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THE MECHANISM OF CHEMICAL REACTION

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1. The Concept of Activated Molecules.—It was first shown by Arrhenius[1] that in order to account for the large effect of temperature on the velocity of chemical reactions it seems advantageous to postulate that the molecules that actually undergo chemical change are in special *activated states*, having a larger energy content than the average molecule. Thus in the case of chemical changes involving a single molecule we assume that reaction is due to the continuous presence of a quota of activated molecules, of high energy content, a certain fraction of which undergo in each unit of time the chemical change in question, and in the case of reactions between two or more molecules we assume that reaction occurs only through the interaction of suitably activated molecules having more than the average energy content.

The quota of molecules in a given activated state is assumed to be replenished, as they are used up in the reaction by the striving of the molecules towards a statistical distribution which accords with the Maxwell-Boltzmann distribution law, the large temperature coefficient of reaction velocity being due to the large increase with temperature in the tendency for molecules to assume high energy contents which is required by this distribution law. During the progress of a reaction the fraction of the molecules in a given activated state will of course fall somewhat below that predicted by the Maxwell-Boltzmann law, if the rate of chemical change is of the same order of magnitude as the rate at which the reëstablishment of the Maxwell-Boltzmann distribution can take place. Indeed, there may easily be extreme cases in which activated molecules are used up by the reaction as fast as they receive their activation, so that the concentration of molecules in the activated state falls practically to zero. This possibility, however, which will be more fully discussed in a later section, does not seem to invalidate the general idea of activated states.

At the present time, the detailed nature of the activated states responsible for any particular chemical reaction is but rarely known. Sometimes, however, there is sufficient evidence to indicate that the transition to the activated form involves a chemical change already made familiar in other connections. Thus, for example, from the fact that the rate of combination between gaseous bromine and hydrogen[2] is proportional to the square root of the bromine concentration we conclude that the activa-

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

[2] Bodenstein and Lind, *ibid.*, **57**, 168 (1907).

tion of bromine involves its dissociation into atomic form. In general, however, we have to assume activated forms which must be regarded as transitory tautomers which could not be isolated from the normal form. Thus, a study of the temperature coefficient for the combination of bromine and hydrogen leads to the belief that a further activation in addition to the dissociation into bromine atoms is necessary, which may mean that the hydrogen also has to be activated and that the activation process leads to a tautomeric form of hydrogen of less energy content than would be necessary for complete dissociation.

In recent years the concept of activated molecules has received further certainty and clarity through the development of the quantum theory, since we now identify these tautomeric *activated* states with *higher quantum states* of the molecule.

2. **Purpose of the Present Article.**—At the present stage of theoretical development, there has been practically unanimous agreement as to the concept of activated states and their role in chemical reaction outlined above.[3] There has, however, been room for a great diversity of speculation as to the actual mechanism of the processes by which the quota of activated molecules is maintained, since the Maxwell-Boltzmann law tells us, indeed, that there must be some tendency for molecules to pass from unactivated to activated states as the latter are used up by chemical reaction, but gives no immediate information as to the speed or mechanism with which this tendency towards the establishment of statistical equilibrium will assert itself. It is the purpose of the present article to discuss the various mechanisms of chemical activation which have been proposed, in order to estimate their possible importance for chemical reaction.

3. **Proposed Mechanisms of Activation.**—The following mechanisms of activation have all of them been suggested at one time or another as sufficient to account for chemical reaction.

a. Activation by collision with another molecule of high enough kinetic energy (ordinary collision).

b. Activation by collision with another molecule which is itself in an activated state, resulting in a transfer of energy of activation (collision of the second kind).

c. Activation by the absorption of monochromatic radiation of the frequency calculated from the temperature coefficient of the reaction rate (simple radiation theory of chemical reaction).

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[3] There is no intention on the part of the writer to deny the possibility of reactions without activation. Such reactions, however, would not have the normal temperature coefficient found in typical chemical reactions, and are not the ones of special interest in the present article.

Attention is called to the difficulty of drawing a clear-cut distinction between the "active molecules" long familiar in chemical theory and the "residual molecules" just invented by Rice, Fryling and Wesolowski, THIS JOURNAL, **46**, 2405 (1924).

d. Activation by interaction with more than one frequency (elaborated radiation theory of chemical reaction).

It is a matter of considerable interest that the above mechanisms of chemical activation were all actually first proposed by chemists before the newer developments of the quantum theory were available. Nevertheless, these methods of activation are as a matter of fact the very mechanisms now discussed in general in the quantum theory for the passage of atoms and molecules from lower to higher quantum states. The rapid progress of the quantum theory makes profitable a frequent reëxamination of the suggestions.

4. **Magnitude of the Energy of Activation.**—As the first step in investigating the mechanism of activation for any particular reaction, we shall wish to know the magnitude of the energy of activation for the chemical change under consideration. To obtain this information we shall use the following equations connecting rate of reaction with energy of activation and temperature. For first-order reactions, we shall write

$$-\frac{dC}{dt} = kC = k' e^{-\frac{E}{RT}} C \qquad (1)$$

E being the energy of activation per mole and k' a constant; and for second-order reactions we shall write

$$-\frac{dC}{dt} = kCC' = k' T^{1/2} e^{-\frac{E+E'}{RT}} CC' \qquad (2)$$

$E + E'$ being in this case the sum of the energies of activation for the two kinds of molecules M and M', and k' again a constant.

Although the above equations are satisfactory as an empirical expression of the facts, and equations at least approximately agreeing with the above have been used by most workers in this field since the investigations of Arrhenius, nevertheless the theoretical deduction of the equations and the justification for identifying the empirical quantity E (or $E + E'$) with energy of activation are still not entirely satisfactory. This is due to the fact that most attempts at derivation have involved special assumptions as to the nature of the activated states, or the mechanism of activation. Thus, for example, if we assume only a single activated state for each kind of molecule entering into the reaction, and a mechanism of activation fast enough to maintain the Maxwell-Boltzmann quota of activated molecules, we can evidently obtain Equation 1 by making the rate of a unimolecular reaction proportional to the number of activated molecules present, and obtain Equation 2 by making the rate of a bimolecular reaction proportional to the number of collisions between activated molecules. Unfortunately, the assumptions involved in such a treatment limit the generality of the conclusions. However, the possibility of deducing the equations in a more general way will be considered in some detail in another place, where we shall find some justification for the general conclusion that the mean energy of activation can be in all cases at least approximately determined from the expression given.

5. Relative Speed of Activation and Reaction.—As a further step in analyzing the mechanism of activation for a given reaction we shall examine the speed with which the activation process must take place. As a minimum requirement it is evident that the number of molecules activated per second must be at least as great as the number which react in that time, since otherwise the steady continuance of the reaction would be impossible. In addition to the above minimum requirement, however, the known facts as to the order of the reaction will in general impose additional restrictions on the possible nature of the activation mechanism.

If the rate of activation is only just sufficient to furnish the number of activated molecules which are necessary for the reaction, it is evident that the overall rate of the reaction will be determined by the rate of activation, and will be affected by changes in concentration in the same way as the rate of activation. In other words, if the rate of activation is very slow, the order of the reaction will be determined by the order of the activation process. On the other hand, if the rate of activation is very high compared with the rate of the reaction, a constant quota of activated molecules equal to that prescribed by the Maxwell-Boltzmann distribution law will in any case be maintained, and the overall order of the reaction will be the same as the order of the reaction in which the activated molecules themselves take part.

In the sequel we shall wish especially to apply these considerations to cases of first- and second-order gas reactions. In the case of a first-order reaction, we shall be able to conclude that the rate of activation either must be very fast compared with the rate of reaction, or must itself be independent of concentration. This, for example, would rule out activation by ordinary collisions as a possible mechanism for first-order reactions, unless it could be shown that the rate of activation by collisions is very fast. In the case of a second-order reaction, on the other hand, we shall be able to rule out any method of activation which is independent of concentration, unless the method of activation is itself very fast compared with the rate of reaction.

6. Experimental Material for Test.—We shall find it profitable to use as far as may be the same reactions for testing out the possibility of the different mechanisms of activation. For this purpose we shall, for obvious theoretical reasons, choose definite first- or second-order gas reactions, proceeding homogeneously throughout the gas, not catalyzed by the walls or by any substance present in the gas. Reactions of higher order than the second will not be considered, since it seems probable that they may often be the result of a combination of individual steps which are themselves of the first or second order.[4]

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[4] See Trautz, *Z. anorg. Chem.*, **102**, 81 (1918).

There has apparently been an undercurrent of feeling in a number of quarters that there are no real examples of homogeneous uncatalyzed gas reactions, but that all gas reactions actually take place either on the wall of the containing vessel or through some obscure mechanism of homogeneous catalysis. If this should really be true, it would seriously limit the value of the conclusions presented in this article, since logical as the deduction of these conclusions might be, their main importance would certainly lie in the explanation they might afford of chemical processes which sometimes actually exist.

