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A THEORY OF CHEMICAL REACTIVITY. CALCULATION OF RATES OF REACTIONS AND EQUILIBRIUM CONSTANTS.

BY SAUL DUSHMAN.

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I. Introduction.

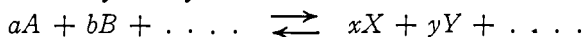
The general problem of chemical reactivity may be treated by two methods, the thermodynamic and the kinetic. The first one, as well known, is capable of dealing only with the equilibrium state, and the conclusions are therefore, independent of the mechanism by which such a state is attained. In the form of van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2} \quad (1)$$

the thermodynamical method leads to a relation between the equilibrium constant K , the heat of reaction Q , and the absolute temperature T , that has proved to be one of the most valuable generalizations of modern chemistry. Stated in another form, this equation gives the relation between the *temperature coefficient of the free energy* of a chemical reaction and the *total energy change* involved in the reaction. Thus, it is impossible, without the use of further assumptions, to derive by means of this equation the actual value of the free energy change from the change in total energy. As well known, Nernst has shown that this may be accomplished by means of his third law of thermodynamics, but, in general the method although theoretically valuable, is difficult to apply because of our lack of knowledge of specific heats at extremely low temperatures. G. N. Lewis and his collaborators have attacked the problem from a purely experimental point of view, and as a result of their work, we have a great deal of accurate data on the actual change in free energy in a large number of reactions.

Attempts have also been made during the past decade or so to treat the problem of chemical reactivity from a kinetic point of view, that is, by considering the mechanism by which the equilibrium state is attained.

Thus we may regard the equilibrium state as one in which the velocities of 2 opposing reactions are equal. If, in addition, we take into account the mass-law relation first deduced by Guldberg and Waage, we can write for the velocity of any chemical reaction



an expression of the form

$$-\frac{dC_A}{dt} = k_1(C_A)^a(C_B)^b \dots - k_2(C_X)^x(C_Y)^y \quad (2)$$

where C denotes the concentration of each substance and k_1 and k_2 are

the so-called *velocity-constants*. At equilibrium, the actual velocity of the reaction is zero. Consequently,

$$\frac{k_2}{k_1} = \frac{(C_A)^a(C_B)^b \dots}{(C_X)^x(C_Y)^y \dots} = K. \quad (3)$$

This equation enables us, therefore, to calculate the free energy of a chemical reaction from determinations of the velocity constants of the opposing reactions.

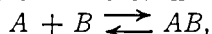
Now what are the factors governing the values of k_1 and k_2 ? "The fact that many reactions occur with a *finite* and measurable velocity, shows us that *all* the molecules are *not* in the same chemical state. If they were, the speed of the reaction would either be zero or practically infinite."¹ It has also been a matter of common knowledge that the velocities of most chemical reactions increase very rapidly with the temperature, so that at ordinary temperatures the rate usually doubles or triples for an increase of 10° .²

Arrhenius³ pointed out that the effect of temperature on the velocity of a reaction could be expressed by means of the empirical equation

$$\frac{d \ln k}{dT} = \frac{A}{T^2} \quad (4)$$

which is analogous to van't Hoff's equation for the temperature-coefficient of the equilibrium constant. In this equation, A is a constant for any particular reaction. In order to account for the effect of temperature on the velocity of a reaction, Arrhenius also introduced the concept of "active molecules," so that AR corresponds to the amount of energy required to "activate" a gram-mol of the reactants.

L. Boltzmann⁴ and subsequently F. Krüger⁵ have attempted to calculate the velocity of a bimolecular reaction in gases by means of kinetic considerations. Thus consider the reaction



where all the substances concerned are gases. Formation of AB can occur only because of collisions between molecules of A and B . Hence, the velocity of this reaction should be given by the value of the collision-frequency of these molecules. With regard to the dissociation of AB , Krüger assumes that this reaction occurs whenever the relative velocity of one of the atoms with respect to the other, inside the molecule AB , exceeds a certain critical value.⁶

¹ W. C. McC. Lewis, "Radiation the Fundamental Factor in all Chemical Change," *Scientia*, **25**, 450 (1919).

² van't Hoff, "Die Chemische Dynamik," 1901, p. 225.

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

⁴ Boltzmann, *Wied. Ann.*, **22**, 39 (1884).

⁵ Krüger, *Nach. Göttinger, Math. Phys. Klasse*, 1908, p. 318.

⁶ For a full discussion of this theory see K. Jellinek, "Physikal. Chem. der Gasreaktionen," 1913, p. 723.

Neither Boltzmann nor Krüger attempted to compare their theoretical conclusions with experimental data, but as the collision-frequency of gas molecules is proportional to \sqrt{T} , while the experimentally observed effect of temperature on reactions is to increase the velocity constant exponentially, it is evident that the velocity cannot depend upon collision-frequency alone.

This phase of the problem has been attacked by M. Trautz in a series of papers published during the past ten years.¹

Trautz's fundamental conception is that a molecule must be in an *active state* in order to react, and he deduces the fraction of the molecules which are in the active state at any temperature from the following considerations.

Combining Equations 1 and 3 above, it follows that

$$\begin{aligned} \frac{d \ln K}{dT} &= \frac{d(\ln k_1 - \ln k_2)}{RT^2} = \frac{Q}{RT^2} \\ &= \frac{q_1 - q_2}{RT^2} \end{aligned} \quad (5)$$

where $q_1 - q_2 = Q$.

If now we write

$$\left. \begin{aligned} \frac{d \ln k_1}{dT} &= \frac{q_1}{RT^2} \\ \frac{d \ln k_2}{dT} &= \frac{q_2}{RT^2} \end{aligned} \right\} \quad (6)$$

we obtain a relation between the temperature coefficient of the velocity constant and the *heat of activation*, q_1 (or q_2) of the corresponding reactants. Furthermore, the *difference between the heats of activation of the reactants and resultants corresponds to the thermochemically observed heat of reaction*. Now, if we assume that the molecules have to acquire an energy of activation given by q_1 before the reaction corresponding to k_1 can occur, it readily follows from Maxwell's distribution law that the fraction, α , of the molecules which at any temperature, T , possess this amount of energy is given by

$$\alpha = \epsilon^{-\int \frac{q_1 dT}{RT^2}}$$

It is evident that for a small range of temperature where q_1 may be assumed to be constant.

$$\int \frac{q_1 dT}{RT^2} = -\frac{q_1}{RT}$$

¹ A review of this work has been given by Trautz himself in *Z. anorg. Chem.*, 106, 81-127 (1919), where further references are given to his previous publications. Trautz's work has also been discussed by K. Jellinek (*loc. cit.*) and K. F. Herzfeld, *Ann. Phys.*, 59, 635 (1919).

Thus we can write for α , the fraction of the molecules which are in the active state, the relation

$$\alpha = e^{-q/RT} \quad (7)$$

where q denotes the heat of activation at the temperature T . In general, q will, of course, vary with the temperature, owing to differences in specific heat between activated and inactivated forms, and Trautz has indicated the manner in which the magnitude of this specific heat correction may be calculated in certain cases. This correction is, however, usually small, and if we define q as the heat of activation at any given temperature T , the value of α is fixed by the value of $d(\ln k)/d(1/T)$ at this temperature.

Trautz and also Stern¹ have drawn attention to the fact that in some cases, at least, another factor must be taken into account as possibly influencing the mutual reactivity of 2 molecules. This is known as the *steric* factor. Thus the molecules in order to react may not only have to be in an active state as defined by their internal energy content, but may have to collide at definite portions of their surfaces. In the case of complex molecules, such as are met with in organic chemical reactions, such a factor must undoubtedly be taken into account, but in the case of ordinary gas reactions, it has not been found necessary to consider this factor, so that for the purpose of the present discussion, its value may be considered as practically unity (the maximum value).

By taking account, in the above manner, of the fact that only a definite fraction of each type of molecule is capable of reacting at any given temperature, Trautz and W. C. McC. Lewis² have shown that the rate of a bimolecular reaction in gases may be calculated from the frequency of collision between the active molecules as deduced from kinetic theory considerations. Some other examples of the application of this theory are given in a subsequent section of this paper.

While the treatment of bimolecular reaction velocities from the kinetic point of view has proved very successful, the problem of unimolecular reaction velocities has still remained open, and the reason for this may be readily understood from the following considerations.

As has been pointed out quite recently by Perrin,³ the fact that a reaction proceeds according to the law of a unimolecular reaction means that the rate of this reaction is *independent* of the concentration. Thus, let us consider a dissociation into atoms of the type, $A_2 \rightleftharpoons 2A$.

The *fraction* of A_2 dissociating at any instant at any given temperature is independent of the actual number of molecules of A_2 present in unit volume. Hence, the collision-frequency can have no effect on the velocity of the dissociation, or the probability that a molecule of A_2 will disso-

¹ Stern, *Ann. Phys.*, **44**, 497 (1914).

² *J. Chem. Soc., (London)* **113**, 471 (1918).

³ Perrin, *Ann. physik.*, **11**, 5 (1919).

ciate is independent of the number of collisions with other molecules, and must consequently depend upon some process occurring within the structure of the molecule itself.

Now let us consider the significance of this from another point of view. The ordinary expression for a reaction of the first order is

$$-\frac{d[A_2]}{dt} = k_1[A_2] \quad (8)$$

where $[A_2]$ denotes the concentration of A_2 at the instant, t . It is evident that the value of the velocity constant, k_1 , is independent of the particular units of concentration used, and has the dimension t^{-1} , that is, a frequency. Since the velocity of dissociation increases rapidly with the temperature, we may assume, as Trautz has done, that the fraction, α , of the molecules A_2 which are in the active state increases with the temperature according to Equation 7. It therefore follows that the value of the velocity constant k_1 will be expressed at any temperature by an equation of the form

$$k_1 = \nu \epsilon^{-q/RT} \quad (9)$$

where ν denotes a frequency.

The question therefore arises as to how the value of ν may be determined. Following Herzfeld,¹ we may deduce a relation for ν empirically from the equilibrium constant, K , of such a reaction as the dissociation $H_2 \rightleftharpoons 2H$. For the velocity of dissociation may be assumed to be unimolecular, while that of the recombination must be bimolecular. To the latter case we can then apply the relation deduced above, based on the collision-frequency theory and thus obtain the velocity constant of dissociation k_1 from the relation

$$k_1 = K \cdot k_2 \quad (3)$$

In this manner Herzfeld has deduced the relation

$$k_1 = \frac{kT}{h} \left(1 - \epsilon^{-\frac{h\nu_A}{kT}} \right) \epsilon^{-\frac{q}{RT}}$$

where k is the gas constant per molecule = 1.372×10^{-16} ergs/deg.; h is Planck's constant = 6.55×10^{-27} ergs/sec.; and ν_A is the vibration frequency of the atoms, as derived from specific heat data.

