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THEORIES OF UNIMOLECULAR GAS REACTIONS AT LOW PRESSURES

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Certain recent experiments on the decomposition of propionic aldehyde[1] show an actual falling off at low pressures in the rate of a reaction which is unimolecular at high pressures. It would seem that some kind of collision hypothesis must be used to account for activation in such a case. The old form of the collision hypothesis as developed by Langmuir,[2] Christiansen and Kramers,[3] and Tolman[4] appears entirely inadequate even in the case just cited.[5] It seems possible that the explanation may be found in the suggestion, originally made by Lewis and Smith[6] and somewhat extended since by Christiansen[7] and by Hinshelwood and Lindemann,[5] that the internal degrees of freedom may be of some help in causing activation.[8]

This theory may be put in several different forms, not all of which have been considered in this connection. These will be investigated, and equations for the reaction rate at low pressures will be developed, using the methods and results of classical statistical mechanics.

[1] Hinshelwood and Thompson, *Proc. Roy. Soc.*, **113A**, 221 (1926).

[2] Langmuir, THIS JOURNAL, **42**, 2201 (1920).

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

[4] Tolman, THIS JOURNAL, **47**, 1524 (1925).

[5] Hinshelwood, *Proc. Roy. Soc.*, **113A**, 230 (1926).

[6] Lewis and Smith, THIS JOURNAL, **47**, 1514 (1925).

[7] Christiansen, *Proc. Cambridge Phil. Soc.*, **23**, 438 (1926).

[8] Since this paper was submitted, articles by Fowler and Rideal [*Proc. Roy. Soc.*, **113A**, 570 (1927)] and Thomson [*Phil. Mag.*, [7] **3**, 241 (1927)] have been received here, in which these authors have considered the internal degrees of freedom. They were attempting to explain quite a different phenomenon, and many of their assumptions run counter to ours. In so far as their treatments coincide with ours, they are similar also to the earlier work of Hinshelwood and Christiansen.

General Considerations

There seems to be some ambiguity over the definition of heat of activation. We shall define it as the minimum energy that a molecule must possess in order that it may decompose. Only internal energy is included and not translational, since we assume with Lewis and Smith[9] that a fast-moving molecule is no more likely to decompose than a slowly-moving one. The heat of activation is *not* to be taken as the excess over an average energy, nor as an energy term derived from the temperature coefficient of the reaction by use of the simple Arrhenius equation. In general, it is to be supposed that the energy of activation may be distributed in any manner whatsoever among the various degrees of freedom, exclusive of those concerned with the motion of translation of the molecule as a whole.

With this understanding we may now turn our attention to various possible theories.

Theory I.—The simplest possible hypothesis states that an activated molecule has a certain chance of reacting, independent of the distribution of energy among the degrees of freedom and independent of the amount it has above that necessary for activation. This is the theory which has been considered by Hinshelwood.[5]

Theory II.—It might be necessary for reaction that a *particular* degree of freedom should have a minimum energy, say ϵ_0, but that it is able to obtain this energy, even between collisions, from other parts of the molecule.[10] We shall assume that if the proper degree of freedom gets this energy, the molecule instantly decomposes. Now if the molecule *as a whole* has an energy of ϵ_0 or greater, enough of this energy *may* get to the proper degree of freedom to cause reaction to occur. A molecule is *activated*, then, if its total energy, exclusive of the translational, is at least ϵ_0. However, the chance that it will *react* depends on the amount of energy it has in excess of ϵ_0, for this determines the probability that enough energy will reach the right place.

Other Theories.—There may be various modifications of Theories I and II. (a) It may be that if *any one* of a number of unconnected degrees of freedom gets a certain (unshared) energy, the reaction occurs. (b) Reaction may take place if the energy becomes localized, not in a single degree of freedom, but among a few closely connected degrees of freedom, it being supposed that it makes no difference how it is distributed among this limited number of degrees of freedom. (c) It may be necessary for each of several degrees of freedom simultaneously to attain a minimum energy.

The above are typical, but other cases might readily be imagined. We shall consider chiefly Theories I and II.

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[9] Lewis and Smith, This Journal, **47**, 1512 (1925).

[10] Thomson (Ref. 8) also makes use of this idea.

It is to be remarked that any of the above will, of course, give a unimolecular reaction at high pressures where there is an equilibrium number of activated molecules, for the rate then depends only on the probability that something will occur within a single activated molecule.