As to the possibility that all gas reactions actually occur *only* on the walls of the container, there is certainly now enough evidence to show very definitely that this is not the case. The following examples will suffice. By changes in the ratio of surface to volume of the container, the reaction of hydrogen and bromine,[2] and the decomposition of ozone[5] at 100°, have been shown to be largely unaffected by wall surface. By the more drastic test of adding glass wool, powdered glass, or powdered silica according to the nature of the container, the decomposition of nitrogen pentoxide,[6] chlorine monoxide[7] and nitrous oxide[8] have been shown to be certainly almost completely homogeneous, and the decomposition of hydrogen iodide[9] has been shown to take place only to a limited extent on the walls. Finally, by a method of visual observation it has been shown that chlorine and phosphorus trichloride[10] unite in the gaseous phase to form a supersaturated vapor of pentachloride.

The other possibility, that gas reactions, even if not catalyzed by the wall, always depend on catalysis by minute traces of foreign gas, is an elusive one to dispose of experimentally, since it might be that the reaction was catalyzed by the presence of an amount of material below that analytically determinable, as is certainly true in the case of some reactions catalyzed by water vapor. The following remarks may be made, however. In the first place, in the case of gas reactions of simple and constant order, like the decomposition of nitrogen pentoxide or the union of hydrogen and iodine, the most natural explanation of the order is that it corresponds to the order of the elementary process entered into by the molecules of the reactant, and it would not seem sensible to abandon this explanation by the introduction of a catalytic step until forced to by experimental evidence. In the second place, there are some reactions like the decomposition of nitrogen pentoxide which take place with the same specific rate under a very wide variety of conditions, which would seem improbable

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[5] Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908).

[6] Daniels and Johnston, This Journal, **43**, 53 (1921).

[7] Hinshelwood and Prichard, *J. Chem. Soc.*, **123**, 2730 (1923).

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

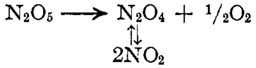
[9] H. A. Taylor, *J. Phys. Chem.*, **28**, 984 (1924).

[10] H. A. Taylor, *ibid.*, **28**, 510 (1924).

if the reaction were due to accidental traces of catalyst. Finally, the esoteric dictum that all reactions have to be catalyzed, suggests an unkind inquiry as to whether the reaction between the reactant and the catalyst also has to be catalyzed by a second catalyst, and the action of this second catalyst promoted by a third catalyst, and so on *ad infinitum.*[11] Certainly the individual steps in any chemical change must themselves be reactions of some definite order, so that experimental material of the kind of interest, at least exists, even if we have not yet discovered it.

a. **Unimolecular Reactions.**—As the most clear cut example of a first-order, unimolecular reaction, we shall take the decomposition of nitrogen pentoxide. This was shown to be first order, over a range of concentrations and at a series of temperatures, by the work of Daniels and Johnston.[6] They also showed by changing the shape and size of their reaction vessels and by the introduction of glass wool that the reaction is not appreciably catalyzed by the wall surface. For a time, however, it was suspected on account of the work of Daniels, Wulf and Karrer[12] that the reaction might be autocatalytic, owing to abnormality in the apparent rate of decomposition in the presence of an excess of ozone. It has since been shown, however, by the work of White and Tolman[13] that the initial specific rate, as soon as the excess ozone is used up, is the same as that throughout the run. This later work also showed the important fact that nitrogen pentoxide mixed with a thousand times its volume of oxygen decomposes at the same rate as the approximately pure nitrogen pentoxide present in the first stages of the runs of Daniels and Johnston, or the pentoxide mixed with decomposition products present at later stages.

The final overall results of the decomposition process can be expressed by the formula



$$N_2O_5 \longrightarrow \underset{\underset{2NO_2}{\upharpoonleft\!\downharpoonright}}{N_2O_4} + {}^1/_2O_2 \qquad (A)$$

In the early stages of a run the decomposition will be practically entirely to form nitrogen dioxide and in the later stages of the run an increasing proportion of tetroxide will be formed.

The thermochemistry of the reaction will be of great significance for our later considerations. The overall reaction is apparently *endothermic,* even if the decomposition goes only to the stage of the tetroxide, as shown in the following equations:

$$N_2O_5 = N_2O_4 + {}^1/_2O_2 - 2690 \text{ cal.} \qquad (B)$$
$$N_2O_5 = 2NO_2 + {}^1/_2O_2 - 16{,}290 \text{ cal.} \qquad (C)$$

where the heat of reaction is in calories per mole at constant pressure in the neighborhood of room temperature. The result given by Equation

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[11] See Perrin, *Trans. Faraday Soc.,* **17,** 605 (1922).

[12] Daniels, Wulf and Karrer, THIS JOURNAL, **44,** 2402 (1922).

[13] White and Tolman, *ibid.,* **47,** 1240 (1925).

B is calculated by combining Thomsen's[14] values for the heat of oxidation of an aqueous solution of tetroxide and heat of solution of tetroxide, with Berthelot's[15] values for heat of sublimation and heat of solution of pentoxide. The value 2690 is of course not exact, but since the calorimetry involved is all pretty straightforward it would seem as if the reaction certainly were endothermic. In the early stages of decomposition, when the tetroxide all dissociates, the reaction is of course strongly endothermic.

The rate of decomposition of nitrogen pentoxide as a function of concentration and temperature can be satisfactorily expressed by the following equations which represent the results of Daniels and Johnston,

$$-\frac{dC}{dt} = kC;\ k = 4.56 \times 10^{13}\, e^{-\frac{24,700}{RT}} \tag{D}$$

where the specific rate k is in reciprocal seconds and the energy of activation is in calories per mole of pentoxide.

The decomposition of nitrogen pentoxide is certainly the best example we now have of a homogeneous, unimolecular gas reaction. The dissociation of phosphine, which has been used in the past to test many theories of reaction velocity, has recently been shown to take place probably almost completely on the walls of the vessel.[16] The newly studied transformation of trimethylene into propylene, however, has apparently been shown by the work of Trautz[17] to be unimolecular and to occur under suitable conditions to a large extent homogeneously throughout the gas, although additional work on the effect on the walls would be desirable. Furthermore, from the recent work of Bodenstein and Lütkemeyer,[18] the dissociation of gaseous bromine into the atomic form appears to have a definite unimolecular rate which can be calculated by combining the rate which they find for the bimolecular recombination with the known value of the equilibrium constant for the reaction. We call special attention to the fact that the rate for this dissociation of bromine, and the rate for the transformation of trimethylene would lead to the same conclusions as we shall obtain in the sequel from the rate of decomposition of nitrogen pentoxide. Some of the considerations to follow could also be applied to reactions in solution, and in so far as this is possible we again obtain similar conclusions.

b. **Bimolecular Reactions.**—We are rather better off in the matter of satisfactory examples of bimolecular gas reactions. The decompositions of nitrous oxide,[8] chlorine monoxide,[7] hydrogen iodide[19] and the reaction between hydrogen and iodine[19] all appear reasonably clear cut. Of these

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[14] Thomsen, "Thermochemistry," Longmans, Green and Co., **1920**, p. 218.

[15] Berthelot, *Ann. chim. phys.*, **6**, 170, 171 (1875).

[16] Hinshelwood and Topley, *J. Chem. Soc.*, **125**, 393 (1924).

[17] Trautz, *J. prakt. Chem.*, **104**, 78 (1922).

[18] Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **114**, 233 (1924).

[19] Bodenstein, *ibid.*, **29**, 295 (1899).

we shall specially use the figures for the rate of decomposition of nitrous oxide as the most satisfactory. *The figures for all four rates of reaction, however, would lead to the same conclusions that we shall obtain from the figures for nitrous oxide.*

It has been shown by H. A. Taylor[9] that the decomposition of hydrogen iodide is to some extent catalyzed on the walls of the vessel. If the proper allowance for this could be made, the corrected rate for homogeneous bimolecular reaction would be somewhat lowered and the heat of activation somewhat increased, but it does not appear as if these corrections would be such as to make any changes in our conclusions.

The rate of decomposition of nitrous oxide was shown by Hinshelwood and Burk to be homogeneous by the drastic test of adding powdered silica, and second order by large variations in the initial pressure of the gas introduced. The work was carried out at a series of temperatures from 838° to 1,125° K. Their results on the rate of decomposition of nitrous oxide as a function of concentration and temperature may be fairly satisfactorily represented by the following equations

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = kC^2; \quad k = 7.60 \times 10^{13}\, T^{1/2}\, e^{-\frac{58{,}450}{RT}} \qquad (E)$$

where the specific rate k is in moles^{-1} cm.^{3} sec.$^{-1}$, and the energy of activation is in calories per two moles of nitrous oxide. The above result is obtained by combining the energy of activation found by Hinshelwood and Burk with the value they give for the constant at 1000° K.

