Nonadiabatic Reactions. The Decomposition of N2O

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Nonadiabatic Reactions. The Decomposition of N_2O

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The experimental and theoretical absolute rates for the nonadiabatic decomposition of N_2O are shown to be in good agreement. The amount of chemical inertia present in other reactions involving the singlet-triplet transition of oxygen is considered. A convenient method of constructing potential functions for polyatomic molecules which fit the spectroscopic data, and which reduce in the proper way for the various dissociation processes, is indicated, and is carried through for the N_2O molecule.

THE method of calculating absolute reaction rates by means of statistical mechanics as developed at the present time[1] involves information obtainable from potential surfaces. For a large number of reactions interest is confined to the lowest surface. There are also cases of importance for which, when magnetic effects are neglected, two potential surfaces intersect. When these effects are considered the surfaces, instead of crossing, approach each other very closely. In such cases the reacting system may pass from one of the noncrossing surfaces to the other in the neighborhood of the point of closest approach instead of proceeding across the potential barrier, and thus may fail to react. The fraction of the systems reaching the activated state which react we take equal to κ. The transmission coefficient, κ, plays exactly the role of c in Eq. (10) of reference 1.

Nonadiabatic reactions have been considered by a number of authors.[2] As an example of such a reaction the dissociation of nitrous oxide into a nitrogen molecule and an oxygen atom will be considered. That the N_2O reaction proceeds abnormally slowly for a unimolecular reaction is well known from the work of Volmer and his collaborators.[3] Wigner and others[4] have remarked that the reaction might be expected to proceed only about 0.001 as fast as the normally expected rate because of the change of multiplicity in the decomposition. In the ordinary thermal process a nonparamagnetic linear NNO molecule passes from a $^1\Sigma$ state through an activated state 53 kg. cal. higher to form $O(^3P)$ and $N_2(^1\Sigma)$.

We next consider the properties of the molecular potential energy. Among the conditions which we require for a satisfactory potential function for N_2O in its normal state are:

(1) Removal of an O atom to infinity must leave the function for a normal N_2 molecule.

(2) Removal of an N atom to infinity must reduce the potential to that for a $^4\Sigma$ NO molecule.

(3) N_2O being a linear molecule with O on one end, the function must yield the same values for an O atom approaching either N atom.

(4) The minimum must correspond to the correct dissociation energy and moment of inertia (interatomic distances).

(5) The potential must yield the known vibration frequencies.

Certain less obvious conditions on the potential are next considered. When N_2O decomposes adiabatically to give a $^1\Sigma$ N_2 molecule the oxygen will of necessity be in a singlet state. Now O (^1D) lies 45.1 kg. cal. above O (^3P),[5] whereas the next higher level, O (^1S) lies 96.1 kg. cal. above the ^3P state. Because O (^1S) is so much higher than O (^1D) we conclude that the state of oxygen in the normal N_2O is such that if it dissociated without change of multiplicity into $^1\Sigma$ N_2 and therefore singlet oxygen the latter would be in a ^1D state. Now N_2 $(^1\Sigma)$ dissociates adiabatically into two nitrogen atoms each in a ^4S state. Thus one thinks of a $^1\Sigma$ N_2O as assembled without change of multiplicity from two

[1] Eyring, J. Chem. Phys. **3**, 107 (1935).

[2] a. Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932). b. Zener, Proc. Roy. Soc. **A137**, 696 (1932); **A140**, 660 (1933). c. Landau, Physik. Zeits. Sowjetunion **1**, 88 (1932); **2**, 46 (1932). d. London, Zeits. f. Physik **74**, 143 (1932). e. Hellmann and Syrkin, Acta Physicochimica **2**, 433 (1935).

[3] a. Volmer and Kummerow, Zeits. f. physik. Chemie **B9**, 141 (1930). b. Nagasako and Volmer, ibid. **B10**, 414 (1930). c. See also Hunter, Proc. Roy. Soc. **A144**, 386 (1934).