Herzfeld is unable to assign any physical significance to this expression, and concludes with the statement that "experimental data are lacking for testing out this relation quantitatively." As will be shown in a subsequent connection, this is not at all the case, as we have data on the equilibrium constants of the dissociation of hydrogen, iodine, bromine, chlorine, phosphorus and arsenic, and it is therefore possible, as indicated above, to calculate the magnitude of ν , the frequency of dissociation of the active molecules in each of these cases. The frequencies thus cal-

¹ Herzfeld, *Ann. Phys.*, 59, 635 (1919).

culated are found to vary from 4×10^{14} to 9×10^{14} , and therefore correspond to ultra-violet frequencies. On the other hand, the vibration frequencies ν_A deduced from specific heat data by Bjerrum and others vary from 10^{13} to 10^{14} .

Trautz assumes that the dissociation of an active molecule of A_2 is due to collisions between the constituent atoms. Applying the kinetic theory of gases, he thus obtains a relation of the form,¹

$$k_1 = 8.72 \times 10^4 \cdot \frac{\sigma^2}{\sigma_1^3} \sqrt{\frac{M + M_1}{MM_1}} T^2 \cdot e^{-\frac{Q_A}{RT}}$$

where σ is the diameter of each atom; σ_1 is the diameter of the molecule; M and M_1 denote the atomic weights of each atom, and Q_A denotes the heat of activation per mol.

There are, however, several objections to this theory. Our ordinary conception based upon a great deal of chemical evidence, leads us to regard the atoms in a molecule as held together by forces exerted by electrons. The dissociation of a molecule must therefore involve a tearing apart of a bond between these electrons, and it is therefore difficult to understand how the atoms could move about freely inside the molecule and suffer continual collisions. Most probably these binding electrons are vibrating at certain definite frequencies, and it is only occasionally, after the critical amount of energy has been supplied to the molecule, that the electrons can vibrate far enough apart to cause an actual separation of the 2 positive nuclei, constituting the atoms.

Furthermore, Trautz assumes that the collision-frequency of the atoms varies with the temperature. On the other hand, from the specific heat phenomena it has been concluded that for each kind of molecule there exists a *definite* frequency of vibration of the atoms which is independent of the temperature.

Lastly, Trautz's formula can be tested by comparison with the value of ν deduced from the experimentally determined values of the equilibrium constants as shown above. Such a calculation shows that the collision-frequency theory of unimolecular reaction-velocities leads to values of ν which are much too low except at extremely high temperatures. The actual quantitative comparison must again be reserved for the subsequent discussion.

W. C. McC. Lewis has suggested an empirical formula for the rate of a unimolecular reaction,² which he bases on the radiation hypothesis. As this theory has already been discussed in a paper by Langmuir,³ further discussion may be omitted in this connection. Briefly stated, Lewis assumes that the process of activation is due to the absorption of radia-

¹ Trautz, *loc. cit.*, Equations 10 and 11.

² Lewis, *loc. cit.*

³ Langmuir, *THIS JOURNAL*, **42**, 2190 (1920).

tion of a definite frequency ν . According to the quantum theory, this energy, which is absorbed from the black-body radiation with which the molecules are in thermal equilibrium, must be absorbed in quanta of the value $h\nu$. Hence it follows that the heat of activation per mol

$$Q_A = Nh\nu \quad (10)$$

where N is the number of molecules per mol = 6.062×10^{23} , and hence

$$\alpha = \epsilon^{-\frac{Nh\nu}{RT}} = \epsilon^{-\frac{h\nu}{kT}}. \quad (10a)$$

A similar assumption had previously been made by Haber for heats of reaction, and Trautz has also assumed, like Lewis, that the heat of activation is absorbed in quanta. As shown by Langmuir, Equation 10a may also be regarded as a direct consequence of the similarity between Wien's equation for black-body radiation, and Arrhenius' equation for the temperature coefficient of reaction velocities. From this point of view, therefore, the origin of the heat of activation, whether it is directly absorbed from the radiant energy in the environment, or is due to some internal process within the molecule itself, is of secondary importance.

On the above hypothesis of black-body radiation as a source of activation, Lewis concludes that the velocity of a unimolecular reaction must be proportional to the density of the black-body radiation of the particular frequency ν corresponding to $Q = Nh\nu$, and suggests the empirical relation

$$k_1 = 10^3 p \epsilon^{-Q_A/RT}$$

where $p = \frac{c^3}{8\pi h\nu^3}$; c is the velocity of light; and ν = frequency calculated by means of Equation 10 from the heat of activation, Q_A ...

From the form of this equation, it is evident that k_1 has the dimensions $\text{cm}^3 \text{ sec}^3 \text{ ergs}^{-1}$, whereas as already mentioned, k_1 involves only t^{-1} . The only reason Lewis obtains a fairly quantitative agreement in applying this equation to the dissociation of hydrogen is because of the introduction of the factor 10^3 , which was apparently necessary because of the particular units of concentration used. As a matter of fact, Lewis¹ finds very recently that the above equation is not in accord with the conclusions based on Planck's radiation theory and leaves the whole problem still open.

II. Theory of Unimolecular Reaction Velocity.

In attempting to obtain a solution for the problem of unimolecular reaction velocities, the writer was guided mainly by 2 considerations.

1. From the known law of variation of reaction velocities with temperature, and from dimensional considerations, the velocity constant of a unimolecular reaction must satisfy a relation of the form,

¹ Lewis, *Phil. Mag.*, 39, 26 (1920).

$$k_1 = \nu \epsilon^{-Q/RT} \quad (9)$$

as has been pointed out above.

2. As Haber has shown, the quantum theory does apply with a fair degree of success to the calculation of heats of reactions. Furthermore, the quantum theory has been shown to be applicable to all processes in which energy absorption or emission is accompanied by the transfer of an electron, whether it be from one atom to another, or from one position to another position in the same atom. In all these cases the conclusion is forced on us that the energy transfer occurs in multiples of a unit quantum $h\nu$, where ν is the particular frequency of the energy radiated or absorbed.

These 2 considerations lead to the conclusion that the constant of a unimolecular reaction has the general form,

$$k_1 = \nu \epsilon^{-\frac{h\nu_A}{kT}}$$

since $Q_A = Nh\nu_A$ and therefore $\frac{Q_A}{RT} = \frac{Nh\nu_A}{RT} = \frac{h\nu_A}{kT}$. This would still leave ν undetermined.

Now the frequency ν denotes the rate at which the active molecules dissociate. It seems reasonable to expect that in some manner this frequency ought to be related to the potential energy of the constituent atoms, that is, to the heat of activation. The writer has therefore assumed that

$$\nu = \nu_A = Q_A/Nh \quad (11)$$

and the rate of a unimolecular reaction is therefore given by the relation

$$-\frac{dC}{dt} = C \cdot \nu_A \epsilon^{-\frac{h\nu_A}{kT}} \quad (12a)$$

so that

$$k_1 = \nu_A \cdot \epsilon^{-\frac{h\nu_A}{RT}} = \frac{Q_A}{Nh} \epsilon^{-\frac{Q_A}{RT}} \quad (12b)$$

where C is the concentration of reacting substances; Q_A is the heat of activation per mol of reactant, and N , h , R , and T have the usual significance.

*This equation we may consider as the fundamental relation for the rate of any unimolecular reaction that is dependent on the temperature.*¹

By substituting in Equation 12b

$$\begin{aligned} N &= 6.062 \times 10^{23} \\ h &= \frac{6.55 \times 10^{-27}}{4.184 \times 10^7} \text{ (cal. sec.)} \end{aligned}$$

we obtain for the rate of any unimolecular reaction at a given temperature T , the expression

¹ See also *J. Franklin Inst.*, 189, 515 (1920).

$$-\frac{dC}{C \cdot dt} = 1.048 \times 10^{10} Q_A \epsilon^{-Q_A/RT} \quad (12c)$$

where Q_A is the heat of activation per mol, in gm.-calories, and $dC/C\epsilon$ denotes the relative change in concentration of the reacting substance per second.

Comparing this equation with Equation 8, we derive the relation,

$$\log k_1 = 10.0203 + \log Q_A - \frac{Q_A}{4.571 T}. \quad (13)$$

That is, from a *single determination* of the velocity constant at any given temperature it should be possible to calculate the heat of activation, or *vice versa*.

The only unimolecular reaction, so far investigated, for which the reaction has been shown to be free of the catalytic effect of the walls, is the dissociation of phosphorus trihydride at temperatures above 920°Å . Table I gives the values of k_1 observed by M. Trautz and D. S. Bhandharkar,¹ for the temperature range 918° to 956°Å . From the smoothed curves obtained by plotting these results they derived the values " k , graph" given in the third column of the table. These are the values which have been used for calculating Q_A by means of Equation 13 and from the average of these results, $Q_A = 72,750$, the values of k_1 given in the last column have been calculated. It will be observed that the agreement is very satisfactory.

Kooy's observations at 845° , 785° and 719°Å . are also given at the bottom of the table. From the fact that in these experiments k_1 (obs.) is greater than k_1 (calc.), it is evident that the reaction at these temperatures must have been catalyzed by the walls. This is also shown by the lower values of Q_A (calc.).

TABLE I.
Rate of Dissociation of PH_3 .

T .	$10^4 k_1$ (obs.).	$10^4 k_1$ (graph.).	Q_A (calc.).	$10^4 k_1$ (calc.).
956	22; 11; 22	18.3	72,760	17.5
953	15; 11	15.0	72,740	15.2
948	17; 10; 10; 11	12.0	72,710	12.4
945	8.5	10.2	72,760	10.8
942	17	9.1	72,780	9.6
940	13; 14	8.3	72,740	8.9
936	2.7; 3; 8.3; 7.6; 8.7	7.1	72,730	7.6
933	12	6.3	72,690	6.6
929	5.6	5.5	72,610	5.6
923	4.4	4.6	72,560	4.4
918	3.6	3.8	72,520	3.5
845	0.54		69,920	0.113
785	0.0021	} Kooy.		0.0041
719	0.00081			0.000055

¹ *Z. anorg. Chem.*, 106, 95 (1919).

From the plot of Trautz and Bhandarkar's values of $\log k_1$ against $1/T$, it is possible to calculate Q_A by means of van't Hoff's equation. The values thus obtained vary between 75,000 and 81,000 cal. per mol when all the data are taken into consideration, and a straight line is drawn so as to include the maximum number of points. Considering the accuracy of the experimental data, the agreement between calculated and observed values of Q_A is therefore as good as can be expected.

M. Bodenstein and G. Dunant¹ have measured the rate of dissociation of phosgene at 3 different temperatures, and find it to be unimolecular. Similarly von Wartenberg² has shown that at approximately 1100° C., the rate of dissociation of water is unimolecular.

However, the heat of activation has not been measured from the temperature-coefficient of k_1 , so that a direct application of the above equation is not possible. But as will be shown in a subsequent section, from the experimental data on the rates of formation and the equilibrium constants, it is possible to calculate the heat of activation for the unimolecular reaction and thus obtain a further check on Equation 13. In each of these cases the calculated values are found to be in good agreement with the observed velocity constants for the rate of decomposition.