7. Tests of Proposed Mechanism.—We are now ready to test the proposed mechanisms of activation given in Section 3. In doing this we shall first try to find out whether the mechanism would be fast enough to account for the above decomposition rates of nitrogen pentoxide and nitrous oxide and would lead to the right order of reaction. We shall then look for special criteria appropriate to the particular mechanism under consideration.

8. Activation by Ordinary Collision.—The activation of a molecule by collision with another molecule of high enough speed is one of the most obvious hypotheses to propose, and has been somewhat definitely advanced by Lindemann[20] as the most probable mechanism of activation. Following the general line of thought of others[21] we shall now calculate the possible speed of activation by this method, and shall find ourselves in agreement with the conclusion that activation by ordinary collision *cannot* take place fast enough to account for all reactions.

An exact calculation of the rate of activation by collision would necessitate a detailed knowledge of the internal behavior of molecules throughout

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

[21] Compare in particular Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

the duration of collision far beyond that which we now possess. It is possible, however, to carry out the desired computation with sufficient accuracy by adding to the usual hypotheses employed in making kinetic theory calculations a reasonable assumption as to the amount of kinetic energy transferable into energy of activation through molecular collision. In agreement with the usual applications of kinetic theory we shall consider that the molecules can be regarded with sufficient approximation as rigid spheres of a definite diameter. For a "head on" collision between two such molecules it can easily be shown from the principles of the conservation of energy and momentum that the maximum kinetic energy which can be transferred into other forms is $\frac{1}{2}\frac{m_1 m_2}{m_1 + m_2} V^2$ where m_1 and m_2 are the masses of the two molecules and V is the relative velocity of the molecules. For collisions which are not "head on" it would seem reasonable to use the same expression for the kinetic energy transferable into other forms, provided we take V as the component of the relative velocity parallel to the line of centers of the two molecules at the instant of contact. On the basis of these assumptions the energy of activation ϵ could be obtained only as the result of collisions in which the component of velocity V parallel to the line of centers at the instant of contact is equal to or greater than that given by the following equation

$$\epsilon = \frac{1}{2}\frac{m_1 m_2}{m_1 + m_2} V^2 \tag{3}$$

It is perhaps not to be expected that activation would actually occur at every collision in which V is greater than this value, since special internal orientations as well as sufficient energy might be necessary. In the calculations we are now to perform, however, we shall assume activation for every such collision. Since the actual difficulty is to discover a method of activation which would be fast enough, this assumption seems at least to be fair to the collisional hypothesis.

It has been shown by Langevin and Rery[22] that the fraction of all collisions in which the component of velocity parallel to the line of centers is not less than V is given by the expression $e^{-\frac{1}{2}\frac{m_1 m_2}{m_1 + m_2}\frac{V^2}{kT}}$. Hence, making use of Equations 3, we may write for the number of molecules activated per second by collision the expression

$$\frac{\mathrm{d}N_{\mathrm{act}}}{\mathrm{d}t} = Z\, e^{-\frac{\epsilon}{kT}} \tag{4}$$

where Z is the total number of collisions made per second by molecules of the kind that are to be activated and ϵ is the energy of activation per molecule.

In the reactions that we are now going to treat we need consider the

[22] Langevin and Rery, *Le Radium*, **10**, 142 (1913).

collisions Z only for the single kind of molecules present at the beginning of the decomposition. Hence, substituting for Z its well-known kinetic theory value, changing from energy of activation per molecule ϵ to energy per mole E and changing to concentrations we may rewrite Equation 4 in the form

$$\frac{\mathrm{d}C_{\mathrm{act}}}{\mathrm{d}t} = A\ C^2\,\sigma^2\sqrt{\frac{4\,\pi\,RT}{M}}\,e^{-\frac{E}{RT}} \tag{5}$$

where the whole expression gives the rate of activation in moles per unit volume per unit time, A is Avogadro's number, C is the concentration of the gas in question, σ the diameter of the molecules and M the molecular weight. In case more than a single kind of gas were present Equation 5 could be modified in an evident manner.

We may now use Equation 5 to calculate the possible rate of activation of nitrogen pentoxide. Expressing concentrations in moles per cubic centimeter, taking Avogadro's number as 6.06×10^{23}, and to be on the safe side taking for the diameter of the molecule the large value 10^{-7} cm., we obtain for the rate of activation at 25° C.

$$\frac{\mathrm{d}C_{\mathrm{act}}}{\mathrm{d}t} = 3.25 \times 10^{14}\,e^{-\frac{E}{RT}}\,C^2 \tag{6}$$

To compare this rate of activation with the rate of reaction, we may note that in the runs made at 25° by Daniels and Johnston the initial concentration was in the neighborhood of 1.5×10^{-5} moles per cc., which substituted in (6) would give a rate of activation of about

$$\frac{\mathrm{d}C_{\mathrm{act}}}{\mathrm{d}t} = 4.9 \times 10^{9}\,e^{-\frac{E}{RT}}\,C \tag{7}$$

Since the experimentally found rate of reaction, however, is given by Equation D above as

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = 4.56 \times 10^{13}\,e^{-\frac{E}{RT}}\,C \tag{8}$$

it is evident that activation by collision cannot supply molecules anywhere near fast enough to account for those used up by the reaction, much less fast enough to maintain the reaction first order as is experimentally found. We may rule out activation by collision as of appreciable importance in accounting for the rate of decomposition of nitrogen pentoxide. The same result would be found for the other unimolecular reactions mentioned in Section 6a.

At first sight it might seem possible that the estimated rate of activation by collision might be increased by the assumption of more than a single activated state or by the assumption of intermediate quantum states having less energy than necessary for full activation. Further consideration, however, makes this appear improbable. The possibility of more than a single activated state has already been introduced into the preceding computations, since we assumed activation for *every* collision in which the available energy exceeded a minimum value. As to the possibility of intermediate states, if E_i should be the energy per mole corresponding to an intermediate state S_i, then it is true that the specific rate of activation of molecules from state S_i would be increased over that from the normal state by a factor $e^{\frac{E_i}{RT}}$ in accordance with Equation 4. On the other hand, in accordance with the Maxwell-Boltzmann distribution law, the number of molecules in state S_i is less than that in the normal state by the reciprocal factor $e^{-\frac{E_i}{RT}}$. Furthermore, many of the collisions made by a molecule in an intermediate state will lead to deactivation so that it may no longer be possible to assume activation for every collision in which the available energy exceeds the minimum amount necessary for activation. A more detailed analysis of these points would be desirable, but it does not seem as if an escape from difficulties could be found along this path.

Let us now pass to second-order reactions and determine whether the activation of the nitrous oxide molecules could take place by the mechanism of collision. The data on the rate of decomposition of nitrous oxide are closely given by Equation E, above, as

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = 7.60 \times 10^{13}\, T^{1/2}\, e^{-\frac{58{,}450}{RT}}\, C^2 \tag{9}$$

The quantity 58,450 calories is the sum of the energies of activation (per mole) brought into the reaction by the two molecules of nitrous oxide which interact. At the present state of our knowledge it is not possible to state in what way this total energy of activation is divided between the two molecules. It seems profitable to carry out the calculations on the assumption (*a*) that reaction occurs as the result of a collision between an activated and an unactivated molecule; (*b*) on the assumption that reaction occurs as the result of a collision between two molecules each having the same energy of activation; and (*c*) on the assumption that reaction occurs as the result of a collision between previously unactivated molecules which obtain their energy of activation from the collision itself.

a. If only one of the molecules entering into the reaction is activated, it has to have the whole energy of activation, 58,450 calories per mole. Substituting this value into Equation 5, and taking the diameter of the nitrous oxide molecule as 3.32×10^{-8} cm., we obtain for the rate of activation by collision

$$\frac{\mathrm{d}C_{\mathrm{act}}}{\mathrm{d}t} = 3.25 \times 10^{12}\, T^{1/2}\, e^{-\frac{58{,}450}{RT}}\, C^2 \tag{10}$$

Comparing with Equation 9 for the rate of reaction, we see that the assumed mechanism could not possibly account for the facts since, in accordance with our previous discussion, the rate of activation would have to be very large compared with the rate of reaction in order to maintain the constant second order which the reaction is experimentally found to have.

b. A second possible mechanism of interest is that each molecule entering into the reaction has been previously activated to the same extent. This would be the point of view favored by Trautz,[4] W. C. McC. Lewis[23] and Dushmann.[24] On this basis the energy of activation for each molecule would only be a half of the total or 29,230 cal. per mole, and the rate of activation by collision would be found, by substituting into Equation 5, to have the value

$$\frac{\mathrm{d}C_{\mathrm{act}}}{\mathrm{d}t} = 3.25 \times 10^{12}\ T^{1/2}\, e^{-\frac{29,230}{RT}}\ C^2 \tag{11}$$

