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THE THEORY OF REACTION RATE

BY GILBERT N. LEWIS AND DAVID F. SMITH[1]

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If a reaction and the reverse reaction have independent specific reaction rates or rate constants, it was shown by van't Hoff[2] that the ratio between these constants must be the equilibrium constant, which varies with the temperature according to the equation

$$\frac{\mathrm{d}\, ln\, K}{\mathrm{d}T} = \frac{Q}{RT^2}, \tag{1}$$

where Q is the heat of the reaction. Writing K as the ratio of the two specific reaction rates, $\mathbf{K}_1$ and $\mathbf{K}_2$, this equation may therefore be broken into two equations

$$\frac{\mathrm{d}\, ln\, \mathbf{K}_1}{\mathrm{d}T} = \frac{A_1}{RT^2} + B$$

and

$$\frac{\mathrm{d}\, ln\, \mathbf{K}_2}{\mathrm{d}T} = \frac{A_2}{RT^2} + B \tag{2}$$

At every temperature B is the same for both reactions, and A_1 and A_2 are quantities such that their difference is the heat of the reaction. This is all that can be learned about reaction velocities from thermodynamics alone.

Arrhenius[3] added the assumption that only a certain fraction of the molecules, the activated molecules, actually react, and that their reaction velocity under all conditions is strictly proportional to their number. The specific reaction rate of the activated molecules, or the chance that one of these molecules will react in unit time, may be designated by $\mathbf{K}^*$. If the fraction of all the molecules in the activated state is represented by w^*, the observed rate constant must be

$$\mathbf{K} = \mathbf{K}^* w^* \tag{3}$$

Furthermore, Arrhenius assumed that there is an equilibrium between active and inactive molecules, and that the ratio between them changes with the temperature in accordance with Equation 1. Now this ratio, when it is small, may be taken equal to the fraction of active molecules w^*, and by Equation 1

$$\frac{\mathrm{d}\, ln\, w^*}{\mathrm{d}T} = \frac{q}{RT^2}, \tag{4}$$

where q is the heat required to convert the inactive into the active form. Combining Equations 3 and 4 we then have

$$\frac{\mathrm{d}\, ln\, \mathbf{K}}{\mathrm{d}T} = \frac{q}{RT^2}, \tag{5}$$

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[1] National Research Fellow in Chemistry.

[2] Van't Hoff, "Studies in Chemical Dynamics," Chemical Publishing Co., Easton, Pa., **1896.**

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

which is identical with Equation 2, B being zero and A being now identified as the heat of activation.

In the *radiation hypothesis* it has been assumed (1) that the activation of molecules is due to radiant energy, namely, the radiant energy which is present in a system by virtue of its temperature, or radiant energy which comes from without in the case of a photochemical reaction, and (2) that the frequency, ν, of the radiant energy which is capable of promoting the reaction may be calculated from the heat of activation by the formula, $Nh\nu = q$.

The second of these assumptions is certainly false. Lindemann[4] showed that the temperature coefficient of the inversion velocity of sucrose is such that, by this assumption, the speed of inversion would be enormously greater in sunlight than in the dark, which is not the case. It was further pointed out by Langmuir[5] that if activation can be produced only by radiation which lies within a narrow spectral region, there is not enough of such radiation passing through a system at ordinary temperatures to account for the observed rates of numerous reactions.

This last argument might be regarded as favoring the older hypothesis that molecular collisions are the chief agency in the activation of substances, but Christiansen and Kramers[6] in a recent analysis of this question conclude that neither radiation nor collisions can furnish sufficiently frequent activation to account for observed reaction velocities. Considering a number of reactions which are classed as unimolecular, they calculate that the rate of activation by collisions cannot be more than one ten-thousandth, and that by radiation cannot be more than one millionth of that required to account for observed rates of reaction.

They are therefore forced to conclude that the greater part of the activation results from the heat set free in the reaction itself. In other words, these reactions are in a certain sense explosive. To quote from this paper: "We imagine the exothermal reaction $n \longrightarrow n' + n''$, and consider that after activation through collision (or through radiation) an elementary reaction has taken place. Then we know that the products of the reaction, immediately after the decomposition, must contain the energy of activation as well as the reaction energy measured by direct calorimetry (at least if no radiation is emitted in the spontaneous decomposition, as we must assume on account of the large constant of the decomposition rate). Then, evidently, the reaction products rich in energy can activate new molecules through collision, which means the occurrence of so-called reaction-chains."