While this direct evidence of the validity of Equations 12 and 13 is very satisfactory, further confirmation has been obtained from a consideration of the equilibrium data for various types of reactions, as determined experimentally by making use of Equation 3 above.

If we consider a reaction such as the dissociation $H_2 \rightleftharpoons 2H$ we may assume the rate of dissociation to be unimolecular, and the rate of recombination must be bimolecular. If, therefore, we can calculate the velocity constant k_2 of the latter reaction, we ought to be able to determine k_1 , from the experimentally observed values of the equilibrium constant K at different temperatures.

Similarly Langmuir has applied the above theory for unimolecular reaction-velocities to the case of evaporation³ by equating the rate of evaporation as given by this theory to the rate of condensation as derived from kinetic theory considerations.

III. Kinetic Theory of Bimolecular Reaction Velocity.

Before, however, discussing the application of Equations 12 and 13 to the calculation of equilibrium constants, it is necessary to consider more fully the collision-frequency method of calculating the velocity of bimolecular reactions, and some actual applications.

Let us consider a bimolecular reaction of the type $A + B \rightleftharpoons AB$.

Let Q_A and Q_B denote the heats of activation per mol of A and B , re-

¹ Bodenstein and Dunant, *Z. physik. Chem.*, **61**, 437 (1908).

² von Wartenberg, *ibid.*, **56**, 513 (1906).

³ This paper will shortly be published by Langmuir as the next one of this series.

spectively. Then it follows from considerations based on the kinetic theory of gases and Trautz's theory that the number of collisions *between active molecules* of A and B , per unit, volume and unit time, is given by the equation,¹

$$Z = n_A \epsilon^{-\frac{Q_A}{RT}} n_B \epsilon^{-\frac{Q_B}{RT}} \cdot \sigma_{A,B}^2 \sqrt{8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \quad (15)$$

where n_A is the number of molecules A per unit volume; M_A = molecular weight of A , with the corresponding notation for B , and $\sigma_{A,B}$ denotes the average molecular diameter of A and B .

Since every collision between active molecules is assumed to result in the formation of a molecule of AB , it follows that the rate of formation of AB is given by

$$\frac{dn_{AB}}{dt} = Z$$

where n_{AB} = number of molecules AB per unit volume at the time t .

Converting to mols per cm^3 . per sec., it follows that

$$\frac{dC_{AB}}{dt} = \frac{d[AB]}{dt} = N[A][B]\sigma^2 \cdot \sqrt{8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \cdot \epsilon^{-\frac{(Q_A+Q_B)}{RT}} \quad (16)$$

where N is Avogadro's number = 6.062×10^{23} ; and C is the concentration in gram-mols cm^{-3} . This will be denoted in the following portion of paper by square brackets.

Comparing this equation with the ordinary expression for the rate of a bimolecular reaction,

$$\frac{d[AB]}{dt} = k_2[A][B] \quad (17)$$

it follows that

$$k_2 = N\sigma^2 \sqrt{8\pi RT \left(\frac{1}{M_A} + \frac{1}{M_B} \right)} \cdot \epsilon^{-\frac{(Q_A+Q_B)}{RT}} \quad (18a)$$

The total heat of activation $Q_A + Q_B$ is given by the relation

$$\frac{d \ln (k_2/\sqrt{T})}{d(1/T)} = -\frac{(Q_A + Q_B)}{RT}$$

which, as has already been mentioned above, was first suggested (in a slightly different form) by Arrhenius and has been subsequently applied by Trautz and Lewis.

In the case of a bimolecular reaction of the type $2A \rightarrow A_2$ the collision-frequency between the molecules A is given by the relation²

$$Z' = n_A^2 \sigma^2 \sqrt{\frac{4\pi RT}{M_A}} \quad (20)$$

Hence, the velocity constant of a reaction of this type is, in general, given by the equation,

¹ J. H. Jeans, "The Dynamical Theory of Gases," 1916, Chapter X.

² See Jeans, *loc. cit.*

$$k_2' = N\sigma^2 \sqrt{\frac{4\pi RT}{M_A}} \cdot e^{-\frac{2Q_A}{RT}}. \quad (21a)$$

For the purpose of calculation, Equations 18a and 21a may be written in the more convenient form,

$$\log k_2 = 28.4427 + 2 \log \sigma + 0.5 \log T - 0.5 \log \frac{M_A \cdot M_B}{M_{AB}} - \frac{Q_A + Q_B}{4.57T} \quad (18b)$$

$$\log k_2' = 28.2922 + 2 \log \sigma + 0.5 \log T - 0.5 \log M_A - \frac{2Q_A}{4.57T}. \quad (21b)$$

In these equations k_2 and k_2' are expressed in terms of gram-mols, $\text{cm}^{-3} \cdot \text{sec}^{-1}$, and the constants have been calculated by substituting the proper values for the universal constants N and R .

W. C. McC. Lewis has made use in his calculation of the velocity of decomposition and formation of hydrogen iodide (HI), of equations for k_2 and k_2' which are not exactly the same as those given above, although leading to results which are in fair agreement with the experimental data. The expressions which he derives for the collision frequency Z , are not in accord with those given by Jeans and also by Trautz. For this reason, and in order to show the validity of Equations 18b and 21b, it has been considered advisable to discuss in this connection the decomposition and formation of hydrogen iodide as well as some other bimolecular reactions.

Velocities of Formation and Decomposition of Hydrogen Iodide.—The velocities of these reactions have been shown by Bodenstein¹ to be bimolecular, according to the equation $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$, and the values of k_2 and k_2' have been determined by him over quite a range of temperatures.

From Equation 19 it is possible to calculate values of $Q_{\text{H}_2} + Q_{\text{I}_2}$ and compare these with the values deduced from the slope of $\log(k_2/\sqrt{T})$ against $1/T$, and in a similar manner $2Q_{\text{HI}}$ can be calculated from the temperature-variation of k_2' .

The average values thus obtained from the plots of $\log k_2/\sqrt{T}$ and $\log k_2'/\sqrt{T}$ against $1/T$ are as follows:

$$\begin{aligned} 2Q_{\text{HI}} (\text{obs.}) &= 45,700 \text{ cal.} \\ Q_{\text{H}_2} + Q_{\text{I}_2} (\text{obs.}) &= 40,520 \text{ cal.} \end{aligned}$$

Tables II and III give the values of k_2 and k_2' , respectively, as determined by Bodenstein for different temperatures. As his values are given in gram-mols per 22,412 cc. and minutes, the values tabulated have been derived from Bodenstein's by multiplying by the factor 22412/60 in order to convert them into the units used in Equations 18b and 21b.

In applying these equations to the calculation of the heats of activation

¹ Bodenstein, *Z. physik. Chem.*, 29, 295 (1899).

from k_2 and k_2' , respectively, the values of the molecular diameters used were as follows:¹

$$\begin{aligned}\sigma_{I_2} &= 4.52 \times 10^{-8} \text{ cm.} \\ \sigma_{H_2} &= 2.0 \\ \text{Average value} &= 3.26 \\ \sigma_{HI} &= 3.50.\end{aligned}$$

Since every collision between an active molecule of H_2 and one of I_2 results in the formation of $2HI$, while every collision between 2 active HI molecules results in the destruction of $2HI$, it is necessary to multiply the values of k_2 and k_2' calculated by means of Equations 18*b* and 21*b* by the factor 2.

Substituting the proper values for σ and M in these equations and introducing the factor 2, we can therefore write the equations for the velocity constants of the reactions under consideration, as follows.

Rate of Formation of HI.

$$\log k_2 = - \frac{(Q_{H_2} + Q_{I_2})}{4.57T} + 0.5 \log T + 13.62.$$

Rate of Dissociation of HI.

$$\log k_2' = - \frac{2Q_{HI}}{4.57T} + 0.5 \log T + 12.63.$$

The values of $(Q_{H_2} + Q_{I_2})$ and $2Q_{HI}$ calculated from these equations are given in Tables II and III.

TABLE II.
Rate of Formation of HI.

T .	Log k_2 (obs.).	$(Q_{H_2} + Q_{I_2})$.
556	0.6474-2	41,550
579	0.1200-1	42,050
599	0.7366-1	41,800
629	0.4021	42,050
647	0.7183	42,310
666	1.1508	42,270
683	1.3911	42,610
700	1.8077	42,350
716	2.1462	42,200
781	3.1261	42,630

Av. = 42,130

Obs. = 40,520

¹ The value for σ_{I_2} is that calculated by O. Sackur (*Ann. Phys.*, 40, 87 (1913)) by means of the Clausius-Mossotti equation; the value for σ_{H_2} is that ordinarily used, while σ_{HI} has been calculated from the critical data by means of the formula,

$$\sigma = \left(\frac{3RT_c}{16\pi NP_c} \right)^{1/3} = 10^{-8} \times 2.01 \times \left(\frac{T_c}{P_c} \right)^{1/3} \quad (22)$$

where T_c and P_c denote the critical temperature and pressure, respectively.

TABLE III.
Rate of Decomposition of HI.

T.	Log k_2' (obs.).	$2Q_{HI}$.
556	0.5463-4	44,360
575	0.0854-3	44,320
629	0.4801-2	44,710
647	0.9339-2	44,660
666	0.3416-1	44,070
683	0.7089-1	44,760
700	0.0636	44,760
716	0.3983	44,700
781	1.5971	44,550

Av. = 44,540

Obs. = 45,700

As will be observed, the agreement between the values of the heats of activation calculated by means of Equations 18b and 21b and the value obtained from the average temperature-coefficient of the reaction-velocity constants is very satisfactory.

Velocity of Decomposition of Nitrous Oxide.—M. A. Hunter¹ has measured the velocity of decomposition of nitrous oxide. This is a bimolecular reaction according to the equation $2N_2O \rightarrow 2N_2 + O_2$. The values of $k_2'' = 1/t.(x/1-x)$ at different temperatures are given in Table IV. In this equation, x denotes the degree of dissociation at one atmosphere pressure, and t is in seconds.

Converting to mols. cm^{-3} . sec^{-1} . $k_2' = k_2'' \times 22,412$.

The value of σ_{N_2O} has been taken as 4.3×10^{-8} $cm.^2$. Hence, Equation 21b assumes the form,

$$\log k_2' = 12.737 + 0.5 \log T - \frac{2Q_{N_2O}}{4.57T}$$

TABLE IV.
Rate of Decomposition of N_2O .

T.	k_2'' .	Log k_2' .	$2Q_{N_2O}$.
986	0.0003	0.8275	60,420
1078	0.00495	2.0450	60,170
1168	0.0436	2.9899	60,220

Av. = 60,270

The value of $2Q_{N_2O}$ calculated by means of Equation 25 agrees well with that calculated from the sloped $\log(k_2'/\sqrt{T})/d(1/T)$ which is found to be 61,500.