Dividing by Equation 9 for the rate of reaction, we obtain

$$\frac{\text{Rate of activation}}{\text{Rate of reaction}} = 0.043\ e^{\frac{29,230}{RT}} \tag{12}$$

Hence, even at the highest temperature (1125°) at which Hinshelwood worked the number of molecules activated per second would be 20,000 times as great as the number that react. It is evident that such a rate of activation would be sufficient to maintain practically the Maxwell-Boltzman distribution, and thus keep the reaction second order. Hence, as far as these considerations go, activation by collision is a definite possibility for the decomposition of nitrous oxide, provided each of the molecules entering the reaction carries half the total energy of activation. The other bimolecular reactions mentioned in Section 6b would lead to the same conclusion. Furthermore, general arguments can be presented to show that preliminary activation by collision would probably be fast enough to account for any bimolecular reaction in which each of the molecules must be in a particular quantum state which carries an appreciable part of the total energy of activation.

c. In the case of second-order reactions, the special possibility arises that the molecules which react are not previously activated but become so through the same collision which leads to reaction, the activated molecules thus being used up as fast as they are formed, the order of the reaction being second because it is the same as the order of the activation process. This is a point of view which has appealed favorably to Hinshelwood.[8,25] To account for the decomposition of nitrous oxide on this basis we might assume that every collision leads to reaction in which the available energy $\frac{1}{2}\frac{m_1 m_2}{m_1 + m_2} V^2$ is greater than 58,450 calories per mole. Since two molecules would disappear as the result of each such collision, the rate of reaction would evidently be twice the rate given by Equation 10, or

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = 6.50 \times 10^{12}\ T^{1/2}\, e^{-\frac{58,450}{RT}}\ C^2 \tag{13}$$

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[23] Lewis, *J. Chem. Soc.*, **113**, 471 (1918).

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

[25] Hinshelwood and Hughes, *J. Chem. Soc.*, **125**, 1841 (1924).

This value is so near the actual rate of reaction as given by Equation 9 that it does not seem absolutely out of the question that this might be a possible mechanism for the reaction. In fact we should only have to assume a diameter of the nitrous oxide molecule of 11×10^{-8} to account for the actual rate on this basis. Similar conclusions can be drawn with respect to the other bimolecular rates mentioned and it is certain that we do not have any data at the present time reliable enough to disprove the possibility in question. Nevertheless, our general knowledge as to the behavior of molecules would lead the writer to feel that bimolecular reactions are more likely to be a result of the interaction of molecules which are already in quantum states higher than the normal.

As a résumé, we may state that activation by collision could not take place fast enough to account for the rate of decomposition of nitrogen pentoxide, and probably not to account for other unimolecular reactions; but, as far as we can now see, might take place fast enough to account for the decomposition of nitrous oxide and for other bimolecular reactions. This latter, however, should not be interpreted as definite evidence that activation by collision *is* the mechanism for bimolecular reactions. Our calculations gave what seemed to be near the upper limit to the possible rate of activation by collision, and the actual rate might be very much lower, especially if the activation process should prove to be in the nature of an electron displacement from one orbit to another, rather than in an increase in atomic vibrations as a whole. Furthermore, our natural desire for theoretical simplicity would lead us to suspect the same main mechanism of activation for both unimolecular and bimolecular reactions until definite evidence shows this to be impossible.

9. Activation by Collisions of the Second Kind.—One of the most interesting theoretical and experimental developments of the quantum theory of atoms and molecules has been the discovery of the existence of collisions between activated and unactivated molecules, in which at least a portion of the energy of activation is transferred to the previously unactivated molecule, thus raising it to an activated state.[26,27,28] Such collisions have received the somewhat unfortunate name "collisions of the second kind."

Christiansen and Kramers[21] in a recent very significant article have essayed the development of a general theory of chemical kinetics based on the assumption of activation by such collisions. Their idea is that the molecules resulting from a chemical change will first be formed in an activated condition and only later fall to their normal state. Hence, through collisions of the second kind the molecules produced by the reaction might

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[26] Klein and Rosseland, *Z. Physik*, **4**, 46 (1921).

[27] Franck, *ibid.*, 9, 259 (1922).

[28] Cario and Franck, *ibid.*, **11**, 161 (1922).

activate fresh molecules of the original reactant and prepare them to undergo the chemical change.

The suggestion that collisions of the second kind may play a part in ordinary chemical reactions is doubtless an important one. The idea that the molecules produced by a chemical change are first formed in an activated condition is a familiar one in chemical kinetics,[29] and activation by transfer of energy from these newly formed molecules had already been successfully postulated by Bodenstein[30] to account for the abnormal behavior of the hydrogen chlorine reaction, even before there were any theoretical or experimental proofs of the existence of collisions of the second kind. Nevertheless, it seems to the present writer that many difficulties would have to be overcome before this method of activation could be accepted as the general and exclusive mechanism in the case of typical thermal reactions.[31]

The theory of Christiansen and Kramers can be understood with the help of the following schematic representation of the course of a chemical change in which a molecule of reactant R breaks down into products P and Q.

$$R \rightleftharpoons R' \longrightarrow \begin{cases} P' \longrightarrow P \\ Q' \longrightarrow Q \end{cases} \quad \text{(Decomposition)} \qquad (14)$$

$$P' + R \longrightarrow P + R' \quad \text{(Collision of second kind)} \qquad (15)$$

In accordance with Expression 14 the reactant can exist in two forms, the normal form R and an activated form R'. The activated form breaks down spontaneously into activated forms of the products P' and Q' and these in turn change into the normal forms P and Q. This latter change, however, can sometimes take place, at least in the case of one of the products, through a collision of the second kind, with a molecule of the reactant R, thus leading to the activation of a new molecule through the mechanism indicated by Expression 15.

In case the reaction deviates from a first-order course the number of such activations need not be the same as the number of molecules that decompose, but in case the reaction actually takes a first-order course, Christiansen and Kramers introduce the special assumption that each decomposition in accordance with (14) is *always immediately* followed by a successful activation in accordance with (15). When this latter assumption is true, it is evident that the full quota of activated molecules R' allowed by the Maxwell-Boltzmann law will be maintained, since the loss of a molecule by decomposition is immediately made good by the specially assumed mechanism and, hence, the ordinary agencies responsible

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[29] Marcelin, *Ann. phys.*, **11**, 5 (1915).

[30] Bodenstein, *Z. Elektrochem.*, **22**, 53 (1916).

[31] Collisions of the second kind are of course of prime importance in cases of photochemical catalysis.

for the transitions $R \longrightarrow R'$ and $R' \longrightarrow R$ are able to maintain the same statistical equilibrium that would exist in the absence of reaction. Under these circumstances we may write for the concentration of activated molecules of the reactant the expression given by the Maxwell-Boltzmann distribution law

$$C' = \frac{p'}{p} e^{-\frac{E}{RT}} C \tag{16}$$

where C and C' are the concentrations of molecules R and R', respectively, p and p' the corresponding *a priori* probabilities, and E the energy of activation which is absorbed when one mole of molecules changes from R to R'. The dependence of rate of decomposition on concentration and temperature would then be given by the equation

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = A\,C' = A\,\frac{p'}{p} e^{-\frac{E}{RT}} C \tag{17}$$

where the constant A is the chance per unit time for the spontaneous decomposition $R' \longrightarrow P' + Q'$. The analogous treatment for bimolecular reactions is obvious.

Although this treatment of Christiansen and Kramers leads to a final expression (17) which is formally satisfactory, there are undoubted difficulties with the assumed mechanism.

In the first place, the assumption of a 100% efficiency in the process of reactivation by collisions of the second kind, as Christiansen and Kramers themselves remark, necessitates the further assumption that the activated molecules P' give up their energy only to molecules of R. This is hard to believe in general, since there are certainly cases where a molecule of P' would make hundreds or thousands of collisions with molecules of other kinds before it meets a molecule of R. [See however, the very recent work of Donat, *Z. Physik*, **29**, 345 (1924).]

In the second place, in the case of endothermic reactions, the mechanism certainly cannot be as simple as presented above, since in such reactions a molecule of product in dropping to its normal state would not give up enough energy to raise a molecule of the reactant from its normal to its activated state. Hence, at the very least, in the case of endothermic reactions, collisions of the second kind would presumably have to be supplemented by an additional activational step. If this supplementary activational step should occur before the collision of the second kind, then the concentration of molecules of reactant in a state suitable to make successful collisions with the activated product would be very much lower than the total concentration of reactant, and the number of collisions during which the activated product would have to withold its energy would be enormously increased. On the other hand, if the collisions of the second kind should be followed by a supplementary activation, it is evident that this step would have to be one of very high specific velocity, since the concentration of molecules in the intermediate state would be very much lower than the total concentration of reactant. In either case it is evident that activation by collisions of the second kind gives no complete and easy explanation of the mechanism of *endothermic* reactions.

