[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Theory of Trimolecular Reactions[1]

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Introduction

There are two different types of reactions that have third order specific rate constants. In the first, two molecules or atoms react in the presence of a third body, which serves to carry off the excess energy, and the stoichiometric equation is of the form $A + B + C \longrightarrow AB + C$; or $A + B + C \longrightarrow E + F + C$. In the second type all three molecules are chemically involved in the reaction, so that none of the reaction products is the same as any reactant. It is this latter type, which we shall call trimolecular reactions, with which we are concerned in this paper. The first type has been treated in a paper soon to be published.[3]

There are known four reactions which seem to be trimolecular in the sense defined above. These are the reactions of nitric oxide with oxygen, chlorine, bromine and hydrogen, respectively. The classical kinetic theory of collisions has been completely unable to explain the rates of these reactions, which seem to be abnormally slow. In addition, the rate of reaction of nitric oxide with oxygen shows a negative temperature dependence. In trying to explain these phenomena Kassel[4] has extended the classical theory to include corrections for the fact that the molecules involved are not perfect gases. Although it is possible to explain the negative temperature dependence of the nitric oxide–oxygen reaction by making special assumptions, the calculated rates of this and other trimolecular reactions differ from the experimental by a factor of 10^9.

The reasons for this discrepancy are readily found in the assumptions that must be made in the usual kinetic theory treatment. Each molecule is considered as a sphere with three degrees of freedom of translation and no rotations or vibrations. One calculates the frequency of collision of such spheres and then determines the probability that while these two spheres are together a third sphere will collide with one of them, which is again considered as a sphere for the purposes of this calculation. When this calculation is carried through it is found that the number of triple collisions defined in this manner is roughly $^1/_{1000}$ of the number of binary collisions. Now there are several reasons why we should not expect such a treatment to give us much information about the rates of chemical reactions. In the first place, there is an obvious inconsistency in the assumption that although one of the molecules is part of a collision complex with another molecule it still acts like a complete sphere toward a third molecule. More serious, however, are the facts that molecules are not spherically symmetrical, that they are generally rotating and that they have internal degrees of freedom. During the reaction some of these degrees of freedom suffer changes and any rigorous statistical treatment must include them. The hard sphere picture assumed that these effects were negligible. When we investigate them more carefully we find that this is not so, and that their omission accounts completely for the failure of the old collision theory.

Some recent papers have considered the relation of these rotations and internal degrees of freedom to the rates of reactions. Rice and Gershinowitz[5] showed that if one took them into account one could explain the small steric factors found in the bimolecular associations of large molecules. Eyring[6] has treated the problem from a more general point of view and has shown that, if we assume that the reacting molecules form an intermediate complex which has the properties of an ordinary molecule except in the one degree of freedom in which dissociation is taking place, the rate of the reaction is determined by the concentration of this complex. In this paper we shall be concerned with a detailed application of the method of Eyring to trimolecular reactions.

General Theory

It has been shown[7] that the specific rate k_1 of any reaction for which the rate determining step

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[1] Presented at the New York meeting of the American Chemical Society, April, 1935.

[2] Parker Traveling Fellow of Harvard University.

[3] Eyring, Sun and Gershinowitz, *J. Chem. Phys.*, in press.

[4] Kassel, *J. Phys. Chem.*, **34**, 1777 (1930); and "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, 1932, Chapters IV and IX.

[5] Rice and Gershinowitz, *J. Chem. Phys.*, **2**, 853 (1934).

[6] Eyring, *ibid.*, **3**, 107 (1935).

[7] Ref. 6, Equation 10.