Velocity of Decomposition of Nitric Oxide. The rate of this reaction has been measured by Jellinek³ and found to be bimolecular in accordance

¹ Hunter, *Z. physik. Chem.*, **53**, 441 (1905).

² Kaye and Laby, *Tables*, **1911**, p. 33.

³ Jellinek, *Z. physik. Chem.*, **61**, 422 (1908).

with the equation $2NO \rightarrow N_2 + O_2$. The velocity constants in terms of $\text{mols. cm}^{-3} \cdot \text{sec}^{-1}$, as calculated by Trautz¹ are given in Table V. The value σ_{NO} calculated from the critical data is 2.82×10^{-8} cm. Substituting in Equation 21b we obtain the reaction,

$$\log k_2' = 12.757 + 0.5 \log T - \frac{2Q_{NO}}{4.57T}$$

Table V gives the values of $2Q_{NO}$ calculated by means of this equation, and for comparison the values observed, from the temperature-coefficient of $\log k_2$.

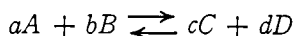
From the fact that these last values vary widely, it is evident that the values k_2' obtained by Jellinek cannot be very accurate. This was probably due to the experimental difficulties involved in the measurements. Furthermore, the values of k_2' given for the extreme temperatures are such that they may properly be regarded as extrapolated from the data obtained at intermediate temperatures. Assuming $2Q_{NO} = 65,000$ we have calculated the values of k_2' which are given in the last column of the table. The agreement with the values given by Jellinek may be considered to be as satisfactory as the original data.

TABLE V.

<i>T</i> .	k_2' (obs.).	$2Q_{NO}$ (calc.).	$2Q_{NO}$ (obs.).	k_2' (calc.).
1620	191,750	67,220	..	383,700
1525	47,059	67,440	70,870	105,300
1355	3,843	66,510	59,060	6,651
1252	1,073.6	64,510	40,410	883.1
1206	624.6	63,390	33,700	314.6
1108	228.3	60,360	26,040	28.1
962	39.82	55,630	24,290	0.3

IV. Theory of Chemical Equilibria.

The possibility of calculating equilibrium constants of chemical reactions from the kinetic point of view has already been discussed above. On the basis of this theory every equilibrium state may be regarded as the resultant effect of 2 opposing velocities. Ordinarily, in a reaction of the type,



the reaction would be regarded as of the order $(a + b)$ in one direction and of the order $(c + d)$ in the opposite direction. But from the kinetic point of view, all reactions in gases must be regarded as either unimolecular or bimolecular. It can readily be shown from considerations based on the kinetic theory of gases that collisions between 3 or more molecules must be exceedingly infrequent as compared with collisions between 2 molecules. This idea has also been emphasized by Trautz in several papers. Accordingly it ought to be possible to deduce equi-

¹ Trautz, *Z. physik. Chem.*, 68, 310 (1908).

librium constants from the consideration of the velocities of unimolecular or bimolecular reactions which lead to this equilibrium state.

An attempt to apply this concept to different types of reactions has been made in the following portion of the paper. The results may be considered as fairly successful in most cases and may therefore be assumed to be an additional confirmation not only of the kinetic point of view but also of the fundamental equation for the velocity of unimolecular reactions which was given in a previous section.

Case I. Reactions of the Type, $A_2 + B_2 \rightleftharpoons 2AB$.—This case is interesting because the reaction may be considered bimolecular in each direction.

Equations 18*b* and 21*b* are therefore applicable directly to the calculation of the equilibrium constants.

From these equations and the fundamental Equation 3 it follows that

$$\log K_c = \log \frac{\sigma^2}{2\sigma_1^2} + 0.5 \log \frac{M_{A_2} \cdot M_{B_2}}{M_{AB}^2} - \frac{Q}{4.57T} \quad (23)$$

where σ is the molecular diameter of AB ; σ_1 is the average molecular diameter of A_2 and B_2 ; and Q = thermochemical *heat of reaction*, = $2Q_{AB} - (Q_{A_2} + Q_{B_2})$.

Since σ is ordinarily not very different from σ_1 , we can neglect the term $\log \sigma^2/\sigma_1^2$ and Equation 23 reduces to the simple form,

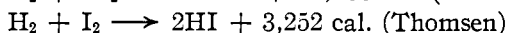
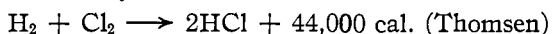
$$\log K_c = - \frac{Q}{4.57T} + I \quad (24)$$

$$\text{where } I = 0.5 \log \frac{M_{A_2} \cdot M_{B_2}}{4M_{AB}^2}. \quad (25)$$

Furthermore, since the reaction involves no change in volume, $\log K_c = \log K_p = \log K'_p$, where $K_p = \frac{p_{A_2} \cdot p_{B_2}}{p_{AB}^2}$ in terms of atmospheres, and K'_p denotes the same expression in terms of millimeters of mercury.

The dissociation of hydrobromic, hydrochloric and hydriodic acids and nitric oxide, are typical illustrations of this class of reactions. In Table VI the values of $\log K$ are given for different temperatures, together with the values of Q (calc.) derived by means of Equations 24 and 25. The last column gives the values of Q (obs.) as calculated from van't Hoff's equation.

The thermochemically observed heats of reaction are



The agreement between calculated and observed values of Q is satisfactory in the first 2 cases, but is apparently bad in the case of hydrogen

iodide. The reason for the discrepancy in the latter is, however, to be expected since the heat of the reaction

$$Q = 2Q_{\text{HI}} - (Q_{\text{H}_2} + Q_{\text{I}_2})$$

and is therefore the difference of 2 large numbers.

TABLE VI.
Equilibrium of Type $A_2 + B_2 \rightleftharpoons 2AB$.

Reaction.	T.	Log K.	I.	Q (calc.).	Q (obs.).
$\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}^a$	1810	- 5.72			
			-0.79	40,800	} 45,160
	923	-11.32		44,400	
	753	-13.60		44,100	
	703	-14.67		44,600	
303	-13.37		43,700		
$\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}^b$	303	-18.43	-0.96	24,190	} 24,000
	1297	- 5.20		25,140	
	1381	- 4.87		24,680	} 30,000
	1495	- 4.53		24,210	
$\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}^c$	328.3	- 2.85.	-1.206	2,467	} 2,900
	556	- 1.93		1,840	
	601	- 1.87		1,824	
	647	- 1.80		1,757	
	683	- 1.75		1,700	
	716	- 1.70		1,616	
	781	- 1.60		1,407	

^a I. W. Cederberg, "Die Thermodynamische Berechnung Chemischer Affinitäten," 1916, p. 79. The values for the range 923-703 were determined indirectly from the equilibrium data on the reaction $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + \text{Cl}_2$ and the equilibrium data for the dissociation of H_2O .

^b *Ibid.*, p. 84.

^c *Ibid.*, p. 87.

The equilibrium, $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$, has been studied by Nernst,¹ and Jellinek and Finckh. The constant I has the value -0.302 in this case, and the equation for the equilibrium constant is, therefore,

$$\log K = - \frac{2Q_{\text{NO}}}{4.57T} - 0.302.$$

The following table gives the observed values of $\log K$, and the values of Q (calc.) and Q (obs.).

TABLE VII.

T.	Log K.	-Q (calc.).	-Q (obs.).	Log K (calc.).
1811	4.0724	36,200	..	4.92
1877	3.9576	36,600	44,400	4.73
2033	3.4864	35,200	..	4.35
2195	3.2182	35,300	..	4.00
2580	2.5368	33,500	42,500	3.36
2675	2.4582	33,800	..	3.23

¹ Nernst, *Z. anorg. Chem.*, 45, 116 (1905); 49, 212, 229 (1907).

The agreement is not very good. The thermochemically observed heat of dissociation of 2NO at 290°C . is 43,200 according to Thomsen and Berthelot. The values of $\log K$ calculated from this value are given in the last column. At $T = 2195$, Nernst finds about one per cent. conversion of air into nitric oxide, whereas the amount calculated by means of $\log K = 4.00$ would be 0.4%.

Case II. Reactions of Type, $\text{A}_2 \rightleftharpoons 2\text{A}$.—The dissociations of hydrogen and iodine into atoms are typical reactions of this class. We shall assume that the dissociation of the molecules is a unimolecular reaction, while the re-combination is bimolecular. Furthermore, we shall assume that *all the atoms are active*, so that recombination results at *every collision* between atoms, and consequently the heat of activation of the molecules is the same as the thermochemical heat of dissociation.

From Equations 21a and 12b it follows that

$$\begin{aligned} \log \frac{[\text{A}]^2}{[\text{A}_2]} &= \log K_c = \log \frac{k_1}{k_2'} \\ &= \log \frac{Q}{N^2h} - 2 \log \sigma - 0.5 \log(4\pi R) + 0.5 \log M_A - 0.5 \log T - \frac{Q}{4.57T} \\ &= \log Q - 2 \log \sigma - 0.5 \log T + 0.5 \log M_A - 18.2718 + \frac{Q}{4.57T} \quad (26) \end{aligned}$$

where K_c is the equilibrium constant in terms of mols./cm³.

Since $p_A = C_A.RT$, it also follows that

$$\log K_P = \log K_c + \log T + 1.914 \quad (27)$$

where p is expressed in *atmospheres*.

Similarly, if p is expressed in millimeters of mercury,

$$\log K'_P = \log K_c + \log T + 4.795. \quad (28)$$

In Table VIII under Q (calc.) are given the values of Q deduced by means of these equations from the observed values of the equilibrium constants for different reactions of this class. The values of Q (obs.) have been calculated from the equation,

$$Q = 4.57 \frac{d \log (K_c \sqrt{T})}{d(1/T)} = 4.571 \frac{d \log (K_P / \sqrt{T})}{d(1/T)}. \quad (29)$$

Regarding the values of σ , the atomic diameter, it has been assumed that this is the same as the molecular diameter. Wherever possible, the values of σ used are those calculated by means of equations developed in the kinetic theory of gases, either from viscosity determinations, or from critical data.¹ In other cases, such as those of P and As, the atomic diameter

¹ See the writer's articles on "The Kinetic Theory of Gases," *Gen. Elec. Rev.*, 18, 951, 1042 (1915); Table VI, p. 1049, gives values of σ calculated for different gases.

For those gases for which this paper does not give any value of σ , use has been made of, Kaye and Laby's "Tables of Physical Constants" and Sackur's paper (*Loc. cit.*)

has been calculated from the density, ρ , by means of the equation,

$$\sigma = \left(\frac{M_A}{N\rho}\right)^{\frac{1}{2}} = 1.18 \times 10^{-8} \left(\frac{M_A}{\rho}\right)^{\frac{1}{2}}. \quad (30)$$

TABLE VIII.
Reactions of Type $A_2 \rightleftharpoons 2A$.