[4] a. Wigner, Nachr. Ges. Wiss. Göttingen, p. 375 (1927). b. Pelzer and Wigner, Zeits. f. physik. Chemie **B15**, 445 (1931–32). c. Eyring, Chem, Rev. **10**, 103 (1932). d. G. Herzberg, Zeits. f. physik. Chemie **B17**, 68 (1932).

[5] Bacher and Goudsmit, *Atomic Energy States* (New York, McGraw-Hill, 1932).
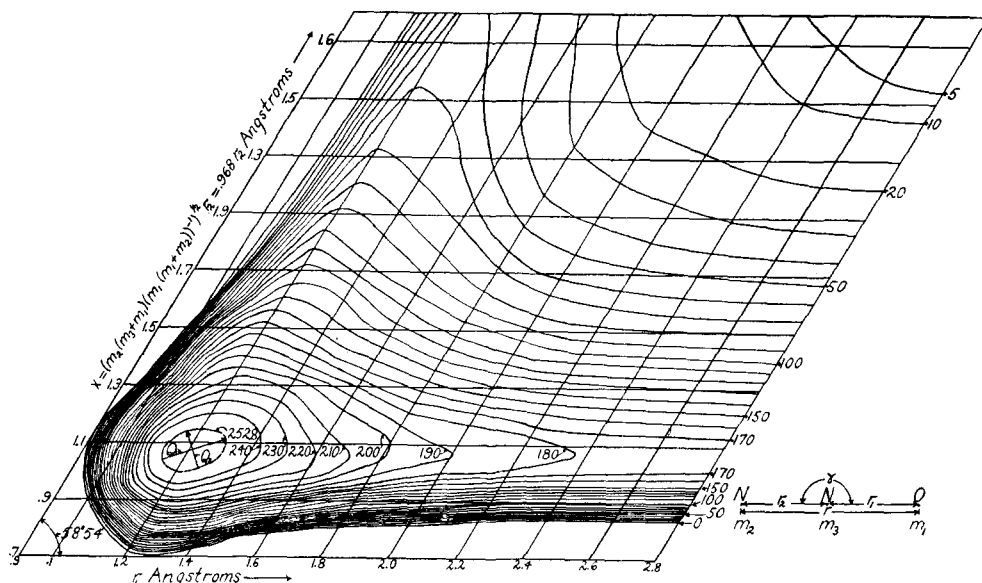
FIG. 1. Potential energy surface for N₂O for linear configurations. Contours, 10 kg. cal. intervals.

[4]S nitrogen atoms and one [1]D oxygen atom. When a [4]S nitrogen is removed from N₂O adiabatically it must leave a [4]Σ NO molecule behind which is formed from a [4]S nitrogen atom and a [1]D oxygen atom. This corresponds to the NO ($\sigma\pi^4\pi^2$, [4]Σ⁻) of Mulliken.[6] We use as his estimated values for the constants for the corresponding Morse curve an equilibrium distance $r_0 = 1.28$A, a vibration frequency $\omega = 3000r_0^{-3} = 1430$ cm⁻¹ and a heat of dissociation plus zero-point energy of 40 kg. cal. The zero-point energy of 2 kg. cal. leaves 38 kg. cal. for the heat of dissociation.

We shall use a potential function $V(r_1, r_2, \gamma)$ for N₂O in which the coordinates and masses are as indicated in Fig. 1.