Before we can proceed to the main part of this paper it is necessary to make a general statement concerning the method we propose to use in calculating the rate of activation. As already stated, we shall assume that interchanges of energy between molecules occur only at collisions, and we shall consider only the case in which this is the sole means of activation. Hinshelwood[11] shows that the rate of activation may be calculated from the rate of deactivation. This idea we intend to use, but we desire to go a little further than he does. If the pressure is high only a small fraction of the activated molecules react, most of them becoming deactivated by collisions with other molecules. The rate of activation is then obviously practically equal to the rate of deactivation. The latter may be calculated from the number of collisions of activated molecules, assuming deactivation at every collision. Now, when the pressure is low, it is no longer true that the rate of activation is equal to the rate of deactivation, because an appreciable number of the activated molecules react instead of becoming deactivated; however, this does not affect the rate of activation, and we can calculate the rate of deactivation which would exist if there were an equilibrium number of activated molecules present, and set it equal to the rate of activation. If the assumption of deactivation at every collision is not absolutely true, the last sentence does not hold, for then, by the principle of entire equilibrium, part of the source of activated molecules will be other activated molecules, whose numbers are depleted at low pressures. Now, it may be that although most of the activated molecules lose energy on collision, a small number actually gain it. One might even suppose that the entire supply of the more highly activated molecules (their number being exceedingly small) was maintained in this way from other less highly but nevertheless activated molecules. This would make no difference in the case of Theory I because of the smallness of number of the high-energy molecules. In Theory II, however, the high-energy molecules have much more tendency to react and this may more than counterbalance the other factor. It will, therefore, be necessary to make an *a posteriori* calculation to show that our assumption is justified, or to indicate how much it may lack of being true.

We may now proceed, confining ourselves throughout to the situation existing at the beginning of a reaction, where we may consider that we have a pure gas, the reaction products not yet beginning to have an effect.

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[11] Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford, **1926**, p. 127.

Reaction Rate at Low Pressures According to Theory I

Let N be the number of molecules per unit volume, and W the fraction of activated molecules as calculated from the distribution law, assuming equilibrium. NW, then, is the actual number per unit volume of activated molecules at high pressures, but not at low. The number of collisions per unit volume per unit time made by activated molecules at high pressures is aN^2W, where a is a constant known from the kinetic theory of gases. This is also the rate of deactivation per unit volume at high pressures and the rate of activation at any pressure. The rate of deactivation for low pressures is found by considering the number per unit volume, Z, of actually existing activated molecules, and is given by the expression aNZ. The number of molecules decomposing per unit volume per unit time is bZ, where b is a constant. A steady state will exist in which the rate of activation is almost exactly balanced by the combined rates of deactivation and reaction.[12] We then have $aN^2W = aNZ + bZ$. Solving for Z we find

$$Z = aN^2W/(aN + b) \tag{1}$$

Now let K be the fraction of molecules decomposed per second; $K = bZ/N$. Let K_∞ be the fraction decomposed per second at high pressures, or the unimolecular rate constant. $K_\infty = bNW/N = bW$. We have, therefore, substituting for Z, from Equation 1, and then for b, from the last equation, in the expression for K, and making algebraic reductions,[13]

$$K = \frac{K_\infty N}{N + K_\infty/(aW)} = \frac{K_\infty p}{p + K_\infty kT/(aW)} \tag{2}$$

where p is the pressure, k the gas constant per molecule and T the absolute temperature.

From the kinetic theory of gases it is known that[14]

$$a = 4s^2\sqrt{\pi kT/m} \tag{3}$$

where s is the molecular diameter and m the mass of a molecule.

From classical statistical mechanics[5]

$$W = \frac{1}{\Gamma\left(\frac{n}{2}\right)}\left(\frac{\epsilon_0}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon_0}{kT}} \tag{4}$$

where ϵ_0 is the energy of activation and n is the number of internal degrees of freedom. This is based on the assumption, the equivalent of which is commonly made in the deduction of the law of equipartition of energy,[15] that the energy is expressible as a sum of squares of coördinates and momenta with constant coefficients, or that Hooke's law of force holds

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[12] Ref. 11, p. 115.

[13] Christiansen [*Trans. Faraday Soc.*, **21**, 518 (1926)] also gets an equation of the same general form.

[14] Jeans, "Dynamical Theory of Gases," Cambridge, **1916**, p. 267.

[15] Ref. 11, **1916**, ed., pp. 80, 87.

within the molecule. This enables us to use total energy in expressions which were originally derived for the kinetic energy. In so doing we count one degree of freedom for each coördinate which enters the energy expression, and one for each momentum.