Reaction.	$\sigma \times 10^8$.	T.	Log K'_p .	Q (calc.).	Q (obs.).
$H_2 \rightleftharpoons 2H^a$	2.0	1200	0.3617-9	93,500	...
		1800	0.8195-4	95,450	...
		2300	0.2041-1	98,800	90,000
		3000	1.2095	101,500	...
log K_c .					
$I_2 \rightleftharpoons 2I^b$	4.52	1073	0.1106-7	36,290	...
		1173	0.6920-7	36,460	34,530
		1273	0.1987-6	35,790	35,830
		1373	0.6395-6	36,560	36,540
1473	0.0086-5	36,690	35,570		
log K_p .					
$Br_2 \rightleftharpoons 2Br^c$	3.74	1000	0.336-5	46,620	...
		1500	0.866-2	46,970	47,220
$Cl_2 \rightleftharpoons 2Cl^d$	3.30	1940	0.0004-4	88,300	...
		2270	0.0043-2	82,490	120,000
		2610	0.5228-1	77,230	118,500
log K'_p .					
$P_2 \rightleftharpoons 2P^e$	2.85	1073	0.5441-2	49,050	...
		1173	0.3801-1	49,330	46,960
		1273	0.0792	49,450	46,540
		1373	0.6812	49,900	46,800
1473	1.2041	50,500	47,520		
$As_2 \rightleftharpoons 2As^f$	2.79	1073	0.2041-1	46,840	...
		1173	0.9085-1	47,570	39,400
		1273	0.4983	46,550	39,080
		1373	1.0086	49,110	39,470
1473	1.4472	49,820	39,160		

^a I. Langmuir, *THIS JOURNAL*, **37**, 418 (1915).

^b Stock and Bodenstein, *Z. Elektrochem.*, **16**, 961 (1910). The value for σ is that given by Sackur, *Ann. Phys.*, **40**, 87 (1913).

^c Bodenstein, *Z. Elektrochem.*, **22**, 327 (1916). The original article has not been available; log K_p has therefore been calculated from the interpolation formula as given in the abstract, which is as follows:

$$\log K_p = -\frac{10100}{T} + 1.75 \log T - 0.000409 T + 4.726 \times 10^{-8} T^2 + 0.548.$$

^d M. Pier, *Z. physik. Chem.*, **62**, 385 (1908). The values of K_p are calculated from his data on the degree of dissociation at the 3 temperatures given in the table. The value of σ is that given by Sackur (*loc. cit.*).

^e G. Preuner and I. Brockmüller, *Z. physik. Chem.*, **81**, 129 (1913). These values of σ are calculated from the density of red phosphorus ($\rho = 2.20$).

^f G. Preuner and I. Brockmüller, *loc. cit.* Values of σ calculated from density ($\rho = 5.73$).

The agreement between $Q(\text{calc.})$ and $Q(\text{obs.})$ is splendid in the case

of iodine and bromine. For these reactions the experimental data are, however, much more accurate than for the other reactions. In the case of the dissociation of hydrogen Langmuir concluded that the heat of dissociation at constant volume ($T = 3000$) is 87,000 cal. and at constant pressure, 90,000. The experimentally observed values range from 80,000 to 100,000 approximately, but assuming the value $Q = 87,000$ Langmuir has calculated the values of K'_p given in the table. Using the value $Q = 97,000$, as derived from the average for $Q(\text{calc.})$ we obtain the following values of $\log K'_p$:

$T.$	$\log K'_p.$
1200	0.7675-10
1800	0.7455-4
2300	0.3708-1
3000	1.5724

These calculated values are in fair agreement with the experimental data.

In the case of chlorine, the data for the degree of dissociation are those given by Pier. Trautz concludes, on the basis of the radiation hypothesis, $Q = 86,000$, while the average of the calculated values given in Table VII is $Q = 83,000$. Assuming the latter value, we obtain the following values for x , the degree of dissociation.

$T.$	$\log K_p$ (calc.).	x (calc.).	x (Pier.).
1940	0.8074-5	0.0081	0.01
2270	0.2025-3	0.04	0.10
2610	0.2748-2	0.138	0.50

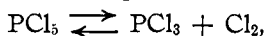
Pier, however, states himself that his data lay no claim to great accuracy, and judging from the indirect method which he used in deriving the degree of dissociation, his values are probably too high.

Preuner and Brockmüller's values of dissociation constants of P_2 and As_2 were also obtained by an indirect method, from the determinations of the density of the vapors at different temperatures. These determinations show that phosphorus in the vapor state consists of a mixture of P_4 , P_2 and P , in varying proportions. The same holds true for arsenic. By making plausible assumptions as to the proportions of these present at any temperature, Preuner and Brockmüller have derived the values for the dissociation constants of P_2 and As_2 given in the table. These values must therefore be regarded as only approximately correct and the difference between $Q(\text{calc.})$ and $Q(\text{obs.})$ may therefore be well within the range of experimental errors.

Case III. Reactions of Type, $AB \rightleftharpoons A + B$.

In the case of collisions between atoms it was assumed that every collision is effective in the production of a molecule. For these reactions, therefore, it is possible to calculate ν , the dissociation frequency of the

active molecules, from the value of Q , the thermochemical heat of dissociation. On the other hand, before a reaction can occur between two molecules, it is necessary that they should be in an active state, as has already been shown in the case of HI formation from H_2 and I_2 . Hence, in dealing with a case such as the equilibrium,



it is not justifiable to calculate ν directly from the thermochemically observed heat of dissociation of phosphorus pentachloride. From considerations similar to those used in calculating the equilibrium constants for the previous 2 cases, it readily follows that for a dissociation of the type, $AB \rightleftharpoons A + B$, where A and B are in the molecular state,

$$\log \frac{[A][B]}{[AB]} = \log K_c = \log \frac{k_1}{k_2} = \log \frac{\nu}{N\sigma^2} - 0.5 \log(8\pi RT) + 0.5 \log \frac{M_A \cdot M_B}{M_{AB}} - \frac{Q}{4.57T} \quad (31)$$

where σ = average diameter of molecules A and B ,

$$Q = Q_{AB} - (Q_A + Q_B)$$

= difference between heats of activation,

$$\text{and } \nu = Q_{AB}/(Nh).$$

Substituting the proper values for the universal constants, this equation may also be written in the form:

$$\log K_c = \log \frac{\nu}{\sigma^2} - 0.5 \log T + 0.5 \log \frac{M_A \cdot M_B}{M_{AB}} - \frac{Q}{4.57T} - 28.443. \quad (32)$$

From this equation, $\log K_p$ and $\log K'_p$ can be calculated by means of Equations 27 and 28, respectively.

In order to determine ν , it is necessary to obtain the value of the heat of activation of the molecule AB . Where the velocity of either the rate of dissociation or rate of formation is known for 2 or more temperatures, it is evidently possible to calculate Q_{AB} with a fair degree of accuracy, and thus determine the validity of the above equations.

Reaction $COCl_2 \rightleftharpoons CO + Cl_2$.—This is the only reaction of the type under consideration for which, as far as the writer is aware, any rate measurements are available. M. Bodenstein and G. Dunant¹ have obtained a few measurements on the rate of formation and rate of dissociation of phosgene. At $T = 876$, the rate of dissociation is so rapid that equilibrium is attained in less than 2 minutes. The measurements at $T = 826$ and $T = 776$ showed that the dissociation is a unimolecular reaction. Only at the latter temperature, does the dissociation proceed at a slow enough rate for accurate measurements. The results obtained at this temperature are given in the following table:

¹ *Z. physik. Chem.*, **61**, 437 (1908).

	<i>t</i> (Seconds).	Degree of dissociation.
<i>T</i> = 776.....	82.8	0.305
	110.4	0.322
	186.0	0.452
	342.0	0.532
	342.0	0.553
	∞	0.67

Since the observed velocity of dissociation is the resultant effect of the actual velocity of dissociation less the velocity of recombination, the above data were plotted and from the slope at $t = 0$, the value of k_1 , the rate of dissociation, was found to be 3.6×10^{-3} .

Hence, according to Equation 13 for the rate of a unimolecular reaction,

$$Q_{\text{COCl}_2} = 61,000.$$

From this result, it follows that the rate of dissociation at $T = 826$ ought to be 4.5×10^{-2} while the plot of degree of dissociation against time (as in the previous case) shows that for $t = 0$, k_1 must be greater than 2×10^{-2} .

Since the observed thermochemical heat of dissociation of phosgene is 20,000 cal. approximately, it follows from the above result, that

$$Q_{\text{CO}} + Q_{\text{Cl}_2} = 41,000 \text{ cal.}$$

For $T = 776$, Bodenstein and Dunant's measurements on the rate of formation of phosgene show that for the concentrations used in their experiments

$$-\frac{d[\text{Cl}_2]}{[\text{Cl}_2]dt} = 2 \times 10^{-2} \text{ (approx.)}$$

On the other hand, by means of equations similar to those already applied to the rate of formation of hydrogen iodide, it is possible to calculate the rate of formation of phosgene at any temperature from the total heat of activation of the reactants. Assuming $\sigma^2 = 10^{-15}$, such a calculation for the velocity of formation of phosgene at $T = 776$ leads to the result $k_2 = 490$, and for the concentrations actually used,

$$-\frac{d[\text{Cl}_2]}{[\text{Cl}_2]dt} = 5 \times 10^{-2}.$$

Furthermore, from the values $k_1 = 3.6 \times 10^{-3}$ and $k_2 = 490$, it follows that

$$K_c = \frac{k_1}{k_2} = 7.4 \times 10^{-6},$$

whereas, the observed value is 12.8×10^{-6} .

These results are therefore in satisfactory agreement with the theory that the rate of dissociation of phosgene follows the law of unimolecular reaction velocity as given above, while the rate of formation may be calculated by means of the collisions frequency theory as in the other cases cited above.

It will be observed that in the case of this reaction,

$$Q_{\text{COCl}_2} = 61,000.$$

$$\text{Hence } \nu = 6.39 \times 10^{14}.$$

$$\text{Assuming } \sigma^2 = 10^{-15}.$$

$$\text{Log } \nu/\sigma^2 = 29.81.$$

Substituting this value in Equation 32 and also the values for the molecular weights, and converting from $\log K_c$ to $\log K'_p$, we obtain the equation,

$$\log K'_p = 3.923 + 0.5 \log T - \frac{Q}{4.57T}.$$

The values of Q calculated by means of this equation from Bodenstein and Dunant's data on K'_p , and also $Q(\text{obs.})$ as derived from van't Hoff's equation, are as follows:

T .	$\text{Log } K'_p$.	Q (calc.).	Q (obs.).
776	0.9112-1	19,360	..
826	0.2518	19,360	19,400
876	0.6819	18,870	27,250

The agreement at the 2 lower temperatures is splendid. For $T = 876$, $\log K'_p$ calculated from the slope corresponding to $Q = 19,400$ is 0.562. The discrepancy is therefore not very great even in this case.