The following definitions are introduced for convenience, where it is to be understood that the partial derivatives are to be evaluated at the point $r_1 = 1.22$; $r_2 = 1.10$; and $\gamma = 180°$.

$$k_1 = \left(\frac{\partial^2 V}{\partial r_1^2}\right), \quad k_2 = \left(\frac{\partial^2 V}{\partial r_2^2}\right), \quad k_{12} = \left(\frac{\partial_2 V}{\partial r_1 \partial r_2}\right), \quad k_3 = \left(\frac{\partial^2 V}{\partial \gamma^2}\right),$$

$$\mu_1 = (m_1 m_2 + m_1 m_3)(m_1 + m_2 + m_3)^{-1},$$

⁶ Mulliken, Rev. Mod. Phys. 4, 51 (1932). (See Fig. 48.)

$$\mu_2 = (m_1 m_2 + m_2 m_3)(m_1 + m_2 + m_3)^{-1},$$
$$\mu_3 = m_1 m_2 (m_1 + m_2 + m_3)^{-1},$$
$$b_{33} = r_1^2 r_2^2 (\mu_1 \mu_2 - \mu_3^2)(\mu_1 r_1^2 + \mu_2 r_2^2 + 2\mu_3 r_1 r_2)^{-1}$$

and

$$\lambda_i = 2\pi c \omega_i,$$

where c is the velocity of light and ω_i is the ith frequency of N₂O in wave numbers.

Now a straightforward solution of the mechanical problem for three atoms (see Cross and Van Vleck)[7] relates the frequencies to the force constants by the following equation.

$$\begin{vmatrix} \mu_1 \lambda^2 - k_1 & \mu_3 \lambda^2 - k_{12} & 0 \\ \mu_3 \lambda^2 - k_{12} & \mu_2 \lambda^2 - k_2 & 0 \\ 0 & 0 & b_{33} \lambda^2 - k_3 \end{vmatrix} = 0. \quad (1)$$

The fact that N₂O is linear is responsible for Eq. (1) reducing to a linear and a quadratic equation. The k's are now determined to fit the observed frequency as given by Plyler and Barker.[8] For the two equal (degenerate) bending frequencies these authors give 589 cm⁻¹, so that $k_3 = 6.4 \times 10^{-12}$ ergs mol.⁻¹ rad.⁻². They give

⁷ Cross and Van Vleck, J. Chem. Phys. 1, 350 (1933).
⁸ Plyler and Barker, Phys. Rev. 38, 1827 (1931).

$\omega_1 = 1285.4$ and $\omega_2 = 2224.1$ cm^{-1} for the other two frequencies. These two values, then, fix the two roots, λ^2, of the quadratic. Since there are three k's to determine however, and since in any case k_{12} must be comparatively small, we try taking it equal to zero. This leads to complex values for k_1 and k_2 which are impossible. Thus we cannot neglect the interaction between the two outer atoms. We eliminate one k by the requirement that $k_1/k_2 = 15.85 \times 10^5 (22.2 \times 10^5)^{-1}$, which is the ratio of the force constants of a normal NO and a normal N$_2$ molecule.[9] This gives $k_1 = 12.0 \times 10^5$, $k_2 = 16.7 \times 10^5$ and $k_{12} = 0.9 \times 10^5$. The units are in ergs mol.$^{-1}$ cm^{-2}.

For the equilibrium distances in the N$_2$O molecule we take the values proposed by Pauling,[10] i.e., for the N–N distance $r_2 = 1.10$A, and for the N–O distance $r_1 = 1.22$A. These values give a moment of inertia of 66.7×10^{-40} as compared with 66.0×10^{-40} found by Barker.[11]

We now give a potential function for N$_2$O which satisfies all the conditions enumerated except the third. It is

$$V = D_1 f(a_1, r_1, b_1) + D_2 f(c_2, r_2, d_2)$$

$$+ \sum_{i=3}^{7} D_i f(a_i, r_1, b_i) f(c_i, r_2, d_i)$$

$$+ D_8 f(a_8, r_1, b_8) f(c_8, r_2, d_8) \sin^2 \gamma. \quad (2)$$

Here

$$f(a, r_1, b) = \exp - (2a(r_1 - b)) - 2 \exp - (a(r_1 - b))$$

and

$$f(c, r_2, d) = \exp - (2c(r_2 - d)) - 2 \exp - (c(r_2 - d)).$$

If to (2) we add all the additional terms obtained by replacing r_1 by r_3 and γ by δ, where δ measures the angle between r_2 and r_3, then the third condition is also satisfied. The inclusion of these terms considerably complicates our potential without changing it appreciably in the region in which we are interested so that they are omitted.