Now in answer to this argument we may point out in the first place that

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[4] Lindemann, *Phil. Mag.*, **40**, 871 (1920).

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

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

the specific reactions which Christiansen and Kramers consider are not exothermic but endothermic, nor are we aware of the existence of any reaction in which a single molecule breaks into two molecules with the evolution of energy (excepting, of course, our somewhat hypothetical activated molecule). Nevertheless, the calculated heat of activation is always greater than the normal heat of the reaction, and therefore some energy will be set free in the decomposition of the activated molecule, and this in coöperation with the other activating agencies, might suffice to produce the "reaction-chain" which they assume.

However, there is another argument against the theory of the reaction-chain which seems conclusive. The decomposition of nitrogen pentoxide is one of the chief reactions considered by Christiansen and Kramers. Now the work of Daniels and Johnston[7] and of Lueck[8] showed that the decomposition of nitrogen pentoxide occurs at about the same rate in the gaseous phase, and when dissolved in carbon tetrachloride or in chloroform. Now in these solvents the products of the reaction will collide much more often with solvent molecules than with molecules of nitrogen pentoxide, and in order to account for the fact that the reaction rate is the same in the solvents as in the pure gas it would be necessary to make the extremely improbable assumption that the solvent molecules are quite incapable of taking energy from the molecules "rich in energy" resulting from the decomposition.

So also if we were to assume that the energy set free in the decomposition of the activated molecule goes into radiant energy, then it would be necessary to believe the two solvents to be completely transparent to such radiation. There are doubtless reactions in which the decomposition of one molecule causes the decomposition of neighboring molecules, but such reactions will not be of the first order, for the specific reaction rate will change with the dilution, and will approach a constant value only at high dilutions where the decomposition of one dissolved molecule will not affect the others.

The paradox thus presented we might attempt to explain away by recalling that it is only an hypothesis that reactions proceed through active molecules, and that there is a definite heat required for activation. But this method also fails, for if we consider such a dissociation as that of nitrogen tetroxide, we know that two moles of nitrogen dioxide possess on the average 14,000 cal. more energy than one mole of the tetroxide. A molecule of the latter must therefore acquire an energy far above the average before it can dissociate, even if we assume the heat of activation to be zero. On the other hand, it was shown by Argo[9] from measurements

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[7] Daniels and Johnston, THIS JOURNAL, **43,** 53 (1921).

[8] Lueck, *ibid.*, **44,** 757 (1922).

[9] Argo, *J. Phys. Chem.*, **18,** 438 (1914).

of the velocity of sound in a mixture of the dioxide and tetroxide that the equilibrium between these substances must be established with extreme velocity. By the same method Keutel[10] obtained figures which show that the average life of a molecule of the tetroxide at ordinary temperatures is not greater than 0.001 second. Here again the calculations of Christiansen and Kramers would show that neither by collision nor by radiation could the molecules of nitrogen tetroxide acquire the energy necessary for dissociation with sufficient frequency to account for the observed reaction rate.

Having by this simple illustration reduced the paradox to its simplest terms, it becomes evident either that we must think of some third way of providing a molecule with energy, in addition to the methods of collision and radiation (and no such way has ever been suggested), or the frequency with which molecules may acquire abnormally large energies by collision or radiation must be very much higher than that calculated by Christiansen and Kramers. It is the latter explanation that we shall adopt and attempt to demonstrate. Before doing so, however, it seems desirable to consider with some care the meaning that we must attach to "heat of activation" and to "active and inactive molecules."

The Heat of Activation

In order to define more exactly the heat of activation, W. C. McC. Lewis has introduced the idea of the critical increment, or the difference between the energy of an activated molecule and the average thermal energy of the molecules. The latter term at least must change markedly with the temperature. Tolman[11] writes for the change of the specific reaction velocity with the temperature, $\frac{\mathrm{d}\, ln\, \mathbf{K}}{\mathrm{d}T} = \frac{E_{\text{activated}} - E_{\text{average}}}{RT^2}$. In using an equation of this type it must, however, be borne in mind that the development of the formula of Arrhenius, given in Equation 5, was based on the simplifying assumption that active molecules are few compared with the inactive molecules (which implies that q is large compared with RT). In the general case if w^* is the fraction of active molecules and $1 - w^*$ is the fraction of inactive molecules, then the application of Equation 1 gives

$$\frac{\mathrm{d}\, ln \frac{w^*}{1 - w^*}}{\mathrm{d}T} = \frac{q}{RT^2} \tag{6}$$

or, by Equation 3,

$$\frac{\mathrm{d}\, ln \frac{\mathbf{K}}{\mathbf{K}^* - \mathbf{K}}}{\mathrm{d}T} = \frac{q}{RT^2} \tag{7}$$

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[10] Quoted by Bodenstein, *Z. Elektrochem.*, **24,** 185 (1918). We have not had access to the original dissertation.