Theoretical Considerations Regarding the Heat of Activation in Dissociation.—The case of the dissociation of phosgene has been discussed in detail because it illustrates the fundamental principles which it ought to be possible to apply to all similar reactions in order to calculate the relation between the total energy and that available as work (free energy). In practically all the other reactions which are discussed in the rest of this paper, no experimental data are available from which heats of activation may be calculated. It is therefore necessary to obtain some general relation by which the heat of activation of a unimolecular reaction may be determined with some degree of approximation. From the manner in which ν , corresponding to Q_{AB} , enters into the calculation of $\log K$, it is evident first, that an error of even 50% in the value of this term will not seriously affect the calculated value of Q , the heat of the reaction. Furthermore, in the cases already discussed we have observed that the heat of activation varies from 36,000 in the case of iodine to approximately 100,000 in the case of hydrogen. We may therefore consider the latter as an upper limit for most cases, while, in general, a more nearly average value will be about 70,000. Also, the molecular diameter for most gases varies from 2.5 to 3.5×10^{-8} . Assuming as an average value $\sigma^2 = 10^{-16}$ and $Q_{AB} = 70,000$, we obtain for $\log \nu/\sigma^2$ the value 29.865. Taking into account the lack of accurate data with respect to both ν and σ we have therefore assumed as a general relation, the value $\log \nu/\sigma^2 = 30$.

As a matter of fact, the values of $\log K$ are not known in a large number of cases, with any greater degree of accuracy.

There is, however, another consideration which leads to the conclusion that, except in one or two cases, the heats of activation for dissociation must range between 100,000 and 40,000. From the form of the equation for a unimolecular reaction, it is evident that there must be a direct relation between the heat of activation and the temperature range in which the dissociation can be measured. Furthermore, in order that equilibrium may be attained in a short time, the actual rate of dissociation or recombination must be extremely high. That is, $\log k_1$ must exceed a certain minimum value. Now for all practical purposes a reaction cannot be measured when the relative change in concentration of the reactant is less than 10^{-9} per second. The reaction is so slow under these conditions that it takes 10^6 seconds (*i. e.*, about 11.5 days) for the concentration to change 0.1%. On the other hand, the reaction will go to completion in 10 seconds or less if $k_1 = > 10^{-1}$. Hence, in those cases where equilibrium is attained in a very short time, we can write as an approximate equation for calculating Q_{AB} ,

$$\text{Log } Q_{AB} - \frac{Q_{AB}}{4.57T} = -11. \quad (33)$$

Table IX gives values of Q_{AB} corresponding to different values of T calculated according to this equation. The last column gives the corresponding lower limit of T at which dissociation may possibly be first detected.

TABLE IX.		
$Q_{AB}/1000.$	T (upper limit).	T (lower limit).
1	71.5	45.5
10	145	95
20	286	188
30	425	280
40	560	370
50	697	461
60	832	552
70	966	643
80	1100	732
90	1234	822
100	1368	912
125	1700	1135
150	2030	1358
200	2684	1801

Thus, the fact that phosgene dissociates rapidly at $T = 876$, means, according to this table that Q_{COCl_2} is between 60,000 and 70,000. Where the limits of temperature are known between which the degree of dissociation varies from practically zero to unity, it is possible to assign limits to Q_{AB} . Thus, in the case of the dissociation of phosphorus pentachloride

the degree of dissociation is 0.05 at $T = 439$, and 0.98 at $T = 631$. From Equation 33 we therefore obtain the value $Q_{\text{PCl}_5} = 45,000$. On the other hand, it has been experimentally observed that N_2 shows no trace of dissociation, even at 2500°K . Hence, we would conclude that the heat of activation in this case is at least 200,000 cal.

The conclusion that the heat of activation for most unimolecular dissociation reactions ranges between 50,000 and 100,000 cal. per mol is also confirmed by the experimental data which are available with respect to the velocities of dissociation of ammonia, arsine, stibine and sulfur trioxide, which have been found to be unimolecular.

The rate of dissociation of ammonia at $T = 1384$ has been measured by Perman and Atkinson.¹ From their determination, $\log k_1 = 0.4500 - 3$, we obtain by means of Equation 13 the result $Q_{\text{NH}_3} = 112,000$. In view of the possible catalytic effect of the walls (as was actually observed at lower temperatures), we can conclude that the heat of activation of ammonia is about 120,000.

The decomposition of arsine is catalyzed by the arsenic deposited on the walls. Using the data quoted by M. Trautz,² the values of k_1 at $T = 717$ and 577 , at the very beginning of the reaction (where the least catalytic effect is to be expected) are as follows:

$T.$	$k_1.$
717	7.0×10^{-4}
577	2.2×10^{-4}

The value Q_{AsH_3} calculated for the higher temperature by means of Equation 13 is 59,000, whereas the value calculated by means of van't Hoff's equation from the determinations of k_1 at $T = 717$ and $T = 577$ is 68,000. We can therefore conclude that for the decomposition of arsine, the heat of activation is about 65,000 cal. per mol.

In the case of stibine, the values of $\log k_1$ as quoted by Trautz, and the calculated values of the heat of activation, are as follows.

$T.$	Log. $k_1.$	Q_{SbH_3}
323	0.809-5	27,390
348	0.448-4	28,640

This reaction is also catalyzed by the antimony (Sb) deposit, so that it can be concluded that the heat of activation of stibine is over 30,000 cal. per mol.

The rate of decomposition of sulfur trioxide has been measured by M. Bodenstein. For $T = 1132$, $k_1 = 1.1 \times 10^{-4}$. Hence $Q_{\text{SO}_3} = 98,330$ as a minimum value. In a similar manner it follows from Bodenstein's measurements of the rate of dissociation of hydrogen selenide that the heat of activation in this case must be greater than 40,000 cal. per mol.

¹ *Proc. Roy. Soc.*, **74**, 110 (1904).

² *Z. anorg. Chem.*, **104**, 69 (1918).

Mittasch has measured the rate of dissociation of nickel tetracarbonyl in contact with a nickel surface.¹ Since it decomposes very slowly at $T = 313$, and fairly rapidly at $T = 343$, we can conclude that the heat of activation for the uncatalyzed reaction must be greater than 30,000 cal. per mol.

In view of these considerations we have, therefore, assumed in the following calculations, $\log \nu/\sigma^2 = 30$. Hence, Equation 32 can be written in the more general form,

$$\log K_c = 1.55 - 0.5 \log T + 0.5 \log \frac{M_A \cdot M_B}{M_{AB}} - \frac{Q}{4.57T}. \quad (34)$$

$\text{SO}_2\text{Cl}_2 \rightleftharpoons \text{SO}_2 + \text{Cl}_2$.—The data obtained by Trautz² are given in the following table. According to Equation 34

$$\log K_p = 4.085 + 0.5 \log T - \frac{Q}{4.57T}.$$

The values of Q calculated by this equation are given in the table. The value of Q observed from the temperature-coefficient of $\log K_p/\sqrt{T}$ is 6160, while Trautz calculates for the heat of reaction at 290° the value 11,146. The discrepancy between these 2 values would tend to throw some doubt on the accuracy of the experimental data.

T .	$\text{Log } K_p$.	Q (calc.).
375.0	0.3784	8560
381.9	0.4958	8520
409.9	0.8525	8500
464.2	1.1158	9130

$\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$.—From Equation 34 we deduce the relation

$$\log K'_p = 7.1875 + 0.5 \log T - \frac{Q}{4.57T}.$$

The following table gives the values of Q calculated according to this equation from the data on $\log K'_p$.³ The value of Q calculated by means of Equation 29 is 21,280.

T .	$-\text{Log } K'_p$.	Q .
439	0.4764	18,030
443	0.2371	17,710
485	0.3456-1	17,460
495	0.3615-1	17,860
574	0.8736-3	16,900
623	0.1997-3	16,470
631	0.1386-3	16,510

$(\text{CH}_3\text{COOH})_2 \rightleftharpoons 2\text{CH}_3\text{COOH}$.⁴—In this case we have collisions be-

¹ Mittasch, *Z. physik. Chem.*, 40, 5 (1902).

² *Z. Elektrochem.*, 14, 540 (1914).

³ C. Holland, *ibid.*, 18, 234 (1912).

⁴ C. Holland, *loc. cit.*

tween like molecules, so that Equation 34 cannot be applied directly. Introducing the necessary correction, we obtain the equation

$$\log K'_p = 7.392 + 0.5 \log T - \frac{Q}{4.57T}$$

which has been used for calculating Q in the following table.

T .	$-\text{Log. } K'_p$.	Q .
413	0.7079-2	13,980
423	0.3985-2	13,740
433	0.3350-2	13,940
458	0.9907-3	14,060
473	0.7043-3	13,910
485	0.5085-3	13,850
493	0.4436-3	13,930
533	0.1867-3	14,470
578	0.1164-4	12,920
579	0.2573-4	13,260

Q observed from slope is 14,560 cal.

$\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$.¹—In this case, the modified form of Equation 34 leads to the relation

$$\log K_p = 4.4534 + 0.5 \log T - \frac{Q}{4.57T}$$

T .	$-\text{Log } K_p$.	Q .
273.0	1.8129	9790
291.3	1.1399	9090
322.9	0.0969	8570
346.6	0.4713-1	8230
372.8	0.8751-2	7690

Q observed from slope is 13,400 cal.

$\text{P}_4 \rightleftharpoons 2\text{P}_2$.—This equilibrium has been investigated by G. Preuner and I. Brockmüller.² The data, as in the case of the equilibrium $\text{P}_2 \rightleftharpoons 2\text{P}$ already discussed, lay no claim to great accuracy. From the values of $\log K'_p$ at different values of T , Q has been calculated according to the equation

$$\log K'_p = 7.399 + 0.5 \log T - \frac{Q}{4.57T}$$

T .	$\text{Log } K'_p$.	Q .
1073	0.8129	39,730
1173	1.3979	40,400
1273	1.9031	41,020
1373	2.3222	41,090
1473	2.6990	42,320

The value of Q observed from the slope of $\log K'_p/\sqrt{T}$ against $1/T$, is 32,800.

¹ Data given by G. N. Lewis, THIS JOURNAL, 37, 2308 (1915).

² *Loc. cit.*

$\text{As}_4 \rightleftharpoons 2\text{As}_2$.—The data for this equilibrium are also given by Preuner and Brockmüller. In this case,

$$\log K'_p = 7.591 + 0.5 \log T - \frac{Q}{4.57T}$$

T.	Log K'_p .	Q.
1073	0.4814	42,300
1173	0.9542	43,800
1273	1.3522	45,300
1373	1.6990	46,800
1473	2.000	48,300

Q observed from slope is 26,200 cal.

It will be observed that the agreement in the case of the dissociation of $(\text{CH}_3\text{COOH})_2$ and phosgene is very good; for sulfuryl chloride the agreement is as good as can be expected from the experimental data, while in the case of P_4 , As_4 , phosphorus pentachloride and N_2O_4 , there is a considerable difference between the calculated and observed heats of reaction.