is the passage over a potential barrier can be written

$$k_i = cF_a'/F_n \cdot kT/h \cdot \text{exp.}(-E_0/RT) \qquad (1)$$

In this equation, F_n is the product of the partition functions of all the individual molecules that agglomerate to make the activated complex. The latter has the partition function $F_a{}^1$ which included the contributions of all normal coördinates except that one along which decomposition is occurring. The partition function for this coördinate together with the average velocity of passage across the barrier in the forward direction gives the factor $kT/h \cdot \text{exp.}(-E_0/RT)$, where E_0 is the difference in energy at the absolute zero between the normal molecules (before activation) and the activated complex. It is this E_0 which is independent of temperature, which we shall call the activation energy at zero. At any other temperature than absolute zero it is not the same as Tolman's activation energy, which is defined as the difference between the average energy of the molecules that react and the average energy of all the molecules,[8] and which is a function of temperature.[9] The factor c is the transmission coefficient, *i. e.*, the probability that a system which has once passed over the saddle point on the potential barrier really reacts and does not cross it in the reverse direction. All the information now available, both experimental and theoretical, indicates that c is generally near unity. This c is particularly interesting in that it is the only factor in k_i which depends on mechanical properties of the molecule not entering into ordinary statistical mechanics.

The known trimolecular reactions involve only diatomic molecules. Each of these has three degrees of freedom of translation, two of rotation, one of vibration and the electronic and nuclear degrees of freedom. Each molecule, therefore, has a partition function of the form[10]

$$F_i = g_i i_i \left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} \left(\frac{8\pi^2 I_i kT}{\sigma_i h^2}\right) (1 - \text{exp.}(-h\nu_i/kT))^{-1} \qquad (2)$$

where m_i is the mass of the molecule, I_i its moment of inertia, σ_i the symmetry number and ν_i the frequency. g_i and i_i are the weights of the electronic and nuclear states, respectively. The partition function for the normal state of a system in which a trimolecular reaction is taking place will be given by the product of three partition functions like the above.

If we assume that the activated complex of the three molecules is non-linear it will have, besides its nuclear and electronic degrees of freedom, three of translation, three of rotation, and $3n - 6$ or 12 internal degrees of freedom, which we shall for the present assume to be vibrations, although it may turn out that some of them correspond to free rotations at ordinary temperatures. One of these internal degrees of freedom is that in which dissociation is taking place and is included in the factor $kT/h \cdot \text{exp.}(-E_0/RT)$. We have, therefore, for the partition function of the activated complex, excluding this degree of freedom

$$F_a{}^1 = g_a i_a \left(\frac{2\pi(m_1 + m_2 + m_3)kT}{h^2}\right)^{3/2} \cdot \frac{8\pi^2}{\sigma_a} \left(\frac{(8\pi^3 A^* B^* C^*)^{1/3} kT}{h^2}\right)^{3/2} \Pi_{j=1}^{11} (1 - \text{exp.}(-h\nu_j/kT))^{-1} \qquad (3)$$

where A^*, B^* and C^* are the three principal moments of inertia of the activated complex and the other symbols correspond to those defined before.

We have then for the specific rate of such a reaction

$$k_r = \frac{c g_a i_a \left(\frac{2\pi(m_1+m_2+m_3)kT}{h^2}\right)^{3/2} \frac{8\pi^2}{\sigma_a} \left(\frac{(8\pi^3 A^* B^* C^*)^{1/3} kT}{h^2}\right)^{3/2} \Pi_{j=1}^{11} (1 - \text{exp.}(-h\nu_j/kT))^{-1} \frac{kT}{h} \text{exp.}(-E_0/RT)}{\Pi_{i=1}^{3} g_i i_i \left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} \frac{8\pi^2 I_i kT}{\sigma_i h^2} (1 - \text{exp.}(-h\nu_i/kT))^{-1}} \qquad (4)$$

If we separate out those quantities that are functions of temperature and let the remaining terms be represented by A, we may write

$$k_r = cA \frac{\Pi_{j=1}^{11} (1 - \text{exp.}(-h\nu_j/kT))^{-1}}{\Pi_{i=1}^{3} (1 - \text{exp.}(-h\nu_i/kT))^{-1}} \times \frac{\text{exp.}(-E_0/RT)}{T^{7/2}} \qquad (5)$$

We may rewrite this as

$$\frac{k_r \Pi_{i=1}^{3} (1 - \text{exp.}(-h\nu_i/kT))^{-1} T^{7/2}}{\Pi_{j=1}^{11} (1 - \text{exp.}(-h\nu_j/kT))^{-1}} = cA \times \text{exp.}(-E_0/RT) \qquad (5a)$$

If we take the logarithm of this expression and differentiate with respect to $1/T$ we get

$$\frac{d}{d(1/T)} \ln \left(\frac{k_r \Pi_i (1 - \text{exp.}(h\nu_i/kT))^{-1} T^{7/2}}{\Pi_j (1 - \text{exp.}(-h\nu_j/kT))^{-1}}\right) = -\frac{E_0}{R} \qquad (6)$$

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(8) Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, p. 269.