[11] Tolman, THIS JOURNAL, **42,** 2506 (1920).

This is a completely general equation in which q represents the difference in the average energy of active and of inactive molecules. Before this equation can be integrated, however, we must know something more about the meaning of active and inactive molecules. In the original theory of Arrhenius these were regarded as different chemical species in tautomeric equilibrium. If we adopt this view, then the two types of molecules having the same molecular weight will presumably have the same specific heat, and under equal conditions the same entropy. If we assume this as a first approximation, then q would be constant, the integration constant would be zero, and we should find

$$ln \frac{\mathbf{K}}{\mathbf{K}^* - \mathbf{K}} = -\frac{q}{RT}, \tag{8}$$

or

$$\mathbf{K} = \mathbf{K}^* \frac{1}{1 + e^{\frac{q}{RT}}} \tag{9}$$

Only when q is large compared with RT does this reduce to the simpler equation

$$\mathbf{K} = \mathbf{K}^* e^{-\frac{q}{RT}} \tag{10}$$

Equation 9 would be of considerable importance if we should find evidence that the active molecules are to be regarded as a tautomeric form of the inactive. But in the absence of such evidence it would seem safer to assume for the present that the difference between active and inactive molecules consists in a difference of energy content. For our present purpose we shall assume that a molecule cannot undergo transformation or dissociation unless it possesses a minimum internal energy, which we may call ϵ^*. By internal energy we shall mean all the energy which it possesses over and above what it would possess at very low temperatures, except its energy of rectilinear translation. The latter, by the principle of relativity, can have nothing to do with the possibility of a change inside the molecule.

Any molecule containing an amount of internal energy equal to or greater than ϵ^* may be called an activated molecule. It may not be in a position to undergo the particular reaction which we have in mind, for this may depend upon the orientation of the several parts of the molecule, upon the location of this energy within the molecule, or upon other factors of a similar nature. In other words, the molecule may not satisfy *all* the conditions requisite for the reaction in question, but at least it satisfies the energy requirement.

The distribution of energy among the molecules of a substance will be different for different substances. The simplest case that we can consider is one in which the distribution of energy among the several molecules is given by the formula which is deduced from classical kinetic theory for molecules possessing two degrees of rotational freedom. This formula is

$$\frac{dw}{d\epsilon} = \frac{1}{kT} e^{-\frac{\epsilon}{kT}} \tag{11}$$

where dw is the fraction of the molecules (or the probability of one molecule) possessing an internal energy within the range ϵ to $\epsilon + d\epsilon$, and k is the gas constant for one molecule. If we represent by w^* the chance that a molecule will have an energy greater than ϵ^*, we may obtain w^* by the integration of Equation 11 between ϵ^* and ∞, which gives

$$w^* = e^{-\frac{\epsilon^*}{kT}} \tag{12}$$

And now if we assume, as in Equation 3, that the specific reaction velocity is under all circumstances proportional to the fraction of activated molecules, we have the equation

$$\mathbf{K} = \mathbf{K}^* e^{-\frac{\epsilon^*}{kT}} \tag{13}$$

or

$$\frac{d\, ln\, \mathbf{K}}{dT} = \frac{\epsilon^*}{kT^2} \tag{14}$$

In this case, therefore, we see that the heat of activation is not the heat required to activate the average molecule, but rather is the heat required to raise a molecule from zero internal energy to the condition of activation.

When we consider other more complicated types of distribution of energy the equations are not easily integrable, but they are all alike in the one respect that they all reduce to Equation 14 when ϵ^* is large compared with kT. In other words Equation 14 is true for certain types of substances at all values of ϵ^* and kT, and is true for all reactions when the activation energy is large and the temperature is low.