So we obtain finally, by substitution of Equations 3 and 4 in 2,

$$K = \frac{K_\infty}{1 + \beta_1/p} \tag{5}$$

where

$$\beta_1 = \frac{K_\infty \sqrt{m}\,(kT)^{\frac{n-1}{2}}\, e^{\frac{\epsilon_0}{kT}}\,\Gamma\left(\frac{n}{2}\right)}{4\sqrt{\pi}s^2\,\epsilon_0^{\frac{n-2}{2}}}$$

It is to be noted that the temperature coefficient of the rate constant is related to the heat of activation by the equations[5]

$$\frac{\mathrm{d}\log K_\infty}{\mathrm{d}T} = \frac{\mathrm{d}\log W}{\mathrm{d}T} = \frac{\epsilon_0 - \frac{n-2}{2}kT}{kT^2} = \frac{U}{kT^2} \tag{6}$$

where U would be the energy of activation per molecule, as originally defined by Arrhenius and used by many writers in this field.

Reaction Rate at Low Pressures According to Theory II

This case differs from the former chiefly in that we must consider the activated molecules with different amounts of energy separately. We will let $W_\epsilon\mathrm{d}\epsilon$ be the fraction of molecules having total internal energy between ϵ and $\epsilon + \mathrm{d}\epsilon$ as calculated from the normal distribution law for the case of equilibrium, so that $W = \int_{\epsilon_0}^{\infty} W_\epsilon\mathrm{d}\epsilon$, W having the same meaning as before. We will assume that the number of molecules per unit volume per unit time entering the range between ϵ and $\epsilon + \mathrm{d}\epsilon$ is given by $aN^2W_\epsilon\mathrm{d}\epsilon$, the number which would leave that range if equilibrium existed (that is, the number of collisions). The justification of this we will defer, as explained above.

We will let $Z_\epsilon\mathrm{d}\epsilon$ be the *actual* number of molecules per unit volume in the range between ϵ and $\epsilon + \mathrm{d}\epsilon$, so that $Z = \int_{\epsilon_0}^{\infty} Z_\epsilon\mathrm{d}\epsilon$. The number per unit volume per unit time leaving the range through deactivation will then be $aNZ_\epsilon\mathrm{d}\epsilon$, while the number lost through reaction will be $b_\epsilon Z_\epsilon\mathrm{d}\epsilon$; b_ϵ will differ for different energies in a way to be determined.

We then have $aN^2W_\epsilon\mathrm{d}\epsilon = aNZ_\epsilon\mathrm{d}\epsilon + b_\epsilon Z_\epsilon\mathrm{d}\epsilon$, so

$$Z_\epsilon = \frac{aN^2W_\epsilon}{aN + b_\epsilon} \tag{7}$$

Now let $K_\epsilon\mathrm{d}\epsilon$ be the total number of molecules in the range ϵ to $\epsilon + \mathrm{d}\epsilon$ which decompose per second, divided by the total number of molecules. Then, $K_\epsilon\mathrm{d}\epsilon = b_\epsilon Z_\epsilon\mathrm{d}\epsilon/N = aNW_\epsilon b_\epsilon\mathrm{d}\epsilon/(aN + b_\epsilon)$ by Equation 7, and

$$K = \int_{\epsilon_0}^{\infty} K_\epsilon d\epsilon = \int_{\epsilon_0}^{\infty} \frac{W_\epsilon b_\epsilon d\epsilon}{1 + b_\epsilon kT/(ap)} \qquad (8)$$

where p/kT has been substituted for N. It will be noted that for high pressures b_ϵ is negligible compared to aN and we have

$$K_\infty = \int_{\epsilon_0}^{\infty} W_\epsilon b_\epsilon d\epsilon \qquad (9)$$

By the general principles of statistical mechanics[16] under the same assumptions as before

$$W_\epsilon d\epsilon = \frac{1}{\Gamma\left(\frac{n}{2}\right)} \left(\frac{\epsilon}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon}{kT}} \frac{d\epsilon}{kT} \qquad (10)$$

We now have to evaluate b_ϵ.