(9) See for example Ref. 6, Equation (4) and Gershinowitz and Rice, *J. Chem. Phys.*, **2**, 273 (1934).

(10) For a discussion of the forms of these partition functions see Ref. 6, p. 108.

whence we see that if we plot

$$[\ln k_r + \ln \Pi_i (1 - \exp.(-h\nu_i/kT)^{-1} + 7/2 \ln T - \ln \Pi_j (1 - \exp.(-h\nu_j/kT))^{-1}]$$

against $1/T$, the slope of the resulting straight line will give $-E_0/R$. From equation (5) we can obtain some general information on the dependence of the rate on temperature. Let us first neglect the effect of the internal degrees of freedom. This is tantamount to assuming that they are all vibrations of high frequency. We see, then, that if E_0 is small or zero the rate of the reaction will decrease as the temperature increases. If E_0 has an intermediate value, at sufficiently low temperatures the rate will increase with temperature; as the temperature increases it will approach a maximum and then start to decrease. If some of the internal degrees of freedom of the activated complex are free rotations or low frequency vibrations, their effect will be to increase the rate as temperature increases, thereby offsetting the $T^{7/2}$ in the denominator. In the applications that follow we shall see how to determine these factors in any specified case.

TABLE I

B P M, Briner, Pfeiffer and Malet Ref. 11. B, Bodenstein and co-workers, direct measurements Ref. 12. B R, Bodenstein and Ramstetter, calculated, Ref. 13.

	$k_{\text{obsd.}} \times 10^{-9}$			$k_{\text{calcd.}} \times 10^{-9}$	
T, °K.	B P M	B	B R	Non-adiabatic	Adiabatic
80.1	41.8			308	42.3
90.1	40.1			217	29.8
143.1	20.2			57.9	7.95
163.1	16.6			40.9	5.62
193.1	12.6			27.5	3.78
228.1	10.1			18.9	2.60
253.1	8.62			15.0	2.06
273.1	7.88	8.94		12.6	1.73
293.1	7.38			12.0	1.65
303.1		7.06		11.2	1.54
323.6	6.62			10.6	1.46
333.2		5.58		10.0	1.37
348.1	5.85			9.79	1.34
363.1		4.51		8.95	1.23
413.4		3.98		8.15	1.12
470.0		3.34		7.62	1.05
514.2		3.05		7.44	1.02
563.6		2.82		7.27	1.00
592			2.78		
603.8			2.77		
613.2		2.82		7.63	1.05
627			2.69		
651.5			2.89		
656			2.93		
661.9		2.54		7.69	1.06

The Reaction $2NO + O_2 \longrightarrow 2NO_2$

This reaction affords an excellent test of the theory. The experimental data are more complete and more accurate than those for any other third order reaction. The rates have been measured from 80.1 to 348.1°K. by Briner, Pfeiffer and Malet[11] and from 273.1 to 661.9°K. by Bodenstein and co-workers.[12] From the rate of the reverse reaction and the equilibrium constant Bodenstein and Ramstetter[13] have calculated the rate between 592 and 656°K. These data are given in Table I. The second column gives the rate constants of Briner, Pfeiffer and Malet, the third column the direct measurements of Bodenstein and the fourth column the calculated rates of Bodenstein and Ramstetter. The first two sets of data do not check exactly in the temperature range in which they overlap. Since the rates of Briner, Pfeiffer and Malet were determined by a flow method we have considered the data of Bodenstein to be more accurate and have given them greater weight.