As already stated, the data on As_4 and P_4 are probably not very accurate. These are practically the only cases in which $Q(\text{obs.})$ is greater than $Q(\text{calc.})$. It is also possible, however, that in some cases a steric factor should be taken into account as mentioned in the introduction, so that instead of ν/σ^2 we ought to write $\nu/\alpha\sigma^2$ where α denotes the fraction of the collisions between active molecules that is effective. Thus for the dissociation of phosphorus pentachloride if we assume $Q = 21,280$, we find that $\log \nu/\alpha\sigma^2 = 31.5$ (approx.). Hence $\alpha = 0.03$, that is, about 3% of the collisions are effective. Similarly in the case of N_2O_4 , if we assume $Q = 13,400$, we obtain the result $\log \nu/\alpha\sigma^2 = 33.26$, and therefore $\alpha = 0.55 \times 10^{-3}$ at $T = 273$, while for higher temperatures it is still smaller.

However, practically all the reactions involving nitrogen compounds show similar discrepancies between calculated and observed data. The reason for this may possibly be looked for in the peculiar structure of the nitrogen molecule and some of its compounds.¹ The writer is, however, unable at present to form any more definite ideas on this point.

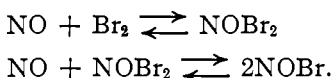
Reactions of Type, $2\text{A}_2\text{B} \rightleftharpoons 2\text{A}_2 + \text{B}_2$.

In this case we can assume that the dissociation is a bimolecular reaction, although the available data on rates of dissociation of this class of compounds is very meager. The measurements made by Hunter on the rate of the reaction $2\text{N}_2\text{O} \longrightarrow 2\text{N}_2 + \text{O}_2$, have already been mentioned above. This is a clean-cut case of a bimolecular reaction. On the other hand, Von Wartenberg has carried out a few determinations of the rate of dissociation of water at about 1100° and finds it to be unimolecular,²

¹ I. Langmuir, *THIS JOURNAL*, **41**, 868 (1919); G. N. Lewis, *ibid.*, **38**, 762 (1916).

² *Z. physik. Chem.*, **56**, 513 (1906).

while the reaction between hydrogen (H_2) and oxygen (O_2) is termolecular. Both the dissociation and formation were catalyzed by the walls, so that much stress cannot be laid on this case. According to Trautz's views and the theory developed above for rates of reactions, it is impossible to conceive of a termolecular reaction in a gas phase. Trautz assumes that in such cases we really have a sequence of two reactions. Thus, in the case of the reaction leading to the formation of nitrogenoxybromide,¹ Trautz assumes the intermediate stages:

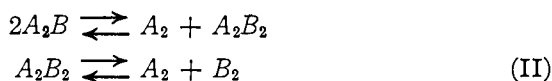


Similar assumptions are also made by him with respect to the formation of nitrogenoxychloride and nitrogen dioxide.

In general, we might assume for reactions of the type under consideration either of the following 2 mechanisms,



or



In Case I,

$$\begin{aligned} \ln \frac{[A_2][B]}{[A_2B]} &= \ln \frac{\nu_{A_2B} \sqrt{\frac{M_{A_2} \cdot M_B}{M_{A_2B}}}}{N\sigma^2 \sqrt{8\pi RT}} - \frac{Q_{A_2B} - (Q_{A_2} + Q_B)}{RT} \\ \ln \frac{[B_2]}{[B]^2} &= \ln \frac{N\sigma_B^2 \sqrt{4\pi RT}}{\nu_{B_2} \sqrt{M_B}} - \frac{2Q_B - Q_{B_2}}{RT}. \end{aligned}$$

Hence

$$\ln K_c = \ln \frac{[A_2]^2[B_2]}{[A_2B]^2} = \ln \left(\frac{\nu_{A_2B}^2 \sigma_B^2}{2N \cdot \nu_{B_2} \cdot \sigma^4} \sqrt{\frac{M_{A_2}^2 \cdot M_{B_2}}{M_{A_2B}^2 \cdot 8\pi RT}} \right) - \frac{Q}{RT}. \quad (35a)$$

In Case II we have similarly,

$$\ln K_c = \ln \left(\frac{\nu_{A_2B_2} \sigma_{A_2B}^2}{2N \cdot \sigma_{A_2, A_2B_2}^2 \sigma_{A_2, B_2}^2} \sqrt{\frac{M_{A_2}^2 \cdot M_{B_2}}{M_{A_2B}^2 \cdot 8\pi RT}} \right) - \frac{Q}{RT} \quad (35b)$$

where the subscript letters on σ denote the average values for the molecules designated.

The 2 mechanisms lead to equations which have similar form and differ only in the values of the frequencies and molecular diameters. Making the assumption as above, that $\log \nu/\sigma^2 = 30$, and assuming that the values of σ are approximately the same for all the molecules, we can

¹ *Z. anorg. Chem.*, 110, 1 (1920).

write the general equation for a reaction of the type under consideration, in the form,

$$\log K_c = 1.256 - 0.5 \log T + 0.5 \log \frac{M_{A_2}^2 \cdot M_{B_2}}{M_{A_2B}^2} - \frac{Q}{4.57T} \quad (36a)$$

where

$$1.256 = 30 - \log(2N) - 0.5 \log(8\pi R)$$

Since $p = CRT$,

$$\log K_p = 3.16 + 0.5 \log T + 0.5 \log \frac{M_{A_2}^2 \cdot M_{B_2}}{M_{A_2B}^2} - \frac{Q}{4.57T} \quad (36b)$$

where p is expressed in *atmospheres*.

Also

$$\log K'_p = 6.04 + 0.5 \log T + 0.5 \log \frac{M_{A_2}^2 \cdot M_{B_2}}{M_{A_2B}^2} - \frac{Q}{4.57T} \quad (36c)$$

where p is expressed in *mm.* of mercury.

These equations have been applied in the following section to the calculation of Q from the published values of K_p (or K'_p) for different equilibria.

(I) $2H_2 + O_2 \rightleftharpoons 2H_2O$.—The values of $-\log K_p$ as obtained by different investigators have been tabulated by G. N. Lewis.¹ The following table gives these data, together with the values for Q calculated by means of the equation,

$$\log K_p = 2.97 + 0.5 \log T - \frac{Q}{4.57T}$$

which was derived from Equation 36b.

T .	$-\log K_p$.	Q (calc.).
1325	13.768	110,900
1393	12.786	110,400
1397	12.624	109,600
1455	11.844	109,000
1480	11.506	108,600
1550	10.928	109,700
1561	10.708	109,000
1863	7.652	104,300
2257	7.219	105,200

From the slope of $(\log K_p - 0.5 \log T)$ against $1/T$, the average value of Q observed is 117,500, while Lewis gives $Q_0 = 114,820$.

(II) $2CO + O_2 \rightleftharpoons 2CO_2$.—From the data given by Lewis² the following values of Q have been calculated by means of the equation

$$\log K_p = 3.73 + 0.5 \log T - \frac{Q}{4.57T}$$

¹ Lewis, *THIS JOURNAL*, **36**, 1982 (1914).

² Lewis, *ibid.*, **37**, 458 (1915).

T.	-Log. K_p .	Q (calc.)
1395	11.8454	109,300
1400	11.7854	109,200
1443	11.1078	108,200
1478	10.7854	108,700
1481	10.9396	110,000
1498	11.8676	106,900
1565	9.8820	108,700
1823	7.4964	107,200

The average value obtained from the slope of $(\log K_p - 0.5 \log T)$ against $1/T$ is 116,100, while Lewis gives $Q_0 = 135,000$.

(III) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$.—This equilibrium has been determined by Bodenstein and Pohl.¹ The values of the constant K_c are given in terms of mols/liter. Converting Equation 36a into the same units and substituting in the term for the molecular weight, the equation for calculating Q becomes,

$$\log K'_c = 4.912 - 0.5 \log T - \frac{Q}{4.57T}$$

The observed values of $\log K'_c$, together with the values of Q (calculated) are as follows:

T.	Log K'_c .	Q (calc.).
801	-4.810	41,000
852	-4.126	40,890
900	-3.500	40,670
953	-2.914	40,570
1000	-2.451	40,510
1062	-1.900	40,410
1105	-1.552	40,330
1170	-1.089	40,300

Q observed from slope is 42,520 cal.

(IV) $2\text{H}_2 + \text{S}_2 \rightleftharpoons 2\text{H}_2\text{S}$.—From the equilibrium data, as given by G. N. Lewis,² the values of Q have been calculated by means of the equation

$$\log K_p = 3.193 + 0.5 \log T - \frac{Q}{4.57T}$$

T.	-Log K_p .	Q (calc.).
1362	1.804	40,860
1473	1.286	40,830
1537	0.980	40,520
1667	0.514	40,520

Q observed from slope is 42,370 cal.

(V) $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$.—From the data given by Lewis³ for the degree of dissociation of nitrogen dioxide at different temperatures, the

¹ Z. *Elektrochem.*, **11**, 373 (1905).

² Lewis, *THIS JOURNAL*, **40**, 373 (1918).

³ Lewis, *ibid.*, **37**, 2311 (1914).

values of K_p have been derived and from these the values of Q calculated by means of the equation

$$\log K_p = 3.737 + 0.5 \log T - \frac{Q}{4.57T}$$

T .	$-\log K_p$.	Q (calc.).
457	4.160	19,360
552	2.838	20,040
767	0.322	20,240

Q observed from slope is 19,240 cal.

The thermochemically observed heat of dissociation of 2NO_2 is given as 26,900 (Abegg) and assumed to be about 24,000 by Lewis.

(VI) $2\text{NO} + \text{Cl}_2 \rightleftharpoons 2\text{NOCl}$.—This equilibrium has been investigated by M. Trautz and C. F. Hinck.¹ From his data for K_c , as given below, corresponding values of Q were calculated, according to the equation

$$\log K_c = 1.655 - 0.5 \log T - \frac{Q}{4.57T}$$

T .	$-\log K_c$.	Q (calc.).
450	8.010	17,140
483	7.590	17,450
503	6.779	16,290
543	6.077	16,170
571.4	5.284	14,540
593.4	4.8894	14,000

Q observed from slope is 24,000 cal.

(VII) $2\text{NO} + \text{Br}_2 \rightleftharpoons 2\text{NOBr}$.—The equilibrium data have been obtained by M. Trautz and V. P. Dalal.² From these the values of Q have been calculated by means of the equation

$$\log K_c = 1.794 - 0.5 \log T - \frac{Q}{4.57T}$$

T .	$-\log K_c$.	Q (calc.).
258.4	7.5376	9600
294.8	6.3716	9340
333.0	5.4776	9150
373.1	4.9208	8950
453.2	3.4815	8200
513.2	2.6990	7400

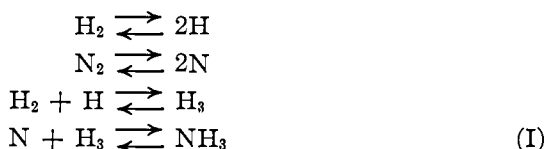
As calculated from the change in K_c with T , Trautz finds that Q varies between 8500 and 18,000 cal., but he concludes that the actual value must be between 8,000 and 9,500 cal.