The constants used in Eq. (2) are collected in Table I.

[9] Mulliken, Rev. Mod. Phys. **4**, 1 (1932).
[10] Pauling, Proc. Nat. Acad. Sci. **18**, 293, 498 (1932).
[11] Barker, Phys. Rev. **41**, 369 (1932).

TABLE I. *Constants used in potential function* (2).

	D	a	b	c	d
1	40.	3.95	1.28	—	—
2	172.82	—	—	3.10	1.09
3	−39.97	3.00	1.12	3.00	1.20
4	−57.89	3.00	1.12	3.00	1.10
5	25.97	3.95	1.22	3.00	1.20
6	74.27	3.00	1.22	4.00	1.10
7	−60.00	2.519	1.22	1.665	1.10
8	46.83	3.00	1.22	3.00	1.10

The adjustment of the constants for a function of the type (2) is a simple matter but should be made in a certain sequence.

(1) The first two terms are simply Morse functions for Mulliken's NO ($\sigma\pi^4\pi^2$, $^4\Sigma^-$) and for the normal nitrogen molecule, respectively.

(2) The third term takes care of k_{12}. The constants a_3 and c_3 are chosen as 3, approximately the value of a_2 in nitrogen. b_3 was chosen to contract the N−O bond while d_3 has the effect of slightly expanding the N−N bond. After these choices were made, D_3 is taken to make $k_{12} = 0.9 \times 10^5$ ergs mol.$^{-1}$ cm^{-2}.

(3) The fourth term is chosen to make $\partial V/\partial r_1 = 0$ at $r_1 = 1.22$A and $r_2 = 1.10$A. Now d_4 is taken equal to 1.10 so that $f(c_4, r_2, d_4) = -1$. Finally a_4 and b_4 are kept with the values of a_3 and b_3 for the same reason as before and D_4 is so chosen as to make $\partial V/\partial r_1 = 0$.

(4) The fifth term is arranged in a manner analogous to the fourth to make $\partial V/\partial r_2 = 0$ for $r_1 = 1.22$A and $r_2 = 1.10$A.

(5) In the sixth and seventh terms k_1, k_2 and E are fitted. Here b_6 and b_7 are set equal to 1.22, the equilibrium N–O distance in N$_2$O, and d_6 and d_7 equal to 1.10 the corresponding N–N distance. Thus, for $r_1 = 1.22$ and $r_2 = 1.10$, for these two terms,

$$f(a, r_1, b) = f(c, r_2, d) = -1$$
$$\partial f(a, r_1, b)/\partial r_1 = \partial f(c, r_2, d)/\partial r_2 = 0$$

and

$$\partial^2 f(a, r_1, b)/\partial r_1^2 = 2a^2 D,$$

while

$$\partial^2 f(c, r_2, d)/\partial_2^2 = 2c^2 D.$$

In this way the contribution to the energy is $D_6 + D_7$. These are then chosen to give N$_2$O the correct dissociation energy and at the same time to give values for the a's and c's in the neighbor-

hood of 3. a_6 and a_7 are now chosen so that $\partial^2 V/\partial r_1^2 = k_1$: and c_6 and c_7 so that $\partial^2 V/\partial r_2^2 = k_2$.

