43] if there is sufficient water to form a uni-

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[42] Coehn and Jung, Z. physik. Chem., **110**, 705 (1924).

[43] Bowen, J. Chem. Soc., **125**, 1235 (1924). Norrish, Faraday Society. Discussion on Photochemical Reactions in Liquids and Gases. (1925), page 575.

molecular layer over the surface, the full effect is exerted, and any excess beyond this minute trace has no further influence.

The explosion of carbon monoxide and hydrogen is presumably a homogeneous change, even if rather ill-adapted for measurements relating to the kinetics of the reaction. In this example, however, there is, just as we should expect, a regular proportionality over an extended range between water content and the speed of the explosion wave. The water here plays a definite stoicheiometric part in the series of changes, the first of which is probably $CO + H_2O = CO_2 + H_2$.

We must, in short, regard purely negative criticisms of the results of kinetic studies of gas reactions as uninformed.

PHOTOCHEMICAL REACTIONS IN GASES

Light is absorbed and emitted by molecules in quanta the size of which is determined by the well-known relation—*energy* $= h\nu$ Thus illumination with monochromatic light provides a means for supplying to the molecules accurately known amounts of energy. It might therefore be expected that a simple relationship would exist between the frequency of the photochemically active light and the heat of activation. Any hope of discovering more about the mechanism of chemical reactions in this way is, however, disappointed. The reason is not difficult to see, and can be explained best with a simple illustration. Let us consider the chlorine molecule. In this two atoms are united by what is called a non-polar link, which probably involves electronic orbits common to both nuclei. Each atom has also its own independent electrons. Stimulation of the molecule by light in the visible region of the spectrum causes these latter electrons to move to higher quantum orbits. Much energy may be absorbed by one or other of the two atoms in this way before the link bebetween them is affected and the molecule decomposed. In fact, the energy taken up may be much greater than the energy of dissociation. Photochemical stimulation puts the energy in the wrong place; it is an extravagant method of molecular activation. We find, quite in keeping with this idea, that the quanta involved in photochemical changes are in general much greater than ordinary chemical heats of activation.[44]

Nevertheless the study of photochemical changes has led to the discovery of certain facts of fundamental importance to chemical kinetics generally. In most cases these reactions conform more or less to the Einstein law of photochemical equivalence. The basis of this law is best stated as follows: (*a*) Light is in the nature of things absorbed by the molecules in quanta of magnitude $h\nu$. (*b*) The quantum of light corresponding to the visible region of the spectrum is a large quantity of energy for one molecule to possess, and, if a molecule does not react at once when the light is absorbed, it is almost certain to lose the energy again in a collision before it has the chance to absorb a second quantum. Thus processes in which molecules absorb more than one quantum of visible light are seldom or never found. (*c*) The light quantum being an amount of energy very many times greater than the average energy of a molecule at ordinary temperatures, it is not likely that the effectiveness of the light in bringing about chemical change will be much influenced by minor variations in the internal state of the molecule. Thus if the light is capable at all of provoking the reaction, it is probable that each quantum will be effective. This is the Einstein law which states that one molecule is caused to react for each quantum of the active light which is absorbed.

In the decomposition of hydrogen bromide and of hydrogen iodide in the gaseous state Warburg[45] found that two molecules are decomposed for each quantum absorbed. Bowen[45] found the same to be true of the decomposition of chlorine monoxide. This is explained by assuming the mechanism:

$$Cl_2O + h_\nu = Cl_2O \text{ (activated)}$$
$$Cl_2O \text{ (activated)} + Cl_2O = 2\ Cl_2 + O_2$$

or

$$Cl_2O + h_\nu = Cl_2 + O$$
$$Cl_2O + O = Cl_2 + O_2$$

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[44] Bowen, ibid., page 543.

[45] See collected summary by Allmand, ibid., p. 444.