It will be profitable to examine the decomposition of nitrogen pentoxide in the light of these considerations. Attention has already been called to the fact that the pure nitrogen pentoxide of Daniels and Johnston,[6] and the nitrogen pentoxide of White and Tolman[13] mixed with a thousand times its volume of oxygen decomposd at the same rate. In the later experiments, however, it is evident that a molecule of activated product would on the average collide about a thousand times with molecules of oxygen before it came in contact with a molecule of nitrogen pentoxide. It would certainly seem very artificial to assume no dissipation of energy throughout all these thousand collisions. It is also significant to note that the experiments of Lueck[32] have shown that nitrogen pentoxide dissolved in carbon tetrachloride and in chloroform decomposes at nearly the same rate as the gaseous pentoxide. Unless we wish to assume a completely different mechanism of activation in the gas and liquid phases this is even stronger evidence against the probability of activation by collisions of the second kind.

In addition to these difficulties, the decomposition of nitrogen pentoxide is apparently *endothermic* to the extent of 2690 cal., if it proceeds to the formation of nitrogen tetroxide and molecular oxygen, and still further endothermic to the extent of 16,290 cal. if it goes, as it does at the beginning of the decomposition, to the dioxide. Furthermore, not only is the change to the final products endothermic, but it seems practically certain that the actual first steps of the decomposition would lead to compounds which are even more endothermic than the final products. Thus the plausible first step[33]

$$N_2O_5 \longrightarrow NO_2 + NO + O_2 \qquad (18)$$

would be endothermic to the extent of 29,740 calories, while a first step leading to atomic oxygen, such as

$$N_2O_5 \longrightarrow N_2O_4 + O \qquad (19)$$

might even be too endothermic to occur at all, since the heat of dissociation of oxygen, although unknown, might easily be greater than the net energy (44,120 cal.) made available by the activation of two molecules of pentoxide. Of course, the possible first steps are not exhausted by (18) and (19); nevertheless, in accordance with the usual, although not universal, principle that intermediate unstable compounds are endothermic, a first

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[32] Lueck, THIS JOURNAL, **44**, 757 (1922).

[33] This, or rather the combination $N_2O_5 \longrightarrow N_2O_3 + O_2$ followed by $N_2O_3 \longrightarrow NO + NO_2$, is the mechanism ascribed to the reaction by Bodenstein, *Z. physik. Chem.*, **104**, 51 (1923).

step less endothermic than the complete reaction is improbable. Hence, it seems very difficult to devise a mechanism of decomposition such that there will not be some shortage of energy below that needed for activation by a collision of the second kind.

Not only do we encounter these general difficulties in trying to explain the decomposition of nitrogen pentoxide with the help of collisions of the second kind, but the specific mechanisms suggested by Christiansen and Kramers meet with special difficulties. Their first proposal is represented by the expressions

$$N_2O_5 \longrightarrow N_2O_3 + O_2 \text{ (slow, determining the velocity)} \quad (20)$$
$$N_2O_3 + N_2O_5 \longrightarrow 2N_2O_4 \text{ (immeasurably fast)} \quad (21)$$

with the addition that new molecules of pentoxide must always be activated by the tetroxide produced in (21). This proposal has the special difficulty that the trioxide is so unstable that its concentration in the gaseous phase is too small to measure, and the tetroxide is known to decompose into dioxide with extraordinary rapidity. Hence, it seems improbable that they could survive the many collisions with indifferent molecules which would intervene before they could play the role postulated by the mechanism. The second proposal of Christiansen and Kramers is represented by the expressions

$$NO_2 + N_2O_5 \longrightarrow NO + N_2O_4 + O_2 \quad (22)$$
$$NO + N_2O_5 \longrightarrow NO_2 + N_2O_4 \quad (23)$$

where it is assumed that the nitric oxide formed in (22) always reacts with pentoxide as shown by (23), and the activated dioxide formed by (23) always reacts as shown by (22). This mechanism is in difficulty, since it assumes 100% efficiency in Reaction 23, when nitric oxide is known to react with oxygen. Furthermore, since the activated dioxide produced by (23) will maintain the full Maxwell-Boltzmann quota of activated dioxide molecules, the rate of reaction should be proportional to the total concentration of dioxide which was found by White and Tolman[13] not to be the case.

Since the decomposition of hydrogen iodide is endothermic, difficulties would also be met in the case of that reaction if we should try to assume collisions of the second kind as the sole mechanism of activation.

As a résumé of the results of this section, it can be stated that the possibility of activation by collisions of the second kind is an important one to consider in explaining rates of reaction, and such activations almost certainly do occur to some extent during the course of some reactions. It does not seem possible, however, to develop a general theory on the assumption that such collisions are the sole mechanism of activation in typical chemical reactions.

10. The Simple Radiation Theory of Reaction.—Much of our present-day interest in the mechanism of chemical reaction has been stimulated by the development of the so-called Radiation Theory of Chemical Reaction, which has been mainly the work of Perrin[34] and W. C. McC. Lewis.[35,36] On the basis of this theory the process of activating a molecule consists in the absorption of a quantum of energy from the store of thermal radiation which surrounds the reacting molecules. This process can be represented by the expression

$$h\nu + R \longrightarrow R' \tag{24}$$

We may write, however, for the distribution of radiation in accordance with the Planck law the expression

$$\rho_\nu = \frac{8\,\pi\, h\nu^3}{c^3}\,\frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{25}$$

and placing the chance of absorbing a quantum of energy proportional to ρ_ν we may write for the rate of activation

$$\frac{\mathrm{d}C'}{\mathrm{d}t} = B\,\frac{1}{e^{\frac{h\nu}{kT}} - 1}\,C \tag{26}$$

where B is a proportionality constant. Noting that $e^{\frac{h\nu}{kT}}$ is usually large compared with unity, and writing

$$E = A\,h\nu \tag{27}$$

for the energy of activation per mole, where A is Avogadro's number, we obtain

$$\frac{\mathrm{d}C'}{\mathrm{d}t} = B\,e^{-\frac{E}{RT}}\,C \tag{28}$$

for the rate of activation.

In the case of first-order, unimolecular reactions it is to be assumed that every molecule or some definite fraction of the molecules would react as soon as activated and hence the rate of reaction would have some definite fraction of the value given for the rate of activation by Equation 28, which agrees in form and content with our original Equation 1 for the rate of first-order reactions. In the case of second-order, bimolecular reactions, it is assumed that the above mechanism of activation is fast enough to maintain the full quota of activated molecules permitted by the Maxwell-Boltzmann distribution law, the rate of reaction then depending on the number of collisions between activated molecules which leads to our original Equation 2 for the rate of a second-order reaction.

Although there are a number of [illegible] see, that the radiation theory in i [illegible] count of the mechanism of all rea [illegible] mire the boldness and beauty of th [illegible] which would unify our pictures of thermal and photochemical reaction, and account in the sim-

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[34] Perrin, *Ann. phys.*, **11**, 5 (1919).

[35] Ref. 23; *Phil. Mag.*, **39**, 26 (1920).

[36] For an excellent review of the present status of the radiation theory, see Harned, *J. Franklin Inst.*, **196**, 181 (1923).

plest possible manner for the orders of reaction by providing a method of activation which is independent of concentration. We must also point out the lack of pertinence in the criticisms of the theory made by Langmuir[37] based on calculations as to the rate at which radiant energy of the activating frequency could be supplied from the walls of the vessel containing the reacting mixture. Langmuir's criticisms assume that the activation of molecules by the absorption of quanta $h\nu$ in accordance with 24, would lead to an exhaustion of energy of frequency ν which could only be made good by inflow of radiation from the walls of the container, and on this basis he calculates that the inflow of energy could not take place fast enough to account for the reaction. As a matter of fact, however, all the radiant energy within the enclosure will continually strive to adjust itself in accordance with the Planck distribution law, and the rapidity with which the deficiency in radiation of a given frequency will be made good is by no means wholly due to inflow from the walls. Furthermore, it should be noted that in no case would the walls have to supply energy at the total rate necessary for activation as indicated by Equation 24, since the energy absorbed in activating the molecules is largely given out again when the reaction is completed. Indeed, in the case of exothermic reactions, such as the decomposition of phosphine for which Langmuir's calculations were made, the net effect of the walls is to remove rather than supply energy.

It should also be noted that the newer concepts of Bohr, Kramers and Slater[38] tend further to relax the difficulty of supplying energy of activation by radiation, since by giving up the principle of the conservation of energy except as a statistical requirement, we can think of the molecule as jumping from its normal to its activated state without any immediate decrease in the radiant energy present in the surroundings. Indeed, the total expected decrease may never become necessary if the molecule quickly re-emits energy in its further transitions.