Let us consider a number of molecules, all of which have energy between ϵ and $\epsilon + d\epsilon$, ϵ being greater than ϵ_0. These we shall designate as molecules of Class A. There will then be a certain chance that a molecule of Class A will have an energy larger than ϵ_0 in a particular degree of freedom. We will call such a molecule a molecule of Class B. If a state of equilibrium existed, these molecules would be shifting over at a certain rate (between collisions) to molecules which, while still of Class A, would not be of Class B. Let us suppose that this rate is proportional to the number of Class B, and is independent (1) of the excess of energy in the particular degree of freedom[17] and (2) of ϵ.[18] Now the rate at which molecules of Class B are formed under equilibrium conditions is equal to the rate at which they revert to molecules of Class A and not of Class B, and hence is proportional to the number of Class B. If all molecules of Class B decompose, this does not affect the rate at which they are formed. Hence the rate of decomposition is proportional to the number of Class B which would normally exist in a state of equilibrium.

We have, then, to determine the fraction of all molecules which have total energy between ϵ and $\epsilon + d\epsilon$ and which would also have, if the distribution law held, one degree of freedom with energy greater than ϵ_0.

The chance that one particular degree of freedom has an energy between ϵ_1 and $\epsilon_1 + d\epsilon_1$ is

[16] Gibbs, "Elementary Principles in Statistical Mechanics," Scribner's, New York, **1902**, p. 93.

[17] This certainly cannot be a bad assumption to make for purposes of approximation, for the distribution law shows that the number of molecules having any appreciable excess over ϵ_0 in the particular degree of freedom is very small compared with the number having a slight excess, and hence those with a large excess do not greatly affect the calculation.

[18] The shape of the curves K_ϵ against $\epsilon - \epsilon_0$ later to be obtained (Fig. 1) would indicate that this should be satisfactory for purposes of approximation, unless the effect of ϵ is quite marked.

$$\frac{1}{\sqrt{\pi}}\left(\frac{\epsilon_1}{kT}\right)^{-\frac{1}{2}} e^{-\frac{\epsilon_1}{kT}} \frac{d\epsilon_1}{kT} \tag{11}$$

The chance that all the rest of the degrees of freedom have among them an energy between $\epsilon - \epsilon_1 - d\epsilon_1$ and $\epsilon - \epsilon_1 + d\epsilon$ is

$$\frac{1}{\Gamma\left(\frac{n-1}{2}\right)}\left(\frac{\epsilon-\epsilon_1}{kT}\right)^{\frac{n-3}{2}} e^{-\frac{\epsilon-\epsilon_1}{kT}} \frac{d\epsilon + d\epsilon_1}{kT} \tag{12}$$

The product of Equations 11 and 12 is evidently greater than the probability that a molecule should have energy between ϵ and $\epsilon + d\epsilon$ and at the same time should have an energy between ϵ_1 and $\epsilon_1 + d\epsilon_1$ in one (specified) degree of freedom.[19] Similarly, if we had written $d\epsilon - d\epsilon_1$, instead of $d\epsilon + d\epsilon_1$ (assuming $d\epsilon_1 < d\epsilon$), then their product would have been smaller. If $d\epsilon_1$ is small compared with $d\epsilon$, then it does not matter which way Equation 12 is written, and we may write it simply

$$\frac{1}{\Gamma\left(\frac{n-1}{2}\right)}\left(\frac{\epsilon-\epsilon_1}{kT}\right)^{\frac{n-3}{2}} e^{-\frac{\epsilon-\epsilon_1}{kT}} \frac{d\epsilon}{kT} \tag{13}$$

It is now evident that the product of Equations 11 and 13 may be integrated with respect to ϵ_1, holding ϵ and $d\epsilon$ constant. This removes the limitation that $d\epsilon_1$ must be small compared to $d\epsilon$.[20]

Multiplying Equations 11 and 13 and integrating with respect to ϵ_1 from ϵ_0 to ϵ will give us $\alpha W_\epsilon b_\epsilon$, where α is a constant, independent of ϵ, which will be determined later.

$$\alpha W_\epsilon b_\epsilon = \frac{1}{\sqrt{\pi}\,\Gamma\left(\frac{n-1}{2}\right)} \frac{e^{-\frac{\epsilon}{kT}}}{(kT)^{\frac{n}{2}}} \int_{\epsilon_0}^{\epsilon} \epsilon_1^{-\frac{1}{2}} (\epsilon - \epsilon_1)^{\frac{n-3}{2}}\, d\epsilon_1 \tag{14}$$