So far we have assumed with Arrhenius that the rate of reaction of the activated molecules depends upon their number and upon nothing else. It is not, however, at all obvious that this will always be true. For example, since we have defined activated molecules as all molecules possessing more energy than ϵ^*, the chance of dissociation of a given activated molecule might be proportional to the energy which it possesses over and above this value, namely to $\epsilon - \epsilon^*$. The specific reaction rate of all molecules having an energy between ϵ and $\epsilon + d\epsilon$ will then be proportional to the fraction of such molecules and to $\epsilon - \epsilon^*$. Let us assume for simplicity that the fraction is given by Equation 11. The total specific reaction rate is then obtained by integrating over all the activated molecules. If A represents a constant,

$$\mathbf{K} = A \int_{\epsilon^*}^{\infty} (\epsilon - \epsilon^*) \frac{1}{kT} e^{-\frac{\epsilon}{kT}} d\epsilon = AkTe^{-\frac{\epsilon^*}{kT}}$$

$$\frac{d\, ln\, \mathbf{K}}{dT} = \frac{kT + \epsilon^*}{kT^2} \tag{14a}$$

This equation differs from the equation of Arrhenius, but the two become identical when ϵ^* is very large compared with kT. In the case of the decomposition of nitrogen pentoxide, which we are going to discuss later, the values of ϵ^* obtained from Equations 14 and 14a differ by a little over 2%, which is probably within the limits of experimental accuracy.

Again, let us assume that the activated molecules do not decompose spontaneously, but only when they meet light quanta. As we shall see in Equation 22, the chance that a molecule meets a light quantum is proportional to the temperature, so that we should write

$$\mathbf{K}^* = BT$$

Substituting this value in Equation 13, taking logarithms and differentiating, we once more obtain the equation

$$\frac{\mathrm{d}\, ln\, \mathbf{K}}{\mathrm{d}T} = \frac{kT + \epsilon^*}{kT^2} \tag{14b}$$

This is identical with Equation 14a. With other assumptions we would obtain other similar equations but, if we make the rate of reaction of the activated molecules any algebraic function of the temperature or the energy content, all of the equations will approach Equation 14 as a limit when the ratio of ϵ^* to kT increases.

The work of Arrhenius, and our whole preceding calculation, have been based upon the assumption that the concentration of active molecules is that which would exist in thermal equilibrium. But when a reaction is occurring the active molecules may decompose so rapidly that such thermal equilibrium is not attained. We shall consider such cases in our subsequent paper, and there show that our conclusions are still valid for any reaction in which the specific reaction rate is constant at a given temperature.

The Maximum Rate of Activation by Collision

Christiansen and Kramers obtained their values for the maximum rate of activation through collision by calculating the number of times per second that a pair of molecules would collide with an energy of relative translational motion equal to the energy of activation. Now the reactions which they consider all involve molecules that possess internal energy in considerable amount. Let us consider the decomposition of nitrogen pentoxide at ordinary temperatures. The heat of activation is calculated to be 24,700 calories per mole, or 24,700/N calories per molecule, where N is the Avogadro number. The chance is very small at ordinary temperatures that two molecules will collide with a mutual translational energy as large as this. But why is it necessary to assume that all of the energy of activation comes from the energy of translation and none from the internal energy which the molecules already possess as a result of previous collisions? The molal heat capacity of gaseous nitrogen pentoxide is not known, but it presumably is nearly 20 cal. per degree. If we subtract the amount of heat capacity due to translational motion, and if we also make some allowance for the falling off of heat capacity at lower temperatures, we still find that the average molecule at room temperature has an internal energy in the neighborhood of 4,000/N cal. Two average molecules possess twice this amount, and the translational energy required for activation is thus considerably reduced. With this new value, the frequency of favorable collisions would be increased about one million-fold and would therefore be far greater than would be required if we wished to assume that the observed rate of the reaction is the result of activation by collision alone.

Of course it may be argued that it is improbable that all of the internal energy of both molecules and all of their mutual translational energy should go into the activation of a single one of the molecules, but a similar argument could be made when translational energy alone is considered, and indeed such arguments would appear very plausible. But we are here concerned only with the calculation of the limit set upon the reaction velocity by the condition that the molecules are able to receive a quantity of energy sufficient for activation. What fraction of the molecules which are able to acquire the activation energy actually do acquire it, and what fraction of the molecules which have this energy would actually decompose to form new substances, are questions quite independent of the one we are now discussing.