(VIII) **Ammonia Equilibrium.**—The reaction $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$ is a more complex case than the equilibria already discussed. In order to apply kinetic considerations to this equilibrium we may make several

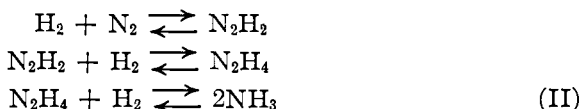
¹ Hinck, *Z. anorg. Chem.*, **93**, 177 (1915).

² Trautz and Dalal, *Z. anorg. Chem.*, **110**, 1 (1920).

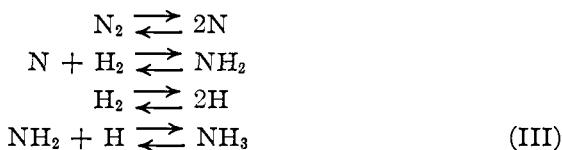
different assumptions as to the mechanism of the reaction. Thus, we may assume one of the following mechanisms.



or



or



Calculating on the basis of the first assumption, we obtain the relation:

$$\log K_c = \log \frac{\nu_{\text{H}_2}^2 \nu_{\text{N}_2}^2 \sigma_{\text{H}}^2 \sigma_{\text{N}}^2}{2\nu_{\text{H}_2} \nu_{\text{N}_2} \sigma_{\text{H}_2}^4 \sigma_{\text{H}_3}^4} - \log (8\pi RT) + 0.5 \log \frac{M_{\text{H}_2}^3 \cdot M_{\text{N}_2}}{M_{\text{NH}_3}^2} - \frac{Q}{4.57T}. \quad (37)$$

Introducing the further assumption that the heat of activation in all cases corresponds to $\nu = 10^{15}$ and $\sigma^2 = 10^{-15}$ approximately for all the atoms and molecules under consideration, we derive the simplified equation

$$\log K_p = 6.59 + \log T - \frac{Q}{4.57T}.$$

Here again, if we use Mechanism II or III and introduce the same assumptions regarding ν and σ we arrive at approximately the same result.

The following table gives the values of the equilibrium constant as tabulated by G. N. Lewis,¹ and also the values of Q calculated by the above equation.

In view of the fact that the term containing ν and σ is of the dimensions ν^2/σ^4 it is evident that any inaccuracy in this value is bound to affect the result much more than in any of the other cases hitherto discussed. It seems not unlikely from all that we know of the nitrogen compounds that ν/σ^2 for these compounds is much greater than 10^{30} . The last column of the table gives the values of Q calculated on the assumption $\nu/\sigma^2 = 10^{31}$. The value of Q_0 given by Lewis is 21,400.

¹ THIS JOURNAL, 37, 2308 (1915).

T.	Log K_p .	Q (calc.).	Q' (calc.).
958	6.524	13,330	22,090
973	6.334	14,410	23,030
1023	6.660	13,720	18,280
1074	6.898	13,360	23,170
1074	6.956	13,070	22,910
1082	7.154	12,200	22,090
1109	7.306	11,790	22,020
1123	7.108	12,980	23,250
1149	7.542	11,050	21,560
1174	7.344	12,410	23,140
1193	7.756	10,400	21,300
1203	7.398	12,470	23,470
1273	8.018	9,736	21,030
1273	7.660	11,820	23,450
1313	8.170	9,212	21,210

Discussion.

Validity of the Equation for Unimolecular Reaction Velocities.—The fundamental assumption in all the calculations made in this paper is that the rate of a unimolecular reaction is given by the expression

$$k_1 = \nu \cdot \epsilon^{-\frac{h\nu}{kT}} = \frac{Q}{Nh} \cdot \epsilon^{-\frac{Q}{RT}} \quad (12b)$$

where Q is the *heat of activation*.

It has been shown that the available data on unimolecular reaction velocities are in good accord with this equation; furthermore, that by means of this equation it is possible to calculate the equilibrium constants of a reaction such as the dissociation of hydrogen (H_2), with a fair degree of accuracy. This, of course, involves a kinetic theory of bimolecular reaction velocities. But the evidence for this latter theory is very strong, as shown by W. C. McC. Lewis, Trautz, and the writer in previous sections.

It will also be shown in a subsequent paper by Langmuir that the above equation can be applied to rates of evaporation and the heats of evaporation calculated from the vapor tension data are in good agreement with the observed heats of vaporization. The equation expresses, therefore, a general relation between the *rate* of a reaction at any temperature and the *energy change* involved in that reaction. However, in the above form the equation is only a first approximation to the true relation which is undoubtedly more complex. It, therefore, *lays no claim to strict validity*. However, as such, it must have a fundamental significance both from the point of view of the quantum theory and from that of chemical reactivity.

The values of ν obtained by means of the relation

$$Q = Nh\nu$$

range from 1.05×10^{14} for $Q = 10,000$, to 1.05×10^{15} for $Q = 100,000$

cal. The frequency corresponding to the D line of the sodium spectrum is approximately 0.5×10^{15} . It, therefore, follows that the heat of activation, in general, corresponds to a frequency which is in the visible or ultra-violet portion of the spectrum. As the latter are usually associated with vibrations of the electrons in the atoms, this result is in accord with the conclusion deduced from other considerations¹ that in chemical reactions the electrons play the fundamental rôle.

Bohr's theory of the structure of a hydrogen molecule represents the first attempt at a calculation of the heat of formation of a molecule from its atoms. In making this calculation Bohr applies the quantum theory to electronic orbits and arrives at a value for the heat of reaction which is too low. However, there is no doubt that the quantum theory must apply to such cases and up to the present we have simply not been able to suggest the exact manner in which it does apply. The relation expressed by Equation 12*b* is another application of the quantum theory to the theory of chemical reactions.

At the present time the writer is unable to answer the question as to the physical significance of the above equation. But he feels that the solution of this problem is intimately bound up with that of the larger problem which Bohr has attempted to solve in the specific case of the hydrogen molecule. As has been stated by Nernst:²

"It is one of the peculiarities of the quantum theory that many very remarkable relations are derived from a very simple assumption, which, however, is not altogether free from arbitrariness."

In attempting to apply Equation 12*b* to homogeneous gas reactions in general, it has been necessary to assume an average value for the heat of activation which is probably not even approximately correct in a number of cases. This, no doubt, accounts to a certain extent for the apparent lack of satisfactory agreement between the calculated and observed heats of reaction in these cases. Again, it has been assumed that every collision between active molecules is effective, but it is self-evident that this cannot be generally true, especially in the case of more complex molecules. For a reaction to occur at a collision, the molecules must not only be in the active state but must also present to each other certain active areas. Thus for a reaction to occur between 2 acetic acid molecules, it is evident that during the collision the 2 hydroxyl groups should be adjacent, and a collision between 2 molecules in which the methyl groups are adjacent would be ineffective in causing polymerization.

Relation of Kinetic Theory to Nernst's Third Law of Thermodynamics.

On the basis of his "Third Law of Thermodynamics," Nernst has de-

¹ Langmuir, *THIS JOURNAL*, 41, 868 (1919).

² Nernst, *Verh. deut. physik. Ges.*, 18, 84 (1916).

rived an expression for the relation between K_p and Q which can be written in the following *approximate* form:¹

$$\log K_p = -\frac{Q}{4.57T} + \Sigma n \cdot 1.75 \log T + \Sigma nC$$

where Q = heat of reaction at constant pressure and temperature, T .

ΣnC = algebraic sum of the "chemical constants."

Various other approximate formulas have been used, and the subject is at present in a more or less confused state.

As well known, Nernst has shown that the values of C can be obtained from the vapor tension data, while Sackur and others have deduced the values from statistical considerations and shown that for any substance

$$C = C_0 + \frac{3}{2} \log M$$

where C_0 is a universal constant.

Very recently Tolman² has also shown that this relation is the only one which is in accord with the principle of similitude.

On the other hand, in the equations for $\log K_p$ derived in the previous sections, the molecular weights occur as $M^{1/2}$, and the integration-constant involves ν , σ^2 and \sqrt{M} . There is, therefore, a difference here which probably accounts to a large extent for the approximate nature of the results obtained by applying the theory of reaction velocities.

Application to Solutions.

The writer has also attempted to apply similar considerations to the calculation of solubilities and rates of reactions in solution, with a fair degree of success in a number of cases and very poor results in other cases.

It is apparent, however, that a simple kinetic theory such as has been used for the case of gas reactions cannot, in general, apply to reactions in solution. The discussion of this must therefore be reserved for a future paper.

In conclusion, the writer wishes to express his appreciation of the interest and encouragement given him in the development of the above theory by Dr. Langmuir.

Summary.

1. A theory of unimolecular reaction velocities is suggested according to which the velocity constant is given by the relation, based on the quantum theory,

$$k_1 = \frac{Q}{Nh} \epsilon^{-\frac{Q}{RT}},$$

¹ I. W. Cederberg, "Die Thermodynamische Berechnung chemischer Affinitaeten," 1916, p. 71.

² THIS JOURNAL, 42, 1185 (1920).

where Q denotes the heat of activation, and N and R have the usual significance, and h is the quantum constant.

2. As shown by Trautz, the heat of activation can also be calculated from the temperature coefficient of k_1 , according to van't Hoff's equation. Combining this relation with that for Q , it is possible to check the above theory on actual experimental data in the case of the dissociation of phosgene (the only uncatalyzed unimolecular reaction whose velocity constant has been measured). The agreement is found to be very satisfactory.

3. As shown by Trautz and others, the velocity constant, k_2 , of a bimolecular reaction in gases can be calculated from considerations based on the kinetic theory of gases. This theory is shown by the writer to be in accord with the experimental data in the case of several reactions.

4. Since the equilibrium constant K of any reaction is given by the value of k_1/k_2 it follows from the above theory that, for any homogeneous gas reaction, it ought to be possible to calculate the free energy from data on the total energy of the reaction, or *vice versa*. In other words, this theory leads to a relation which is similar in certain respects to that derived by Nernst on the basis of his heat theorem.

Working over the available data on homogeneous gas reactions, it is shown that the agreement between values of the heat reaction calculated from equilibrium constants by means of the above theory, are in fair accord, in a large percentage of the cases, with the total heats actually observed. The results also show that the relation suggested for unimolecular reaction velocities can be regarded, at present, as only approximately true.

5. However, from the very fact that it yields such satisfactory agreement in a large number of cases, it must be of fundamental significance and probably represents an ideal relation which would hold true in all cases if it were not for the existence of other factors, at present unknown. The theory also brings out one more relation between the quantum theory and chemical reactions.

SCHENECTADY, N. Y.