For any definite value of n the integral in this expression could be evaluated by successive integration by parts. We will, however, be content with an approximation. We see that $(\epsilon - \epsilon_1)^{(n-3/2)}$ varies much more rapidly, assuming n to be fairly large, than $\epsilon_1^{-1/2}$, and that the important part of the integrand is the part where ϵ_1 is small. We therefore write as an approximation

$$\int_{\epsilon_0}^{\epsilon} \epsilon_1^{-\frac{1}{2}} (\epsilon - \epsilon_1)^{\frac{n-3}{2}}\, d\epsilon_1 = \epsilon_0^{-\frac{1}{2}} \int_{\epsilon_0}^{\epsilon} (\epsilon - \epsilon_1)^{\frac{n-3}{2}}\, d\epsilon_1 = \frac{2\epsilon_0^{-\frac{1}{2}} (\epsilon - \epsilon_0)^{\frac{n-1}{2}}}{n-1} \tag{15}$$

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[19] This is seen in the following manner. Suppose the one degree of freedom to have an energy exactly ϵ_1. Then if all the other degrees of freedom together can have an energy between $\epsilon - \epsilon_1 - d\epsilon_1$ and $\epsilon - \epsilon_1 + d\epsilon$, the total energy of the molecule can lie anywhere between $\epsilon - d\epsilon_1$ and $\epsilon + d\epsilon$. This evidently includes every molecule in which the one degree of freedom has an energy of exactly ϵ_1 and in which the total energy is between ϵ and $\epsilon + d\epsilon$, and some others besides. The same can be seen to be true for any value we choose to take between ϵ_1 and $\epsilon_1 + d\epsilon_1$.

[20] For treatment of a similar problem see Lorentz, "Théories Statistiques en Thermodynamique," Teubner, Leipzig and Berlin, **1916**, p. 12.

To evaluate α we substitute Equation 15 in 14 and integrate with respect to ϵ from ϵ_0 to ∞. This gives us

$$\alpha \int_{\epsilon_0}^{\infty} W_\epsilon b_\epsilon \mathrm{d}\epsilon = \frac{2\epsilon_0^{-\frac{1}{2}} e^{-\frac{\epsilon_0}{kT}} (kT)^{\frac{1}{2}} \Gamma\left(\frac{n+1}{2}\right)}{(n-1)\sqrt{\pi}\,\Gamma\left(\frac{n-1}{2}\right)} \tag{16}$$

Evaluating α from Equations 16 and 9 and inserting the value in Equation 14 we have

$$W_\epsilon b_\epsilon = \frac{K_\infty}{\Gamma\left(\frac{n+1}{2}\right)} \frac{e^{-\frac{\epsilon-\epsilon_0}{kT}}}{kT} \left(\frac{\epsilon-\epsilon_0}{kT}\right)^{\frac{n-1}{2}} \tag{17}$$

From 17 and 10

$$b_\epsilon = \frac{K_\infty \Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)} \frac{e^{\frac{\epsilon_0}{kT}}}{(kT)^{\frac{1}{2}}} \frac{(\epsilon-\epsilon_0)^{\frac{n-1}{2}}}{\epsilon^{\frac{n-2}{2}}} \tag{18}$$

Equation 8 now becomes

$$K = \frac{K_\infty}{kT\,\Gamma\left(\frac{n+1}{2}\right)} \int_0^\infty \frac{e^{-\frac{\epsilon-\epsilon_0}{kT}} \left(\frac{\epsilon-\epsilon_0}{kT}\right)^{\frac{n-1}{2}}}{1+\frac{\beta_2}{p}\frac{(\epsilon-\epsilon_0)^{\frac{n-1}{2}}}{\epsilon^{\frac{n-2}{2}}}} \mathrm{d}\,(\epsilon-\epsilon_0) \tag{19}$$

where

$$\beta_2 = K_\infty \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)} \sqrt{\frac{m}{\pi}} \frac{1}{4s^2} e^{\frac{\epsilon_0}{kT}}$$

This has been integrated by graphical means, and a series of curves for this purpose of the integrand, K_ϵ, against $\epsilon - \epsilon_0$ is shown in Fig. 1. The outer curve is the curve for infinite pressure, and the number near each curve gives the value of β'/p, where $\beta' = 3.16 \times 10^{-3}\beta_2$, ϵ and ϵ_0 being in calories per mole. The temperature used was 576°, n was taken as 11, and ϵ_0 as 54,000 calories per mole. These figures correspond to some of Hinshelwood and Thompson's experiments on propionic aldehyde. The ordinates represent the relative number of molecules having a definite energy and pressure which react in a given time. Due to the character of the function the value of the integrand decreases rapidly with high values of $\epsilon - \epsilon_0$, and although the curve theoretically extends to infinity, actually we can use a finite portion of it.