As in our considerations of the other mechanisms, we must first inquire whether the radiation theory could provide a rapid enough rate of activation to account for actual rates of reaction. The first satisfactory calculations to settle this point we owe to Christiansen and Kramers[21] whose treatment is in essential agreement [illegible] what follows. In accordance with Einstein's[39] views [illegible] and emission of radiant energy, [illegible]lecules would pass from a lower [illegible] by the absorption of a quantum [illegible]

$$\frac{\text{[illegible]}}{dt} = N_n B_{na} \rho_{na} \qquad (29)$$

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[37] Langmuir, THIS JOURNAL, **42**, 2190 (1920).

[38] Bohr, Kramers and Slater, *Phil. Mag.*, **47**, 785 (1924). See also Webster, *Phys. Rev.*, **16**, 31 (1920); Langmuir, Ref. 37; and Darwin, *Nature*, **110**, 841 (1922).

[39] Einstein, *Phys. Z.*, **18**, 121 (1917).

where B_{na} is a constant coefficient depending on the nature of the states S_n and S_a. If we regard S_n as the normal state of our molecule and S_a as the activated state which leads to reaction, it is evident that the rate of activation would be governed by the value of Einstein's coefficient B_{na}. Values of this quantity can be calculated from the intensities of absorption lines when data are available, or with some probability estimated with the help of the Bohr correspondence principle. From absorption data, empirical values of B_{na} were calculated by the present writer[40] and found to vary all the way from 4×10^{14} to 2×10^{19} (in c. g. s. units) for the limited number of transitions where absorption data were available. On the basis of the Bohr correspondence principle, we should expect the value of the coefficient in the case of a charge e performing linear oscillations of effective amplitude Q to be given approximately by the expression

$$B_{na} = \frac{2\,\pi^3\,e^2}{3\,h^2}\,Q^2 \tag{30}$$

By substituting the charge of one electron for e and reasonable value for Q we can also in this way get an estimate of the coefficient. We are led from both points of view to the conclusion that 10^{20} would be a probable upper limit for values of B_{na}.

Let us see whether such a value of Einstein's coefficient could account for the rates of decomposition of nitrogen pentoxide and nitrous oxide. Taking B_{na} as 10^{20}, and using Equation 27 to calculate the activating frequency, we obtain for the rate of activation of nitrogen pentoxide the value

$$\frac{\mathrm{d}C_{\mathrm{act}}}{\mathrm{d}t} = 1.08 \times 10^{7}\, e^{-\frac{24,700}{RT}}\, C \tag{31}$$

while for the rate of reaction we have from (D),

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = 4.56 \times 10^{13}\, e^{-\frac{24,700}{RT}}\, C \tag{32}$$

Hence, it does not seem possible to account for the rate of decomposition of nitrogen pentoxide on the basis of the simple radiation theory. Furthermore, an examination of the available data for other unimolecular reactions shows that the rate of activation would in general be too small on the basis of the simple radiation theory.

Turning now to the decomposition of nitrous oxide, using once more the value 10^{20} for B_{na} and assuming that each of the molecules of nitrous oxide brings into the reaction half the total energy of activation, we obtain for the rate of activation

$$\frac{\mathrm{d}C_{\mathrm{act}}}{\mathrm{d}t} = 1.78 \times 10^{7}\, e^{-\frac{29,230}{RT}}\, C \tag{33}$$

On the other hand, for the rate of decomposition of nitrous oxide we have in accordance with (E)

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = 7.60 \times 10^{13}\, T^{1/2}\, e^{-\frac{58,450}{RT}}\, C^2 \tag{34}$$

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[40] Tolman, *Phys. Rev.*, **23**, 693 (1924).

Combining (33) and (34) we obtain for the relative rates of activation and reaction

$$\frac{\text{Rate of activation}}{\text{Rate of reaction}} = \frac{2.34 \times 10^{-7}}{T^{1/2}\,C}\,e^{-\frac{29,230}{RT}} \qquad (35)$$

Now the highest temperature at which Hinshelwood and Burk worked was 1125° K. and the highest initial concentration at that temperature was 4.11×10^{-6} moles/cc., and by substitution in (35) we find under these conditions that the rate of activation would be over 800 times the rate of decomposition. A similar calculation for the decomposition of hydrogen iodide led to a ratio of over 2000 for the two rates. We may conclude that as far as we can now see, the simple radiation theory *might* lead to rapid enough activation to account for bimolecular reactions, provided each of the molecules entering the reaction brings an appreciable fraction of the total energy of activation.

In addition to the requirement of providing a rapid enough rate of activation, the radiation theory is subject to a very special test, since with the help of Equation 27 we can calculate from the empirically determined energy of activation the frequency of light which should be photochemically active in bringing about reaction. Thus, in the case of the decomposition of nitrogen pentoxide, the energy of activation 24,700 cals. per mole corresponds to a wave length of 1.16μ. It has been definitely shown by Daniels and Johnston,[41] however, that nitrogen pentoxide is *not* decomposed by light of this wave length and, furthermore, that nitrogen pentoxide has no known absorption line or band at this wave length.

As the conclusion of this section, it may be definitely stated that the simple radiation theory which assumes activation by the passage from a single normal to a single activated state through the absorption of a quantum of radiation, cannot give a satisfactory account of unimolecular reactions, both because the rate of activation would be too small and because in at least one case the substance does not respond to radiation of the predicted wave length.

11. The Elaborated Radiation Theory of Reaction.—The elements of promise in the radiation theory of reaction suggest the hope that an elaborated form of the theory might be able to account for the facts. Room for elaboration lies in the possibility of assuming that the mechanism of reaction may not involve merely the absorption of quanta of a single frequency, but might depend (a) on the *simultaneous* absorption of several quanta, (b) on the *successive* absorption of several quanta, (c) on the absorption of quanta having a *range of frequencies*, or (d) on the simultaneous *absorption and emission* of quanta.

In his first quantitative paper in 1919 Perrin[34] suggested the possibility that a bimolecular reaction might involve the simultaneous absorp-

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[41] Daniels and Johnston, THIS JOURNAL, **43**, 72 (1921).

tion of two different quanta at the instant of contact of the molecules, and at the conference of the Faraday Society in 1921,[42] he elaborated this idea to include unimolecular processes[43] and added consideration of the possibility of activation by successive steps,[44] and the possibility of the absorption of several frequencies corresponding to more than one activated state.[45]

Meanwhile, in 1920 the writer[46] had considered a number of the inadequacies of the simple radiation theory and presented an elaborated theory which was broad enough to allow for the simultaneous interaction of more than one frequency,[47] and for activation through intermediate states,[48] and which gave special attention to the possibility of activation by the absorption of a range of frequencies.[49] The results of a simultaneous absorption and emission of quanta will be considered for the first time in the present article.

The task now before us is to consider in the light of the newer developments of the quantum theory whether such a liberalization of the simple radiation theory could provide us with a reaction mechanism that would be fast enough to account for known rates of reaction, and would predict the acceleration of the reaction by wave lengths which are actually found to be photochemically active. We shall examine *seriatim* the results of loosening the strictness of the radiation theory in the four ways a, b, c, d mentioned above.

a. **The Simultaneous Absorption of Quanta.**—If the passage from the normal to the activated state should depend on the simultaneous absorption of several quanta, it is evident that the frequency of light which would be photochemically active could not be calculated by placing the total energy of activation equal to one quantum $h\nu$ as in Equation 27. This has been the main explanation advanced by Perrin for the failure of reactions to respond to predicted frequencies, and if such simultaneous absorptions did occur it would be sufficient to meet the point in question.

There are two considerations, however, which militate against this explanation. In the first place, the whole spirit of the quantum theory gives us no reason to expect that such coupled absorptions would be probable. On the contrary, the development of the quantum theory has led us to correlate each transition with a single frequency determined by the difference in energy of the molecule in its initial and final states, and to expect the

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[42] Ref. 11, p. 546.

[43] Ref. 11, p. 563.

[44] Ref. 11, p. 563.

[45] Ref. 11, p. 552.

[46] Tolman, This Journal, **42**, 2506 (1920).

[47] Ref. 46, p. 2525.

[48] Ref. 46, p. 2519.

[49] Ref. 46, p. 2520.

occurrence of such transitions entirely in accordance with laws of chance and unaffected by the possibility of other transitions. Indeed, the Bohr correspondence principle has brought into special prominence the fact that, although on the classical theory the various mechanical frequencies present in the internal motion of the molecule would be simultaneously absorbed or radiated, on the basis of the quantum theory each mechanical frequency corresponds to a quantum transition with an optical frequency calculable from the energy difference between the initial and final states, and these quantum transitions take place entirely independently.