(6) The final term, of course, adds nothing to energy, slope or curvature in the r_1 and r_2 directions so long as the molecule is linear, i.e., $\gamma = 0$ or π. D_8 is obtained by solving the equation $b_{33}\lambda^2 = k_3$, and putting $D_8 = \frac{1}{2}k_3$. There is some arbitrariness particularly in our choice of a_8 and c_8. This could be removed by fitting the potential function to give more exactly the higher frequencies found by Plyler and Barker in the manner employed by Adel and Dennison for CO_2.[12] A simple central force potential of the type they have used for CO_2 will not, in general, be valid for distances far from the equilibrium position, as they also point out. Our potential can hardly be seriously in error providing adiabatic decomposition gives the products we have supposed.

The method of using polynomials in the f's for the various bonds provides a way for constructing potential functions to fit all the limiting conditions for even the most complicated polyatomic molecules. This should be a generally useful procedure.

Fig. 1 gives the potential surface for linear N_2O plotted from Eq. (2). Here r_1 is plotted against r_2/f where $f = [m_1(m_3+m_2)/m_2(m_1+m_3)]^{\frac{1}{2}}$, and the angle between the abscissae and ordinates is given by

$$\pi/2 - \sin^{-1}\left[m_2m_1/(m_3+m_2)(m_1+m_3)\right]^{\frac{1}{2}}$$
$$= 58° \; 54'.\,[13]$$

The potential function (2) gives for the two nonbending normal coordinates

$$Q_1 = 0.4679(r_1-r_{01}) + 0.8828(r_2-r_{02})$$
and $$Q_2 = 0.7842(r_1-r_{01}) - 0.6206(r_2-r_{02}).$$

Here r_{01} and r_{02} are the equilibrium distances. These give the directions of the major and minor axes of an equipotential line in the immediate neighborhood of the minimum if one plots it in the way used in Fig. 1. Because the potential involves terms higher than the second power in r_1 and r_2, by the time one has reached an equi-

potential corresponding to the zero-point energy (6.66 kg. cal.) the major and minor axes of the near ellipse will have changed. However, even in the present unsymmetrical case, this change in the coefficients of the r's is less than one percent. In the same way we expect our vibration frequencies to show a parallel small anharmonicity.

We next consider how the potential surface for O (^3P) approaching N_2 ($^1\Sigma$) will cut the surface just drawn. At large distances the O attracts the near N in N_2 due to the van der Waals forces and the Coulombic integrals, but it repels it by an amount equal to $\frac{1}{2}$ all the exchange integrals between the two atoms.[14] Now we take the attractive potential as 0.14 of the Morse curve value for NO in its normal state ($\sigma^2\pi^4\pi$, $^2\Pi$ in Mulliken's notation) and the repulsive potential as 0.43 of this value, giving a net repulsion of 0.29 of the Morse curve value.[14a] For this Morse curve we take $\omega = 1906$ cm⁻¹, $r_0 = 1.15$A, $a = 3.05$, heat of dissociation = 121.94 kg. cal. and the zero-point energy = 2.71 kg. cal. In Fig. 2 the curve I is a section following the lowest part of the east west valley of Fig. 1, while curve II is −0.29 times the Morse curve values for normal NO.

ABSOLUTE RATE OF REACTION

Curves I and II intersect when r_1, the N–O distance, is 1.73A. This point of intersection of I and II is the activated state for the decomposition of N_2O. In the activated state the vibration in the r_1 direction becomes a translation, and our potential function gives us for the N to N vibration the value 2005 cm⁻¹, while the degenerate bending vibration has become 361 cm⁻¹. This gives us 3.9 kg. cal. for the zero-point energy in the activated state and an activation energy at the absolute zero of 50.0 kg. cal.

Now not every system passing through the activated state will make the transition from I to II. If we indicate the chance of transition, averaged over the velocity distribution characteristic of the temperature, by κ, we have for the specific reaction rate constant[1]

[12] Adel and Dennison, Phys. Rev. **44**, 99 (1933); **43**, 716 (1933).
[13] Eyring and Polanyi, Zeits. f. physik. Chemie **B12**, 279 (1931).