In evaluating the heat of activation from the temperature coefficient of the reaction rate in the case of Theory II, we note that here

$$\frac{\mathrm{d}\log K_\infty}{\mathrm{d}T} = \frac{\epsilon_0 + \frac{1}{2}kT}{kT^2} = \frac{U}{kT^2} \tag{20}$$

as shown by Rodebush[21] since the rate at high pressures depends on the probability that a *single* degree of freedom have an energy greater than ϵ_0.

We can now use the set of curves in Fig. 1 to justify the assumption we made that the actual rate of formation of molecules in a given energy range was to be calculated from the rate of loss which would exist under equilibrium conditions. The lower the pressure the less justified we would consider this assumption to be. Consider, therefore, the lowest curve of the set shown. A trifle over 11% of the area under it is to the right of the 11,000 mark. At $\epsilon - \epsilon_0$ equal to 5000 the concentration is about 8% of the equilibrium value. We now ask the question: How many of the molecules having an energy per mole of 65,000 cal. ($\epsilon - \epsilon_0 = 11,000$) were formed from molecules having an energy of more than 59,000 cal. per mole, and hence not present in approximately equilibrium numbers? To answer this let us use the principle of entire equilibrium and find what is the chance that a molecule of 65,000 cal. per mole energy should not lose more than 6000 cal. per mole at a collision with an average molecule (or that the other molecule should leave with more than 59,000 cal. per mole). We can do this if we assume that statistical equilibrium

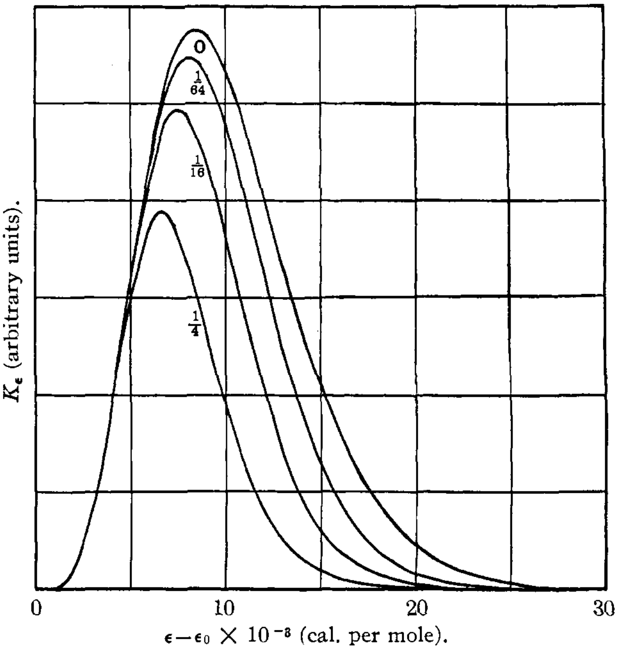

Fig. 1.—Curve $\beta'/p = 0$, relative area $(K/K_\infty) = 1.00$; $\beta'/p = {}^1/_{64}$, $(K/K_\infty) = 0.84$; $\beta'/p = {}^1/_{16}$, $(K/K_\infty) = 0.66$; $\beta'/p = {}^1/_4$, $(K/K_\infty) = 0.44$.

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[21] Rodebush, This Journal, **45**, 610 (1923).

is established between the various degrees of freedom of both molecules at a collision. If statistical equilibrium is not established at a collision, the error would be about the same for low- and high-energy molecules, and the chief result would be that only a fraction of the collisions would be effective in deactivation, which would merely mean that β_2/p would have to be multiplied by a constant factor. While this last point cannot be said to be strictly established, it is obvious that the calculation we propose to make will be a valuable indication of the validity of our assumption.

If two molecules, each having n degrees of freedom, collide, there are $2n$ degrees of freedom involved. The chance that one of the molecules with n degrees of freedom should have an energy between ϵ_2 and $\epsilon_2 + \mathrm{d}\epsilon_2$ is

$$\frac{1}{\Gamma\left(\frac{n}{2}\right)}\left(\frac{\epsilon_2}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon_2}{kT}} \frac{\mathrm{d}\epsilon_2}{kT} \tag{21}$$

The chance that the other molecule should have energy between $\epsilon' - \epsilon_2$ and $\epsilon' - \epsilon_2 + \mathrm{d}\epsilon'$ is

$$\frac{1}{\Gamma\left(\frac{n}{2}\right)}\left(\frac{\epsilon' - \epsilon_2}{kT}\right)^{\frac{n-2}{2}} e^{-\frac{\epsilon' - \epsilon_2}{kT}} \frac{\mathrm{d}\epsilon'}{kT} \tag{22}$$