In order to calculate the theoretical rates for this reaction we must first obtain E_0 from the experimental data, since the theoretical methods of calculating activation energies have not yet been extended to these reactions. We may calculate E_0 by means of equation 6a. To make use of this equation we must determine the nature of the activated state. Figure 1 shows an approximate structure of this activated complex. E_0 can be calculated without making assumptions regarding the dimensions of this complex. Since the oxygens are held together by a single bond there will be free rotation about this bond. Equation (4) then assumes the form

$$k_r = \frac{cg_a i_a \left(\frac{2\pi(m_1+m_2+m_3)kT}{h^2}\right)^{3/2} \frac{8\pi^2}{\sigma_a} \left(\frac{(8\pi^3 A^* B^* C^*)^{1/3}\, kT}{h^2}\right)^{3/2} \Pi_{j=1}^{10}\ (1-\exp.(-h\nu_j/kT))^{-1} \left(\frac{2\pi I_4^* kT}{h^2}\right)^{1/2} \frac{kT}{h}\ \exp.(-E_0/RT)}{\Pi_{i=1}^{3}\, g_i i_i \left(\frac{2\pi m_i kT}{h^2}\right)^{3/2} \frac{8\pi^2 I_i kT}{h^2}\ (1-\exp.(-h\nu_i/kT))^{-1}} \tag{7}$$

where I_4^* is the moment of inertia of the rotation about the O—O bond. If we now substitute for the universal constants their numerical

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(11) Briner, Pfeiffer and Malet, *J. chim. phys.*, **21**, 25 (1924).

(12) Bodenstein, *Z. Elektrochem.*, **24**, 183 (1918); *Z. physik. Chem.*, **100**, 87 (1922).

(13) Bodenstein, *ibid.*, **100**, 106 (1922).

equivalents and denote by m^1 a molecular weight expressed in grams per mole and by I^1 (or A^1) a moment of inertia expressed as $g\text{Å}.^2$ per mole we get

$$k_r = \frac{cg_a i_a \frac{1}{\sigma_a} (m_1^1 + m_2^1 + m_3^1)^{3/2} (A^1B^1C^1)^{1/2} (I_4^1)^{1/2} \Pi_{j=1}^{10} (1 - \exp.(-h\nu_i/kT)^{-1} \exp.(-E_0/RT)}{\Pi_{i=1}^{3} g_i i_i \frac{1}{\sigma_i} (m_i^1)^{3/2} I_i^1 (1 - \exp.(-h\nu_i/kT))^{-1} T^3} \cdot 8.01 \times 10^{18} \text{ cm.}^6 \text{ mol.}^{-2} \text{ sec.}^{-1} \quad (7a)$$

We need now evaluate the vibration frequencies. It can be seen that the complex pictured in Fig. 1 bears some resemblance to the molecule N_2O_4. The vibration frequencies of the latter have been obtained from the infra-red spectrum by Sutherland.[14] As a first approximation, therefore, we may assume that the vibration frequencies of our complex are equal to those of N_2O_4. In the temperature range covered by the data the effect of vibrations with frequencies higher than 900 cm.$^{-1}$ is negligible. The lowest frequency of N_2O_4 is replaced by the free rotation in our complex. We then have to substitute in 7a the seven frequencies, $\nu_1 = 283$ cm.$^{-1}$; $\nu_2 = 380$; $\nu_3 = 500$; $\nu_4 = 600$; $\nu_5 = 752$; $\nu_6 = 813$; and $\nu_7 = 813$ (we have assumed that Sutherland's ν_7 is equal to his ν_4). The frequencies of the diatomic molecules are so high that for the vibration terms we have $(1 - \exp.(-h\nu/kT))^{-1} \approx 1$.

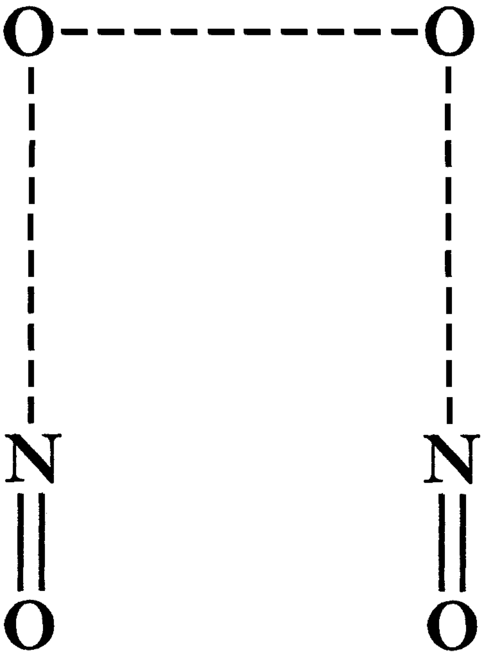

Fig. 1.—One of the configurations of the activated complex of 2NO + O_2 which has a low potential energy. The configurations obtained by a rotation around the O–O bond as an axis have nearly the same energy as this.