[14] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[14a] This method of estimating the potential energy between molecules with these same percentages gives the correct activation energy for the conversion of para- to ortho-hydrogen and very close to the right activation energy in a

$$k' = \kappa \prod_{i=1}^{3} (1 - \exp -h\nu_i^*/kT)^{-1} I^* I^{-1} \prod_{j=1}^{4} (1 - \exp -h\nu_j/kT)(\exp -E_0/kT)kT/h \qquad (3)$$

so that for the ordinary activation energy at temperature T we have

$$E = RT^2 \frac{d \ln k'}{dT} = \left(\sum_{i=1}^{3} \frac{h\nu_i^*}{k} e^{-h\nu_i^*/kT} \left(1 - \exp -\frac{h\nu_i^*}{kT} \right)^{-1} \right.$$

$$\left. - \sum_{j=1}^{4} \frac{h\nu_j}{k} e^{-h\nu_j/kT} \left(1 - \exp -\frac{h\nu_j}{kT} \right)^{-1} + T \right) R + E^0. \quad (4)$$

This gives for $E - E_0$ at 850°, 900°, 938° and 1000°K the values 1.751, 1.799, 1.833, and 1.881 kg. cal., respectively. Thus our calculated value for E is approximately 52 kg. cal., to be compared with the measured value of Nagasako and Volmer[3b] of 53 kg. cal. Hunter[3c] agrees approximately with Nagasako and Volmer for low pressures, but he gives values ranging from 50.5 to 65 kg. cal. increasing with the pressure. He postulates three different mechanisms. We shall discuss his results later.

We are now in a position to calculate k' theoretically except for the factor κ in (3). This will also be estimated theoretically, but before doing this we determine the value to be expected from experiment. For this purpose we take $E_0 = 53,000 - 1.833$ cal. The moment of inertia of the activated complex, I^*, is 10.14×10^{-39}, while I is 6.67×10^{-39}. The appropriate frequencies have all been given. Now taking $k' = 0.00192$, the value given by Nagasako and Volmer for high pressures at 938°K, we find $\kappa = 1.882 \times 10^{-4}$. If, instead of using this E_0 derived from Nagasako and Volmer, we use our value of 50,000 cal. we find $\kappa = 3.5 \times 10^{-4}$.

Now Zener[2b] (see also Landau[2c]) has given the relationship

$$P_{12} = 1 - \exp\{ -4\pi^2 \epsilon_{12}{}^2/hv|s_1 - s_2| \} \qquad (5)$$

for the chance that at the point of crossing of two potential curves, such as I and II in Fig. 2, the system will jump from one curve to the other. Here v is the velocity of the system, $|s_1 - s_2|$ is the absolute value of the difference of the slopes of I and II at the point of crossing. The interaction energy is $\epsilon_{12} = \int \varphi_1 H' \varphi_2 d\tau$ where φ_1 and φ_2 are the eigenfunctions for the two states which cross, and H' is an additional potential term (generally due to magnetic interactions) omitted from the Schrödinger equation in the approximation which gave the φ's as a solution. We find, as a result of this new term in the energy, that instead of crossing the two lower branches of I and II unite to form a single new state and the two upper branches unite to form a second new state. These two new states, instead of touching, are separated by a distance of $2\epsilon_{12}$ at the nearest point of approach, the activated state. The chief condition to be fulfilled for (5) to apply is that $\epsilon_{12} \ll \frac{1}{2}mv^2$, where m is the reduced mass of the system. In applying P_{12} to a chemical reaction we must average over-all velocities. Thus the quantity we require is

$$\bar{P}_{12} = \int_0^\infty \left(1 - \exp \left\{ -\frac{4\pi^2 \epsilon_{12}{}^2 m}{hp|s_1 - s_2|} \right\} \right) \exp(-p^2/2mkT)dp \left(\int_0^\infty \exp(-p^2/2mkT)dp \right)^{-1}. \qquad (6)$$

$\bar{P}_{12}$ is readily found by numerical integration, and if one takes $c = 4\pi^2 \epsilon_{12}{}^2 m^{\frac{1}{2}}/(2kT)^{\frac{1}{2}}h|s_1 - s_2|$ the

wide variety of other cases. The very good agreement between the calculated and experimental values as given below was for this reason not unexpected.

values given in Table II are found for $\bar{P}_{12}$ as a function of c.