The calculation that we have just made is a very rough one and could be made more exact by considering the distribution of internal energy among the several molecules and by calculating the number of favorable collisions through a process of integration. But we shall not do this, partly because we are going to make a calculation of a quite similar type when we discuss activation by radiation, and partly because we shall attempt, in our next paper, to show that while activation by collision is theoretically capable of explaining observed rates, it probably actually plays a minor part in most chemical reactions.

Maximum Rate of Activation by Radiation

The Size of a Light Quantum.—Before we can proceed to any sort of quantitative investigation of the maximum amount of activation which might be effected by radiation, we must obtain some idea of how near to a molecule the radiant energy must come before it can be absorbed. If a molecule is situated in a beam of light and is capable of absorbing it, how large a shadow can it cast? It has commonly been assumed that this zone of influence would be of the same order of magnitude as the dimensions of the molecule itself. But it was shown by Lord Rayleigh[12] that even from the classical wave theory this would not be the case. He came to the conclusion, rather, that even a resonator of infinitesimal size should absorb over an area of the order of $\lambda^2/8\pi$, where λ represents the wave length of the light. For ordinary light this is very much larger than any figure we would choose for the cross section of a molecule.

[12] Rayleigh, *Phil. Mag.*, **22**, 188 (1916).

Now that it has become necessary to discard the older wave theory, and consider some sort of light quanta, our problem may be stated in another way. How near must the center of a quantum of light approach to the center of an atom in order that the latter may absorb the energy of the former? This distance may be called the radius of action of the quantum or, for convenience, simply the radius of the quantum. If we denote this by r, we may define the cross section σ of the quantum by the equation, $\sigma = \pi r^2$. It is unnecessary to assume that this radius can be either measured or defined very sharply, nor need we assume that every molecule, even of those that are sensitive to the given frequency, necessarily absorbs energy every time that it comes within the radius r of the center of the quantum. But we shall assume that no appreciable number of molecules at a greater distance than this can absorb the energy of the quantum.

There is experimental evidence that the size of the quantum as so defined is considerably greater than that which is ascribed to atoms and simple molecules. From data on the extinction of light in its passage through absorbing materials we may calculate the amount of light that would be absorbed by a single molecule. Probably the most powerful absorbent of light hitherto discovered is cold mercury vapor, when the light is produced by resonance in mercury vapor. R. W. Wood[13] found that a thickness of 5 mm. of mercury vapor, at a pressure of one-millionth of an atmosphere, extinguishes one-half of the light of the resonance line at 2536 Å. From this we calculate that from a beam of such light, 1 sq. cm. in cross section, a single atom of mercury would extinguish the fraction 5.8×10^{-14}. Or we may write 5.8×10^{-14} sq. cm. as the area of the shadow cast by a single mercury atom. If we take this as equal to the cross section of the quantum, which we may regard as circular, we find $r = 1.4 \times 10^{-7}$ cm. Ordinary determinations of the radius of the mercury atom give a value only about one-tenth as great. On the other hand, when we use Rayleigh's equation for light of this wave length we find a radius 20 times as great as that which we have just calculated from the experiments of Wood.

There seems no reason for believing that other substances may not be found with even higher opacity than mercury vapor. It is hardly likely that every mercury atom that meets a quantum would be in the right orientation to absorb the energy. We are therefore led to suspect that the size of the quantum may be of about the magnitude given by Rayleigh's formula. Moreover, since this cross section of a quantum has the dimensions of distance squared, and since we know of no other quantity associated with light, of the dimension of distance, except the wave length, it seems not unlikely that the cross section of a quantum varies with the square of the wave length. If this surmise proves to be correct it will not be the first time that a result obtained from classical theory has retained

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[13] Wood, *Physik. Z.*, **13**, 353 (1912).

its value even after the premises upon which it is based have been abandoned.