By reasoning similar to that following Equations 12 and 13, the product of 21 and 22 is the probability that the total energy of the two molecules is between ϵ' and $\epsilon' + \mathrm{d}\epsilon'$, while one of them has energy between ϵ_2 and $\epsilon_2 + \mathrm{d}\epsilon_2$. But the chance that the two together have energy between ϵ' and $\epsilon' + \mathrm{d}\epsilon'$ is

$$\frac{1}{\Gamma(n)}\left(\frac{\epsilon'}{kT}\right)^{n-1} e^{-\frac{\epsilon'\epsilon}{kT}} \frac{\mathrm{d}\epsilon'}{kT} \tag{23}$$

The product of Equations 21 and 22 divided by Equation 23 is the chance that if two molecules have an energy of ϵ' together, a certain one of them has an energy between ϵ_2 and $\epsilon_2 + \mathrm{d}\epsilon_2$. Now we start with two molecules, one of which has an energy of 65,000 and the other the average energy or 9300 cal. per mole, the sum of which is ϵ'. We wish to find the chance that either of them should come out of the collision with an energy greater than 59,000 cal. per mole (ϵ''). We must double the expression [(21) × (22)/(23)] to allow for either molecule having the energy, and integrate.

$$\frac{2\Gamma(n)}{\epsilon'^{\frac{n}{2}}\left[\Gamma\left(\frac{n}{2}\right)\right]^2}\int_{\epsilon''}^{\epsilon'}\left(\frac{\epsilon_2}{\epsilon'}\right)^{\frac{n-2}{2}}(\epsilon' - \epsilon_2)^{\frac{n-2}{2}}\,\mathrm{d}\epsilon_2 \tag{24}$$

For the sake of simplicity, and since it can only cause the probability to come out greater than it should be, we will take ϵ_2/ϵ' as 1, and get

$$\frac{4\Gamma(n)}{n\left[\Gamma\left(\frac{n}{2}\right)\right]^2}\left(\frac{\epsilon' - \epsilon''}{\epsilon'}\right)^{\frac{n}{2}} = 0.081 \tag{25}$$

This seems small enough to justify our assumption as an approximation, especially when it is considered that the molecule we fixed attention on had considerably higher energy than the average reacting molecule.

Discussion of the Results in Connection with the Decomposition of Propionic Aldehyde

Either Equation 5 or 19 allows us to plot a curve for K against p. In order to fit the data one must have values of β_1 or β_2 and K_∞ which must be determined from the data, themselves. In this situation it is convenient to plot log K/K_∞ against log p. In such a plot Theory I gives curves which are absolutely invariable in shape and are shifted horizontally by changes in β_1. We can then plot the data in a similar fashion on transparent coördinate paper and attempt to effect a fit by moving the curve over the data. Since K_∞ from the data may be in error by 10 to 15% we may shift data and curves relatively to each other a short distance in the vertical as well as in the horizontal direction. The value of β_1 may be calculated from the final position of the theoretical curve, and assigning a reasonable value for s and knowing all quantities involved except n, we may find a value for n.

In Theory II a slight change in form occurs if n is changed. We must, therefore, assign a value of n in advance, and the value of β_2 which it is necessary to use in order to fit the data, and which is found by relative shifting of points and curve, as for Theory I, must agree with this value of n and the known values of the other quantities involved in the expression for β_2; however, because of the way in which the molecular diameter and heat of activation enter β_2 we have a leeway in this matter of several fold.

We have used the scheme outlined in constructing Fig. 2, which is for Hinshelwood and Thompson's data[1] at 576°. It will be seen that it is necessary to assign different values to K_∞ for the two theories, and that in either case the theoretical value of K_∞ is considerably higher than the highest experimental value of K. This suggests that information might be obtained not only from experiments at lower pressures, but also by experiments at higher pressures.

The value of K_∞ on Theory I is 0.020 from Fig. 2 (knowing the values of Hinshelwood and Thompson's constants). The value of β_1 used is 57 mm. of mercury. Using $s = 6 \times 10^{-8}$ and $U = 55{,}000$ from Hinshelwood and Thompson's temperature coefficient (see Equation 6), we find that the best value for n is 12, which checks with Hinshelwood's estimate.

The value of K_∞ on Theory II from Fig. 2 is 0.023. Using this, s as above, and $\epsilon_0 = 54{,}000$ (see Equation 20) we calculate that β_2 should be 1900 (n being taken as 11). The value of β_2 actually used is 4000, which is close enough, as a change of 1 in the value of n would introduce a larger discrepancy.