Systems in statistical equilibrium moving up along curve I in Fig. 2 have a chance $\bar{P}_{12}$ of passing to II per crossing in the forward direction.
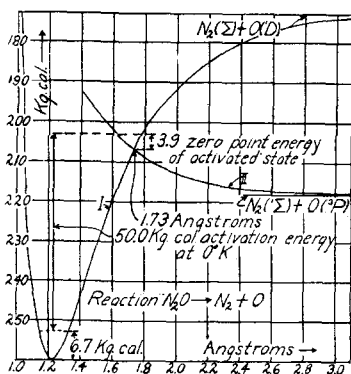
Fig. 2. Section through activated state. N_2O.

If they fail they have a second chance, $\bar{P}_{12}$, of passing to II upon their return. Thus, so long as $\bar{P}_{12}$ is small, the total chance of reaction per system passing through the activated state is $2\bar{P}_{12}$ (more exactly $2\bar{P}_{12} - \bar{P}_{12}^2$). We therefore set $2\bar{P}_{12} = \kappa$. Now $|s_1 - s_2|$ from Fig. 2 is 8.50 $\times 10^{-4}$ ergs mol.$^{-1}$ cm.$^{-1}$. Using the value of κ found when E_0 was taken equal to $53,000 - 1833$ cal. we find, using Table II, that $\epsilon_{12} = 5.05$ cal.

TABLE II.

ϵ	1	0.1	0.01	0.001	0.0001	0.00001
$\bar{P}_{12}$	0.212	.276	.0531	.00774	.001027	.000128
c	0.0^58	0.0^57	0.0^56	0.0^554	0.0^548	0.0^61
$\bar{P}_{12}$	$.0^1107$	$.0^4942$	$.0^4816$	$.0^4728$	$.0^4662$	$.0^5541$ $.0^5299$ $.0^5156$

per mole. Thus the amount, $2\epsilon_{12} = 10.1$ small calories, by which the two upper branches of curves I and II fail to make contact with the corresponding lower branches is not visible on the energy scale we have chosen. Had we used our theoretical value $E_0 = 50,000$ cal., we would have found for ϵ_{12} 7.15 cal. Either of these values for ϵ_{12} fulfill the condition of being small compared with the average kinetic energy $RT/2 = 938$ cal. In our averaging of P_{12} we have included systems having kinetic energies equal to and lower than ϵ_{12}. This introduces some error into our calculation. However, the fraction of all particles having at the activated state a kinetic energy of ϵ_{12} and below is small, and even in this region $\bar{P}_{12}$ is approximately correct. Thus treating this region more carefully could hardly change our results by more than a few percent.

THE NATURE OF ϵ_{12}

Besides the kinetic energy of the electrons and the electrostatic potential energy of electrons and nuclei which are ordinarily considered in obtaining the energy levels which cross and which do not contribute to ϵ_{12}, we have the following types of interactions which do contribute:

(a) The relativity corrections,
(b) A perturbation associated with the kinetic energy of the nuclei,
(c) The interaction of the spin of an electron with its orbital magnetic moment,
(d) Spin-orbit interaction between two different electrons,
(e) Spin-spin interactions of the electrons inside the oxygen atom,
(f) The magnetic interaction of the spins on the nitrogen molecule with those on the oxygen,
(g) Terms responsible for the hyperfine structure.