Let us therefore assume, in the hope that further discoveries will give more support to the assumption than we can now claim for it, that the area of the cross section of the light quantum, as we have defined it, is given by the equation

$$\sigma = \frac{\lambda^2}{8\pi} = \frac{c^2}{8\pi\,\nu^2} \tag{16}$$

The Number of Quanta Available for Activation.—If we are to adopt the quantum theory of light, we may calculate the number of quanta present in unit volume of a hohlraum at a given temperature, or we may calculate the number of quanta having an energy higher than some given energy. If, following Planck, we designate by u_ν, the concentration of energy of frequency lying between ν and $\nu + \mathrm{d}\nu$, and if each quantum has the energy $h\nu$, then u_ν divided by $h\nu$ would represent the number of quanta per unit volume having frequencies lying between ν and $\nu + \mathrm{d}\nu$. This quantity, in turn, we may designate by $\mathrm{d}\rho = (\partial\rho/\partial\nu)\mathrm{d}\nu$, so that

$$\frac{\partial\rho}{\partial\nu} = \frac{u_\nu}{h\nu} \tag{17}$$

In our calculations it will make almost no difference whether we use, for u_ν, Planck's equation or Wien's equation. Largely for this reason, but also for another reason which we cannot enter upon here, we shall employ the latter, namely,

$$u_\nu = \frac{8\pi\,h\nu^3}{c^3}\,e^{-\frac{h\nu}{kT}} \tag{18}$$

or

$$\frac{\partial\rho}{\partial\nu} = \frac{8\pi\,\nu^2}{c^3}\,e^{-\frac{h\nu}{kT}} \tag{19}$$

As a quantum of light passes through the region which we are considering, it will sweep out in unit time a volume equal to the cross section of the quantum multiplied by the velocity of light, c. If in a unit volume the number of quanta of a given kind is represented by $(\partial\rho/\partial\nu)\mathrm{d}\nu$, the whole volume $\mathrm{d}\varphi$ which they sweep out is given by the equation

$$\mathrm{d}\varphi = \sigma c\,\frac{\partial\rho}{\partial\nu}\,\mathrm{d}\nu \tag{20}$$

and, since we have taken the total volume as unity, this expression also gives the ratio of the volume swept out to the total volume. But, if we ignore the very minute Doppler effect, *this ratio is equal to the chance that a molecule situated within the hohlraum will meet a quantum of the chosen type, in unit time.*

The chance φ' that a molecule will encounter a quantum of any frequency above a given frequency ν' will then be

$$\varphi' = \int_{\nu'}^{\infty} \sigma c\,\frac{\partial\rho}{\partial\nu}\,\mathrm{d}\nu \tag{21}$$

Combining with Equations 16 and 19 and integrating, we obtain the very simple expression,

$$\varphi' = \frac{kT}{h} e^{-\frac{h\nu'}{kT}} \tag{22}$$

The Maximum Rate of Favorable Collisions between Molecules and the Quanta of Isothermal Radiation.—It is known that some reactions are produced only by light of almost monochromatic character, the most conspicuous example being the change in an atom caused by light of one of its characteristic spectral lines. On the other hand, the majority of typical chemical reactions are presumably produced by light of a wide range of frequency. However, a discussion of such facts would be entirely alien to the purpose of the present paper, for we are considering the consequences of the single limitation, namely, that a molecule cannot react until it is in a position to acquire a definite activation energy. We thus confine our attention to ascertaining the chance that a molecule possessing a certain internal energy ϵ will encounter a quantum which has a frequency of at least ν' such that

$$\epsilon + h\nu' = \epsilon^*; \quad \nu' = \frac{\epsilon^* - \epsilon}{h} \tag{23}$$

If $dw = (\partial w/\partial\epsilon)d\epsilon$ represents the fraction of molecules with energy between ϵ and $\epsilon + d\epsilon$, and ϕ' is the chance[14] that one molecule of this group will encounter a quantum of frequency higher than ν' in unit time, then the chance dP that some such molecule will encounter some such quantum is given by the equation

$$dP = \phi' \frac{\partial w}{\partial \epsilon} d\epsilon \tag{24}$$

Finally, by integrating this equation we may find the chance P^*, *that any molecule chosen at random from the total number of molecules will, in unit time, meet with a quantum which has sufficient energy to take the molecule from the unactivated to the activated state,*

$$P^* = \int_0^{\epsilon^*} \phi' \frac{\partial w}{\partial \epsilon} d\epsilon = \frac{kT}{h} \int_0^{\epsilon^*} e^{\frac{\epsilon - \epsilon^*}{kT}} \frac{\partial w}{\partial \epsilon} d\epsilon \tag{25}$$

by Equations 22 and 23.

Let us consider a set of molecules which possess no internal energy except that of rotation with two degrees of freedom. For this case classical theory (and also quantum theory, if the moment of rotation is sufficiently large) gives Equation 11,

$$\frac{\partial w}{\partial \epsilon} = \frac{1}{kT} e^{-\frac{\epsilon}{kT}}$$

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[14] Calculations of a somewhat similar character, although far less specific, have been made by Tolman, This Journal, **42,** 2506 (1920).