It will be seen that the data on the decomposition of propionic aldehyde does not allow us to decide which theory is better. We hope to be able to do this soon in the case of azomethane, experiments on which are now under way.

The curves for Theory I at different temperatures should practically coincide. On Theory II, this is not quite the case, but the effect is small (within experimental error). Hinshelwood and Thompson's data for 523°, the other temperature for which they give initial rate constants, fall similarly with reference to theoretical curves but they are displaced in the figure, a certain amount vertically corresponding approximately to the difference in the calculated[22] and experimental values for high pressures in Hinshelwood and Thompson's table.[23]

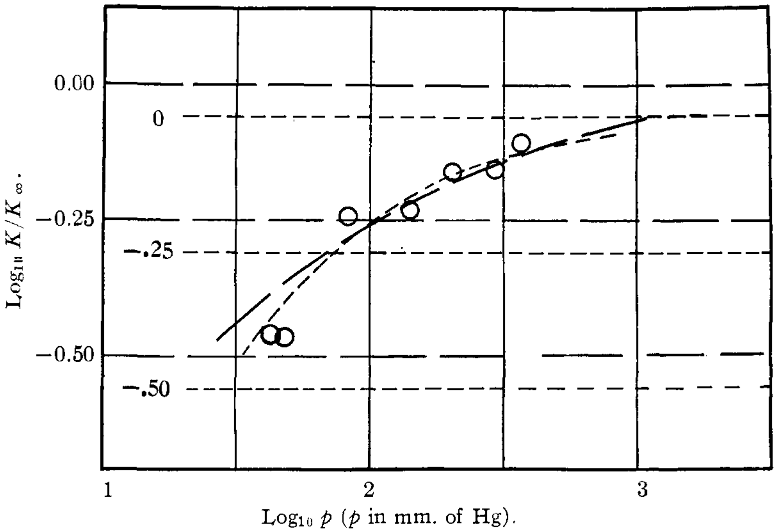

Fig. 2.—Theory I, - - - - - -. Theory II, —— ——.

Other Theories

We may briefly dispose of the other theories mentioned on page 1618 as follows. One may go through a deduction similar to that given for Theory II. In each case this would seem to indicate that for a fixed total number of degrees of freedom this would give results intermediate in character to those of the two theories considered in detail, except (a) which gives exactly the same result as Theory II.

Summary

A collision theory of homogeneous gas-phase, unimolecular reactions at low pressures has been developed. Several possible forms of the theory

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[22] From the temperature coefficient and constants at other temperatures.

[23] Ref. 1, p. 228.

are suggested, and two of them carefully considered These theories take account of the distribution of energy among the large number of degrees of freedom of the rather complex molecules that are known to decompose in unimolecular manner. They determine the way in which the reaction rate would be influenced by the initial pressure and can, therefore, be tested experimentally. All molecules which have a certain minimum total energy which can be calculated from the temperature coefficient are said to be activated. The rate of activation is calculated from the distribution of energy among molecules having n degrees of freedom, and by assuming that the rate of activation is equal to what the rate of deactivation would be under equilibrium conditions, and that each collision of an activated molecule results in deactivation.

When the pressure is high, most activated molecules are deactivated and but a small fraction react. At lower pressures an appreciable fraction of them react, and at very low pressures when most of the activated molecules react the reaction rate becomes very much smaller and bimolecular. By Theory I, the chance of reaction is independent of the excess of energy beyond that required for activation, and this leads to an equation of the form $K = K_{\infty}p/(p + \beta_1)$, where K is the rate constant, K_{∞} the rate constant at high pressures, p the pressure and β_1 a constant involving the number of degrees of freedom, the molecular diameter, the heat of activation, K_{∞}, etc.

Theory II requires not only that a molecule have a minimum total energy, but that such an activated molecule react only if it contains a certain minimum of energy in a particular degree of freedom. It is assumed that the internal energy may be repeatedly redistributed within the molecules between collisions. If a molecule has a large excess of energy beyond that required for activation, there will be a greater probability that this energy will get into a particular degree of freedom to cause reaction. An equation is derived which gives this probability. By fixing the number of degrees of freedom, etc., it is possible to determine the relative reaction rate at various pressures by means of a graphical integration.

The data on the decomposition of propionic aldehyde at various pressures are found to fit the theoretical curves of Theory I and Theory II about equally well. More accurate data extending over a wider pressure range are necessary to decide between the two theories.

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