In addition to this general improbability of the simultaneous absorption of two or more quanta, all our experimental information concerning absorption lines gives no evidence that coupled absorptions ever do occur. The absorption spectrum of a substance is always distinguished by the fact that it contains only such lines as correspond to transitions from states of the molecule of low enough energy content to be present in reasonable concentration, up to known higher energy levels. If coupled transitions should take place, we should expect the appearance of pairs or other combinations of lines, the sum of whose frequencies would be determined by the difference of energy levels. Such lines have never been found.

It seems safe for the present to dismiss the possibility of the simultaneous absorption of quanta as an important addition to the radiation theory of reactions.

b. **The Successive Absorption of Quanta.**—All of the recent increase in our knowledge of atomic and molecular structure which has been obtained with the help of the quantum theory would lead us to expect not a single normal and a single activated state, but rather a series of quantum states of successively increasing energy content. Hence, the process of activation might not consist to any appreciable extent in the absorption of a single frequency corresponding to a jump from the normal to the completely activated state, but rather in the absorption of a variety of frequencies corresponding to jumps from one intermediate state to another. Indeed, in accordance with the Bohr correspondence principle we should expect that the full jump from normal to activated state might often be ruled out.

It is evident that this view of the mechanism would be sufficient to account for the fact that reactions do not respond to the frequency calculated on the assumption of activation in a single step.

On the other hand, it does not seem probable that the mere assumption of intermediate states between the normal and activated state could lead to any marked increase in the rate of activation, such as would be necessary if we are to account for known rates of unimolecular reaction. This arises from the fact that the greater density of radiation which would be effective in causing transitions from an intermediate state to the activated state, compared with that effective in the full transition from the normal state, would be compensated by the smaller number of molecules in the intermediate state, compared with the number in the normal state. Thus, if E_a is the total energy of activation per mole, and E_i the energy necessary to raise molecules to the intermediate state, the density of radiation effective in raising molecules from the intermediate to the activated state would, in accordance with the Planck radiation law, be greater than that corresponding to the whole jump by a factor of approximately $e^{\frac{E_i}{RT}}$ on the other hand, in accordance with the Maxwell-Boltzmann distribution law, the number of molecules in the intermediate state would be less than that in the normal state by the reciprocal factor $e^{-\frac{E_i}{RT}}$. It is hoped that a more detailed analysis leading, however, to the same conclusion will be presented in another place.

The situation may be summed up by the statement that the assumption of intermediate states between the normal and activated state is almost certainly correct, and leads to an explanation of the failure of reactions to respond to calculated frequencies. Nevertheless, the mere assumption of such intermediate states will not alone lead to the great increase in speed of activation necessary to rescue the radiation theory of activation.

c. **The Absorption of a Continuous Range of Frequencies.**—In the earlier article, already referred to,[46] the writer laid special stress on the fact that the actual reactions known in photochemistry do not always take place as the result of the absorption of single spectral lines, but may be produced by the absorption of a continuous range of frequencies. In terms of the quantum theory this is to be interpreted as meaning that instead of a single activated state we have a whole range of activated states of continuously increasing energy content. Such a great increase in the number of activated states would greatly increase the rate of activation and seems to the writer one of the most hopeful modifications which might help in putting the radiation theory on its feet.

In addition to the experimental facts as to the activity of continuous ranges of frequency in causing photochemical reactions, there is an interesting theoretical reason for believing in the possible occurrence of a series of activated states having an almost continuous range of energy contents, which we shall first discuss.

It seems reasonable to assume that the process of activation consists in increasing the energy of vibration of atoms within the molecule. This would correspond with the chemist's rough idea of "loosening a chemical bond" and would undoubtedly make the atoms more free to enter into new chemical combinations. Furthermore, the magnitudes of known energies of activation correspond to frequencies in the near infra-red which we know to be absorbed, for example, by the halogen halides, when changes in atomic oscillation take place. Hence, we shall feel justified in making the hypothesis that the activated condition of the molecule, at least in certain cases, might be one in which the amplitude of atomic oscillation has become so great that the forces holding an oscillating atom in to the molecule are greatly weakened at the exterior limit of its motion.

This hypothesis, however, immediately entails an important consequence. If the oscillations become large enough so that the restoring forces at the exterior limit of oscillation are small, it is evident that the frequency of atomic oscillation will also become small in the same way that the frequency of oscillation of any elastic system decreases as it is strained beyond its elastic limit. For any conditionally periodic system of degree of periodicity s, however, the energy E, fundamental frequencies $\omega_1 \ldots \omega_s$, and the phase integrals $I_1 \ldots I_s$ are connected by the classical equation

$$\mathrm{d}E = \omega_1\, \mathrm{d}I_1 + \ldots + \omega_s\, \mathrm{d}I_s \tag{36}$$

Hence, for any oscillation in which the frequency, say ω_r, has become small, the rate of increase of energy E with the corresponding phase integral I_r will be small in accordance with the equation

$$\frac{\partial E}{\partial I_r} = \omega_r \tag{37}$$

Successive quantized states of the system, however, are those in which the phase integral increases by successive amounts h. It is immediately evident that the energy levels of successive quantized states will lie near together when the frequency involved becomes small. The close succession of quantized states for a Planck oscillator of small frequency is of course a special case of this more general result. In other words, as soon as the amplitude of atomic oscillation within the molecule has become large enough so that the bond holding the atom in question has become greatly weakened, the successive quantized states of the molecule, that is, the activated states of the molecule, will have energy levels lying near together. Indeed, if the oscillations become large enough so that the force restraining the atom at the exterior limit of its motion approaches zero, we obtain a continuous series of activated states. Such a complete weakening of the bond might be necessary for certain reactions and would seem especially reasonable in the case of unimolecular reactions.

Admitting the possibility of the existence of a continuous series of activated states, which on experimental grounds alone seems necessary, it is evident that we must modify the development of the radiation theory of reaction in such a way as to permit unimolecular reactions, including the process of activation, to take place as the result of the absorption of a continuous range of frequencies. This can be done, of course, as shown in the writer's earlier paper, by introducing a specific photochemical reaction rate which depends on the frequency and the integrating over the whole range of frequencies.

If k_ν is the specific photochemical rate of reaction corresponding to the frequency ν, and we assume that ordinary thermal reaction is due to the action of thermal radiation present in the reaction mixture with the energy density given by the Planck radiation law, we may evidently write for the specific thermal rate k_T of a unimolecular reaction the expression

$$k_T = \int_0^\infty \frac{8\,\pi\,h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} k_\nu \,\mathrm{d}\nu \tag{38}$$

This expression was first derived by the author in the article already referred to (Equation 43) and evidently gives the desired extension to the simple radiation theory of reaction. In another place it will, furthermore, be shown that Equation 38 leads to the expected relation between rate of reaction and average energy of activation.

Although Equation 38 gives an undoubted improvement in the formulation of the radiation theory of reaction, nevertheless, the main part of our task would be to determine whether this equation actually leads to rapid enough rates of activation to account for known reaction velocities, thus rescuing the radiation theory of chemical reaction from its main difficulty. Unfortunately, the answer to this question cannot now be given, since it would involve a quantitative knowledge of specific photochemical reaction rates k_ν, which we do not possess. It must be remarked, however, that in an analagous problem Richardson[50] and his co-workers have, at least up to the present, not been able to account for the thermoelectric current emitted by metals as an integrated photoelectric current. Certainly the burden of proof rests on those who would maintain the applicability of Equation 38. Nevertheless, there seems at present no evidence against a large enough number of activated states to account for known rates of reaction. Furthermore, the difficulties in subjecting this equation to a proper test should not be overlooked. The effect of a wide range of frequencies must be studied, since the distribution of active wave lengths cannot be predicted. In particular it is to be remembered, in accordance with the discussion of the preceding section, that activation may occur in steps, so that the far infra-red as well as the near infra-red must be searched. Finally, it must not be forgotten that k_ν is the specific photochemical reaction rate *at the temperature* in question. Hence, since many photochemical reactions have appreciable temperature coefficients,[51] we must determine directly or indirectly the increase in reaction rate when we shine light of the desired wave length into the reacting mixture *at* the reacting temperature.

To sum the results of this section, we may state that there are experimental and theoretical reasons for believing in the possibility of a series of

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[50] Richardson, *Phil. Mag.*, **31**, 149 (1916).