In accordance with equation 6 we plot $[\ln k_r + 3 \ln T - \ln \Pi_{j=1}^{7} (1 - \exp.(-h\nu_j/kT))^{-1}]$ against $1/T$. Fig. 2 shows the results for the data of Bodenstein.[15] We get a straight line parallel to the axis of the abscissa, giving $E_0 = 0$. At first sight this result seems surprising. We must remember, however, that NO and O_2 are both paramagnetic. They, therefore, show some of the properties of free radicals and atoms. It is reasonable, therefore, that there should be no activation energy for their coming together.

In order to proceed with the calculation of the absolute rate we need determine the dimensions of the activated state and calculate the appropriate moments of inertia. At this juncture it may not be amiss to point out that the order of magnitude of the calculated rate does not depend on arbitrary or *ad hoc* assumptions regarding the activated state. The theory automatically gives the absolute rate within a factor of twenty or thirty. Even this accuracy is enormously superior to that of previous calculations. However, by making reasonable assumptions about the vibration frequencies and dimensions of the activated state, assumptions that cannot be made *ad hoc*, because they must check roughly with known data, this uncertainty can be reduced to a factor of about five. The theory is exact, it is simply an application of statistical mechanics; and if we were able to construct potential energy surfaces for these systems we should get exact rates. Until that time comes we must make use of spectroscopic and thermochemical data in order to estimate these surfaces.

We take the following dimensions for the activated complex. The N=O distance is 1.22 Å. and the O—O distance 1.32 Å.[16] The N—O distance is taken as 5 Å., in analogy with the location of the rotation–vibration maximum in the potential energy surface for a diatomic molecule, which gives the dimensions of its activated state.[3] The free rotation about the

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[14] Sutherland, *Proc. Roy. Soc.* (London), **A141**, 342-362 (1933).

[15] The data of Briner, *et al.*, do not fit this curve as well as those of Bodenstein, as can be seen by examining the results in Table I. This may be due to experimental error, since a flow method was used; or perhaps the frequencies which we have chosen for the activated complex are sufficiently off to account for this deviation.

[16] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

O—O bond will have very little effect on the principal moments of inertia and we may therefore calculate these as for a rigid molecule. The moments of inertia of diatomic molecules can be obtained from spectroscopic data.[17] The symmetry number of the activated complex is two, as is that of oxygen. In most chemical reactions the nuclear statistical weights remain constant, hence the i's cancel. Substituting the numerical values into equation 7a we get

$$k_r = c\frac{g_a}{g_n} \times 1.57 \times 10^{17}\,\frac{\Pi_{j=1}^{7}\,(1 - \text{exp.}\,(-h\nu_i/kT))^{-1}}{T^3} \quad \text{cm.}^6\ \text{mole}^{-2}\ \text{sec.}^{-1} \qquad (8)$$

As we have already noted, c seems to be very nearly unity. g_n may easily be evaluated from spectroscopic data. The normal state of NO is a $^2\Pi$. Taking into account the separation of the levels we find that at the temperatures in which we are interested the weight factor is 3.1. Oxygen is in a $^3\Sigma$ state, with a weight of 3. This gives us $g_n = 3(3.1)^2$. The activated state is intermediate between $2NO + O_2$ and $2NO_2$ molecules. Consequently the three triplet states of the activated complex should lead to reaction practically as readily as the singlet state. The ratio g_a/g_n should lie between the limits $4/3 \times (3.1)^2$ and unity. The higher ratio will occur if the non-adiabatic transitions are almost as rapid as the adiabatic. (An adiabatic reaction is one in which the electronic quantum numbers do not change.) The last column of Table I gives the rates when the ratio is $4/[3 \times (3.1)^2]$; the next to the last column, the rates for the ratio unity.