The formation and decomposition of ozone roughly conform to the Einstein law, as also do the combination of chlorine and sulfur dioxide and the bromination of C_6H_{12}.[45] Only one molecule in four of ammonia appears to decompose. This result however may not be very exact.

On the other hand, many molecules of phosgene are formed from carbon monoxide and chlorine for a single quantum, and hundreds of thousands of molecules of hydrogen and chlorine combine for each quantum of light. Reactions of this kind have to be interpreted by what is called the "chain mechanism." An example of the sort of way in which this works is the following:

$$\begin{aligned} Cl_2 &= 2\,Cl \\ Cl + H_2 &= HCl + H \\ H + Cl_2 &= HCl + Cl \text{ ad lib.} \end{aligned}$$

This is illustrative merely. In the hydrogen-chlorine reaction water intervenes also in the reaction chains. In general, there is a primary photochemical reaction followed by a series of purely thermal changes. Weigert and Kellermann[46] have found direct evidence of the existence of these chains by examining cinematographically the condition of the gas after momentary illumination with a spark.

It is a matter open to question, however, whether the reaction chains in the hydrogen-chlorine combination are not partly subject to the influence of the walls of the vessel. Opinion on this matter is divided, and decisive experiments have not been made.

An interesting region of transition between photochemical and thermal reactions is opened up by the experiment of Cario and Franck,[47] in which a mixture of hydrogen and mercury vapor was exposed to the light of the mercury line 2536.7 Å. The mercury atoms, excited by the light, were able on collision to resolve hydrogen molecules into atoms—or at least to convert them into a chemically active form. A number of other experiments of this kind were made by Taylor and Marshall,[48] who activated

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[46] Weigert and Kellermann, Z. physik. Chem., **107**, 1, (1923).

[47] Cario and Franck, Z. Physik, **21**, 161 (1922).

[48] Taylor and Marshall, J. Physical Chem., **29**, 1140 (1925).

the hydrogen in this way and caused it to react with ethylene, carbon monoxide, oxygen and nitrous oxide in the cold. According to Hirst and Rideal,[49] however, these reactions only take place when liquid mercury is present and its surface is illuminated. The reactions according to this are heterogeneous. In any case the possibility of mercury hydride formation must not be ignored.

MISCELLANEOUS REACTIONS

An interesting, if specialised, question is that of the part played by free atoms in chemical kinetics. The rate of decomposition of carbonyl chloride[50] in the region of 700° is proportional to the square root of the concentration of the chlorine present. This suggests that the decomposition depends upon a collision of a carbonyl chloride molecule with a chlorine atom, the concentration of atomic chlorine being proportional to the square root of that of the molecular chlorine, since $[Cl_2] = K\,[Cl]^2$.

Norrish and Rideal[51] suppose the interaction of hydrogen and sulfur in the gaseous state to take place between hydrogen molecules and sulfur atoms, formed by the dissociation of more complex molecules in the sulfur vapor.

Bromine atoms appear to intervene in the very complicated reaction mechanism by which hydrogen and bromine combine.[52] The following stages are supposed to be involved:

$$\begin{aligned} Br_2 &= 2\,Br \\ Br + H_2 &= HBr + H \\ H + Br_2 &= HBr + Br \\ H + HBr &= H_2 + Br \end{aligned}$$

This mechanism leads to the equation

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

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[49] Hirst and Rideal, Nature, **116**, 899 (1925).

[50] Christiansen, Z. physik. Chem., **103**, 99 (1922). Bodenstein and Plaut, ibid., **110**, 399 (1924).

[51] Norrish and Rideal, J. Chem. Soc., **123**, 696, 1689, 3202 (1923).

[52] Bodenstein and Lind, Z. physik. Chem., **57**, 168 (1906).

where m is a constant. This equation was established empirically by Bodenstein and Lind before the theory of the process was proposed.

Reactions of this kind depending upon a quite specialized reaction mechanism are usually too complicated to be analyzed completely into their separate steps in such a way that the heat of activation of each can be found.