Inserting this value in Equation 25 and integrating, we find[15]

$$P^* = \frac{\epsilon^*}{h} e^{-\frac{\epsilon^*}{kT}} \qquad (26)$$

Instead of using the special equation, we may, if we so choose, use the general equation offered by classical statistical mechanics for a system corresponding to n degrees of freedom within the molecule, namely,

$$\frac{\partial w}{\partial \epsilon} = \frac{1}{\Gamma\left(\frac{n}{2}\right)(kT)^{\frac{n}{2}}} \epsilon^{\frac{n}{2}-1} e^{-\frac{\epsilon}{kT}} \qquad (27)$$

and using this value in the integration of Equation 25 we obtain

$$P^* = \frac{1}{h\,\Gamma\left(\frac{n}{2}+1\right)(kT)^{\frac{n}{2}-1}} \epsilon^{*\frac{n}{2}} e^{-\frac{\epsilon^*}{kT}} \qquad (28)$$

Let us consider the case that would correspond roughly to the actual substance nitrogen pentoxide and take $n = 14$, $T = 300°\text{K}$ and ϵ^* as the energy in ergs per molecule corresponding to 24,700 calories per mole. Inserting these values in Equation 28 we find $P^* = 3 \times 10^2$. This figure shows the number of encounters per second between any molecule taken at random and such light quanta as are capable of raising it to the energy of activation. In other words, if every one of these encounters were effective in producing decomposition, the figure we have just obtained would also be equal to **K**, the actual velocity constant of decomposition. The value of **K** actually measured[16] is 4×10^{-5}, so that while Christiansen and Kramers found that radiation offers one million times too few opportunities for activation, to account for the observed rate of the reaction, our calculation shows that there are ten million times as many opportunities as would be necessary to account for the observed rate.

Of course there is a certain arbitrariness in attributing to nitrogen pentoxide the properties of a molecule with 14 degrees of freedom. But even if we had used Equation 26, for a molecule of only two degrees of freedom, we should still have found a possible rate of reaction greater than the observed rate. Every step in the calculation leading to Equation 25 is entirely reliable except for the assumption of Equation 16 for the effective cross section of the quantum. But if instead of this equation we had used the value obtained directly from the measurements of the absorption of light by mercury vapor, our result would not have been affected very materially.

We see therefore that there is no valid argument against the general radiation hypothesis. On the other hand, the special radiation hypothesis,

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[15] A certain resemblance between this equation and one which has been employed by Dushman [This Journal, **43,** 397 (1921)] will be discussed in our subsequent paper.

[16] This is the constant when the second is the unit of time. Daniels and Johnston use the minute as their unit.

as announced in the first papers of Perrin and W. C. McC. Lewis, in which it is assumed that ordinary chemical reaction is caused by nearly monochromatic radiation, is not tenable. Not only is there no experimental evidence in its favor, but it is certain that the number of collisions between molecules and such very restricted light quanta would be inadequate to account for the observed rates of reaction.

At present we can only guess at the various complex factors which determine whether a molecule which has the opportunity of acquiring enough energy for activation actually does acquire it, or whether if it acquires this energy it will suffer chemical change. In the present paper we have only shown that either collisions or radiation provide far more opportunities for activation than would suffice to account for observed rates of reaction. Our reasons for believing that radiation, and not collision, plays the important part in promoting actual chemical reactions we shall present in a subsequent paper.

Summary

This paper discusses the theory that the rate of a given chemical reaction depends upon the concentration of activated molecules. Activated molecules are sharply defined as all of the molecules possessing more than a minimum energy, and this minimum energy is defined as the heat of activation. With these definitions it is shown that an equation of the type obtained by Arrhenius is exactly true in certain simple cases, and is in all cases an approximation which becomes more nearly exact the higher the heat of activation and the lower the temperature. It is shown that both collisions and radiant energy offer opportunities for the activation of molecules far greater than the number required to account for observed reaction rates. An hypothesis is advanced concerning the radius of action of a light quantum, and this leads to a simple equation (Equation 35) for the number of encounters between molecules and the quanta of light which possess sufficient energy to activate these molecules. It is shown that no sound objection has been raised to the general radiation theory of activation, but that the special theory, which assumes activation by nearly monochromatic light, must be abandoned.

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