We see that, as a matter of fact, the experimental rates do indeed fall between these limits, and that the agreement with the calculated values is quite good. There is some discrepancy between the directly measured rates of Bodenstein and the rates calculated by Bodenstein and Ramstetter from the reverse reaction. The latter show that the rate goes to a minimum value and then starts to increase again, whereas the former continue to decrease. Bodenstein was of the opinion that the measurements of the equilibrium and of the reverse reaction are more accurate and that the calculated rates are to be preferred to the direct measurements. The rates that we have calculated are in agreement with those of Bodenstein and Ramstetter in that they also show a minimum. The positions of the minimum would in fact fall together with a slight revision of one vibration frequency. This minimum is due to the fact that as the temperature rises the weight of the vibrational states increases very much and finally overwhelms the T^3 in the denominator of equation 8.

The Reaction $2NO + Cl_2 \longrightarrow 2NOCl$

This reaction may be treated essentially in the same manner as the oxygen reaction. The experimental data for this reaction have been obtained by Trautz and co-workers[18] and by Kiss.[19] These data are given in Table II. They are none too good. The results of the different observers do not always agree. It seems that the reaction is not completely homogeneous and that there are side reactions.[20] Only the order of magnitude of the results seems certain. Where there are several measurements for one temperature we have taken a representative value.

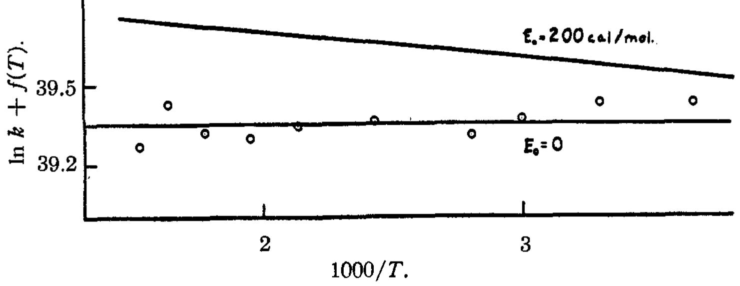

Fig. 2.—E_0 for the reaction $2NO + O_2 \rightarrow 2NO_2$. calculated from the data of Bodenstein. $f(T)$ is $3 \ln T - \Pi_{j=1}^{7}\,(1 - \text{exp.}(-h\nu_j|kT))^{-1}$. The line whose slope gives an $E_0 = 200$ cal. per mole has been inserted just to show how large the scale is.

For the activated complex in this reaction we take a structure similar to that given in Fig. 1, with chlorines replacing the oxygens. For our rate expression we again get equation 7a. The vibration frequencies cannot be fixed as closely as those for the O—N—O—O—N—O complex but by analogy with the data on the spectra of similar molecules we can take as seven representative frequencies one of 200 cm.$^{-1}$; and two each of 300 cm.$^{-1}$, 500 cm.$^{-1}$ and 700 cm.$^{-1}$.

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[17] Jevons, "Band Spectra of Diatomic Molecules," Cambridge University Press, 1932, Appendix II.

[18] Trautz, *Z. anorg. Chem.*, **88**, 285 (1914); Trautz and Wachenheim, *ibid.*, **97**, 241 (1916); Trautz and Henglein, *ibid.*, **110**, 237 (1920).

[19] Kiss, *Rec. trav. chim.*, **42**, 112, 665 (1923); **43**, 68 (1924).

[20] For a critical discussion see Kassel, *op. cit.*, p. 173.

TABLE II

T W, Trautz and Wachenheim, Ref. 18; T H, Trautz and Henglein, Ref. 18; T, Trautz, Ref. 18: K, Kiss, Ref. 19.