[51] For a theory of temperature coefficient of photochemical reaction rate, see Tolman, THIS JOURNAL, **45**, 2285 (1923).

activated states of nearly the same energy content, rather than in a single activated state. It cannot be said at the present time, however, whether this leads to a sufficient increase in rates of activation by absorption of radiant energy to account for certain known reaction velocities.

d. **The Simultaneous Absorption and Emission of Quanta.**—A final possibility to be considered in connection with the radiation theory is that of a simultaneous absorption and emission of quanta of radiation. This might be of special importance in the case of unimolecular reactions, in which the molecule has to be raised in energy content through a critical condition before the chemical change can take place. This could be thought of as resulting from the absorption of one quantum large enough to raise the molecule to its critical condition accompanied by the emission of another quantum of such magnitude as to leave the products of the reaction in their final normal state. The emitted quantum would be larger or smaller than the one absorbed according as the reaction was exothermic or endothermic. The complete process would result in fluorescence and special stress is to be laid on the simultaneous rather than successive nature of the absorption and emission.

A basis for the theoretical treatment of the probability of such combined processes is given by the work of Einstein and Ehrenfest,[52] where it is shown that the number of molecules per second making the transition from the original normal state S_n to the final state S_f must be given by an expression of the form

$$-\frac{\mathrm{d}N_n}{\mathrm{d}t} = N_n\, B_{na}\, \rho_{na}\, (A_{af} + B_{af}\, \rho_{af}) \tag{39}$$

where N_n is the number of molecules in the original normal state, ρ_{na} and ρ_{af} give the radiation density corresponding to the absorbed and emitted quantum, respectively, and the other quantities are the obvious probability coefficients. The work of these authors has also shown that the probability coefficients corresponding to spontaneous emission and negative absorption for the same transition must be connected by the equation

$$A_{af} = \frac{8\,\pi\, h\nu^3_{af}}{c^3}\, B_{af} \tag{40}$$

Substituting Equation 40 in (39) and assuming that the values of ρ_{na} and ρ_{af} are satisfactorily given by the Wien end of the Planck radiation law, we obtain for the rate of transfer of molecules from the original to the final state

$$-\frac{\mathrm{d}N_n}{\mathrm{d}t} = N_n\, B_{na}\, B_{af}\, \frac{8\,\pi\, h\nu^3_{na}}{c^3}\, \frac{8\,\pi\, h\nu^3_{af}}{c^3}\, e^{-\frac{h\nu_{na}}{kT}} \left(1 + e^{-\frac{h\nu_{af}}{kT}}\right) \tag{41}$$

If we apply this equation to a unimolecular reaction, where E is the energy of activation per mole take the concentration C of the original reactant as identical with the concentration of molecules in the initial state S_n

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[52] Einstein and Ehrenfest, *Z. Physik,* **19,** 301 (1923).

and neglect $e^{-\frac{h\nu_{af}}{kT}}$ in comparison with unity, we may rewrite Equation 41 in the familiar form

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = B\, e^{-\frac{E}{RT}}\, C \tag{42}$$

where B has the value

$$B = B_{na}\, B_{af}\, \frac{8\,\pi\, h\nu^3_{na}}{c^3}\, \frac{8\,\pi\, h\nu^3_{af}}{c^3} \tag{43}$$

It is difficult to make a reliable prediction as to the possible magnitude of the all-important quantity B. In considering the simple radiation theory we took the quantity B_{na}, which there referred only to the transition from state S_n to S_a as having a possible magnitude of 10^{20}. If we should be justified, in the present more complicated case, in giving this value both to B_{na} and B_{af} we should obtain greatly increased rates of reaction over those possible on the simple radiation theory—rates certainly of the same order as are necessary (see Equations 31 and 32). We have, however, at the present time no experimental data for settling the magnitude of $B_{na}\, B_{af}$ and a decision on the basis of the correspondence principle is by no means simple.

On the whole it would be safe to sum the results of this section by stating that we can see no reason at the present time why the simultaneous absorption and emission of quanta might not take place as a step in chemical reactions, but there is no evidence to show that such steps are of actual importance in accounting for known rates of reaction.

12. **Conclusions.**—We shall now restate the results obtained above in as specific and definite form as possible. We must call attention, however, to the fact that our conclusions are necessarily based on a variety of assumptions which introduce a certain degree of uncertainty. These assumptions include an acceptance of the general Arrhenius position as to the necessity of activation as a preliminary to reaction in the case of reactions with a large temperature coefficient, the use of Equations 1 and 2 to give at least approximate values of the energy of activation, the use of Equation 4 to calculate the number of molecules that could be activated by collision, the use of estimates of molecular diameters, the use of thermochemical data in the literature, the use of estimates of probable values of Einstein's coefficient of absorption and the choice of certain chemical changes as real examples of unimolecular or bimolecular homogenous gas reactions. Hence, although our conclusions are stated in dogmatic form, we merely offer them as what seem to be the best ideas available at the present time.

Summary

1. Activation by collision with molecules of high enough kinetic energy cannot take place fast enough to account for the decomposition of nitrogen

pentoxide or other unimolecular gas reactions. Activation by collision also could not take place fast enough to account for the decomposition of nitrous oxide or other bimolecular reactions, if the total energy of activation is brought into the reaction by one of the two molecules. Activation by collision might be a possibility for bimolecular reaction if each of the molecules brings an appreciable fraction of the total energy of activation, or if both activation and immediate reaction are the result of the same collision.

2. Activation by collisions of the second kind, involving transfer of energy from activated products of the reaction to molecules which have not yet entered the reaction, is presumably of prime importance in certain abnormal reactions such as the combination of hydrogen and chlorine, and may occur to some extent in other reactions. It does not seem to be the primary method of activation for the decomposition of nitrogen pentoxide or other reactions of constant order.

3. Activation, in accordance with the simple radiation theory, by the absorption of the frequency calculated by assuming the energy of activation to be taken up as a single quantum, cannot take place fast enough to account for the decomposition of nitrogen pentoxide, or other unimolecular reactions, and leads to incorrect predictions as to the frequencies that will be active. It might take place fast enough to account for the decomposition of nitrous oxide and other bimolecular reactions.

4. Activation by the simultaneous absorption of more than one frequency is not a probable mechanism of reaction.

5. The simultaneous absorption of one quantum and emission of another is not ruled out as a possible step in chemical reaction, but there is no evidence to show whether such steps ever do take place in chemical reaction.

6. There are experimental and theoretical reasons for believing that there will often be a number of quantum states of energy intermediate between that of the normal and the activated conditions, and for believing that instead of a single activated state we can sometimes have a whole series of activated states of nearly the same energy content in case the condition of activation corresponds to a very considerable weakening of the forces holding the atoms together in the molecule. As far as we can now see an elaborated radiation theory which includes these ideas as to intermediate and activated states might provide the mechanism for typical unimolecular and bimolecular reactions. The existence of intermediate states would account for the reason why absorption lines are not found in the neighborhood predicted by the simple radiation theory, and the existence of a whole series of activated states might be able to account for the high rate of unimolecular reactions.

In connection with the future prospects of the elaborated radiation theory we also wish to call attention once more to the possible liberating effect of the ideas of Bohr, Kramers and Slater, which retain the principle of conservation of energy only as a statistical requirement. This would permit activation by radiation without any immediate destruction of radiant energy, and indeed might permit us to postpone the necessity of "balancing the energy account" until after the deactivation of the products of the reaction.

7. In conclusion it can be stated that activation may occur to some extent by all the four mechanisms suggested. Indeed, since the great difficulty is to account for the rapidity with which energy of activation is supplied, we must not despise the assistance afforded by any method of activation. However, it seems at the present as if our main hopes must be centered on the elaborated radiation theory if we are to account for unimolecular reactions, and on this theory in general if we desire to have the same mechanism of activation for all typical chemical reactions.

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THE VOLUMETRIC METHOD OF MEASUREMENT OF THE MUTUAL SOLUBILITY OF LIQUIDS. THE MUTUAL SOLUBILITY OF THE SYSTEMS ETHYL ETHER-WATER AND ISO-AMYL ALCOHOL-WATER

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The first part of this investigation was completed in January, 1922, and was presented at a meeting of the Chemical Club of the Laboratory of Physical and Inorganic Chemistry of the First State University of Moscow on May 15, 1922, but remained unpublished. In this first part, in which A. P. Gubkina assisted, was fully discussed the present volumetric method, the measurements being made upon two pairs of liquids: ethyl ether-water and *iso*-amyl alcohol-water. Later, Hill[1] applied the volumetric method to the determination of the mutual solubility of ether and water. The second part of the present investigation was then finished. The method used by the authors was suggested to them by Prof. I. A. Kablukov of the above university.

The methods previously employed for the measurement of the mutual solubilities of liquids are discussed at length by Hill.[1] Aignan and Dugas[2] employed a method analogous to that of the present work, but owing to a different interpretation of their results they reached somewhat different conclusions as to the applicability of this method.

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[1] Hill, THIS JOURNAL, **45**, 1557 (1923).

[2] Aignan and Dugas, *Compt. rend.*, **125**, 498 (1897); **129**, 643 (1899).