Observer	T, °K.	$k_{\text{obsd.}} \times 10^{-6}$	$k_{\text{calcd.}} \times 10^{-6}$	Ratio
T W	273	5.50	0.669	8.2
T H	280	5.57	.782	7.1
	281.6	4.82	.812	5.9
T	282.6	5.60	.827	6.8
	284.4	5.87	.866	6.8
T H	288.0	7.80	.974	8.0
	289.7	7.53	1.01	7.5
K	291.0	7.61	1.06	7.2
	291.1	7.58	1.06	7.2
T W	291.2	9.53	1.06	9.0
T	333.4	19.4	2.84	6.8
	355.1	27.2	4.24	6.4
	365.2	33.7	5.06	6.7
	374.7	41.7	6.01	6.9
	386.2	44.5	7.12	6.3
	401.4	72.2	8.98	8.0
	419.3	107	11.60	9.2
T W	433.9	192	13.66	14.0
	434.3	102	13.70	7.4
T	441.6	156	15.45	10.0
	451.1	182	17.41	10.4
	473.9	153	22.83	6.7
	505.8	453	31.79	14.2
	528.4	665	41.15	16.2
	566.4	1130	59.2	19.0

Figure 3 then shows the resulting plot of $[\ln k_r + 3 \ln T - \ln \Pi_{j=1}^{7} (1 - \exp.(-h\nu_j/kT))^{-1}]$ against $1/T$. The straight line gives an E_0 of 4780 cal. per mole. The data at the lower temperatures have been given greater weight because at the higher temperatures the reverse reaction becomes appreciable.

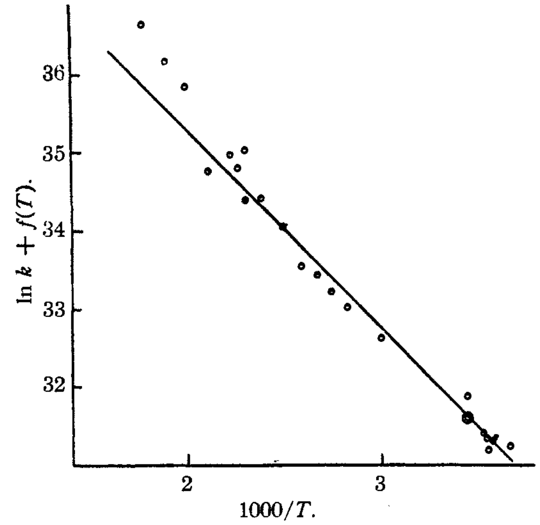

Fig. 3.—Temperature dependence of the rate of the reaction $2NO + Cl_2 \rightarrow 2NOCl$. $f(T)$ is $3 \ln T - \Pi_{j=1}^{7}(1 - \exp.(-h\nu_j/kT))^{-1}$. The double circle represents four experimental values. The measurements at the lower temperatures have been considered more accurate.

In the activated complex the Cl—Cl distance is taken as 2.5 Å., as in a partly dissociated chlorine molecule, and the N—Cl distance as 4 Å. If we now set c equal to one and assume that the reaction can go non-adiabatically we get for our rate expression

$$k_r = 2.83 \times 10^{16} \times \frac{\Pi_{j=1}^{7} (1 - \exp.(-h\nu_j/kT))^{-1}}{T^3} \times \exp.(-4780/RT) \text{ cm.}^6 \text{ mole}^{-2} \text{ sec.}^{-1} \quad (9)$$

The results are given in Table II. We again see that the agreement is good. Better agreement could be obtained by a different choice of frequencies and dimensions for the activated state, but in the absence of more exact experimental data we do not consider such a procedure justifiable.

Other Reactions

There are not enough data for the nitric oxide–bromine reaction to enable us to calculate E_0. However, we should expect that the activation energy and the vibration frequencies would be lower than in the corresponding chlorine reaction. According to equation 4 the rate of the reaction should, therefore, be greater. This is in agreement with the experimental results.[21]

The reaction of nitric oxide with hydrogen has been studied by Hinshelwood and Green[22] and critically discussed by Kassel.[23] It has a high apparent activation energy. The rate of this reaction is much too fast to be accounted for by the simple methods used for the oxygen and chlorine reactions. Either the activated state is much more loosely bound than one would expect or the reaction is not the simple homogeneous trimolecular process that it has been assumed to be. The latter state of affairs seems not unlikely when we remember the similarity between nitric oxide and oxygen and that the hydrogen–oxygen reaction has a very complicated mechanism. At the high temperatures at which this reaction takes place the possibility of a chain mechanism should not be ignored. Further experimental study would seem to be well worth while.

Summary

It is assumed that the rate of trimolecular homogeneous gas reactions is determined by the concentration of an activated complex of the three

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(21) Trautz and Dalal, *Z. anorg. Chem.*, **102**, 149 (1918).

(22) Hinshelwood and Green, *J. Chem. Soc.*, **129**, 730 (1926).

(23) Kassel, *op. cit.*, p. 175.

molecules involved, in which the individual molecules cannot rotate. It is shown that the calculated rates for the reactions of nitric oxide with oxygen, chlorine and bromine agree excellently with experiment, whereas previous theories have been in error by a factor of 10^9. It is shown that the negative temperature dependence of the nitric oxide–oxygen reaction is a natural consequence of the theory. Our calculations indicate that the $2NO + H_2$ reaction may be more complicated than has been supposed.

PRINCETON, N. J. RECEIVED MARCH 23, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Vapor Pressure of Solid and Liquid Nitrous Oxide. The Entropy from its Band Spectrum

BY R. W. BLUE[1] AND W. F. GIAUQUE

In recent years a series of low temperature calorimetric investigations on the entropies of diatomic gases has been reported from this Laboratory. The entropy values calculated by use of the third law of thermodynamics have been compared in each case with very accurate values obtained by calculations based on band spectra data.

Some six years ago, when the interpretation of band spectra reached a stage in its development that permitted accurate and detailed information about the quantum levels of polyatomic molecules, we began an extension of the above work which is expected to include most of the gases boiling below ordinary temperatures. Measurements on several polyatomic substances have been completed. In this paper results on nitrous oxide are presented.

In the case of many diatomic gases the agreement between the third law and spectroscopic values of the entropy has been so excellent as to provide perhaps the best experimental verification of the third law of thermodynamics. However, there are three diatomic gases, hydrogen, nitric oxide, carbon monoxide, in which $\int_0^T C_p \mathrm{d} \ln T$ obtained from the measurements gives less than the known entropy. The deviation in the case of hydrogen has been accurately explained in terms of the lack of equilibrium between the ortho and para states. Johnston and Giauque[2] offered the explanation that the discrepancy of about $^1/_2R \ln 2$ in the case of nitric oxide was due to two forms of the polymer N_2O_2 in the solid state. The difference in the polymer was assumed to arise from a residual effect of the λ doublets known from both theory and experiment to exist in NO molecules. Later Clayton and Giauque[3] proved that a discrepancy of about $R \ln 2 = 1.377$ occurred in the case of carbon monoxide. They offered the explanation that this molecule, structurally resembling nitrogen, has ends so nearly alike that the crystal lattice fails to discriminate at high temperatures. At very low temperatures slow rate prevents the readjustment to an ordered arrangement which characterizes the state of zero entropy. They called attention to the fact that this is a general characteristic of molecules with two or more isotopic atoms occupying otherwise equivalent positions. They predicted that it would occur in cases of low polarity when somewhat similar atoms, or groups of atoms, occupied two or more molecular positions without producing great dissymmetry.

This explanation would serve equally well in the case of the nitric oxide polymer and is preferable to that offered by Johnston and Giauque.

The problem of understanding the circumstances through which lack of equilibrium sometimes invalidates the practical application of the third law is of considerable importance. The treatment of the lack of equilibrium in hydrogen,[4a,b] the zero point entropy of which was first correctly calculated by Giauque and Johnston, is an excellent example of what may be done when the statistical situation is understood. Moreover, we believe that methods can be developed for detecting and quantitatively correcting many such cases.

With this in mind we have studied the case of nitrous oxide, the structure of which was unknown at the beginning of this investigation, but which

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[1] Shell Research Fellow, Academic year 1931–1932.

[2] Johnston and Giauque, THIS JOURNAL, **51**, 3194 (1929).

[3] Clayton and Giauque, *ibid.*, **54**, 2610 (1932).

[4] (a) Giauque and Johnston, *ibid.*, **50**, 3221 (1928); (b) Giauque, *ibid.*, **52**, 4816 (1930).