Now all the effects except (f) involve only a single atom so their magnitudes can be estimated from atomic spectra. Of these interactions only (c) and (e) seem as large as the experimental ϵ_{12}. Condon[15] finds from experimental data that the spin-orbital interaction between O ($^1D_2$) and ($^3P_2$) is 106 cm^{-1}, or 302 small calories per mole for the isolated atom. If this value for ϵ_{12} still held at the activated state, Table II shows us that κ would be around 0.1. Actually, however, what must happen is that from both the ^1D and ^3P states of oxygen molecular orbitals are formed with no angular momentum along the molecular axis, i.e., with $\lambda = 0$, while the other components of the angular momentum precess so rapidly about the molecular axis that coupling with the spin is partly destroyed. We still have spin-spin interaction inside the oxygen atom and between the nitrogen molecule and the oxygen. Of these two effects we should expect the latter to be negligible compared with the former simply on the basis of the distances between the electrons. The rough estimation of this effect of the nitrogen molecule from the point of view used by Wigner[16] in discussing ortho-para conversion indicates that we can neglect it.

The operator for spin-spin interaction is

$$\sum_{i<j} \{4\mu^2((\mathbf{S}_i\mathbf{S}_j)r_{ij}^2 - 3(\mathbf{S}_i\mathbf{r}_{ij})(\mathbf{S}_j\mathbf{r}_{ij}))\}/r_{ij}^5, \quad (7)$$

[15] Condon, Astrophys. J. 79, 217 (1934).
[16] Wigner, Zeits. f. physik. Chemie B23, 28 (1933).

where i and j are summed over the four p electrons, giving six terms in the sum. S_i and S_j are the vectors corresponding to the angular momenta of the spins of electrons i and j, respectively, and r_{ij} is the vectorial distance between the electrons while r_{ij} is this distance. μ is one Bohr magneton, $eh/4\pi mc$. Now the order of magnitude of (7) is $6\mu^2\overline{r_{12}^{-3}}$. If the average of r_{12} is taken to be 1 Angstrom, we obtain 7.3 cal. per mole, the order of magnitude given by our calculations for ϵ_{12}. The theoretical treatment by Breit of spin-spin interaction in He and Li$^+$, taken with the experimental work of Houston and Schüler, has been presented in convenient form by Bethe[17] and indicates that the above estimate for oxygen is right as regards order of magnitude except that there is still a factor depending on the symmetry of the eigenfunctions. This factor for a singlet-triplet interaction is zero. Thus only spin-orbit interaction contributes to ϵ_{12}. A part of the smallness of κ is of course due to tunneling, which requires a corresponding revision upward of ϵ_{12}.

κ FOR OTHER REACTIONS INVOLVING A CHANGE OF MULTIPLICITY FOR OXYGEN

If we can calculate the c defined in connection with Table II, we can obtain $\kappa = 2\bar{P}_{12}$ immediately for any reaction. The four quantities required are the reduced mass of the oxygen against the rest of the molecule being formed or decomposed, the difference of the two slopes at the point of crossing, the temperature, and ϵ_{12}. Now ϵ_{12} will be nearly the same as in N_2O so that only $|s_1 - s_2|$ offers any difficulty.

As a further example we consider the reaction $H_2 + O = H_2O$ at room temperature. Bear and Eyring[18] in their Fig. 3 give, for the value of $|s_1 - s_2|$, 8×10^{-3} ergs mol.$^{-1}$ cm^{-1}. $m = 2.934 \times 10^{-24}$ g mol.$^{-1}$, $\epsilon_{12} = 5.05$ cal. mole^{-1}. We take $T = 300$. This gives $\kappa = 1.5 \times 10^{-5}$.

Thus in general for a reaction involving a change in multiplicity, such as $CO + O = CO_2$, we would expect κ to be equal to 10^{-4} within a factor of about 10.

The specific reaction rate constant[1] for the reaction

$$H_2 + O = H_2O \qquad (8)$$

is

$$k' = \kappa \frac{i^*g^*}{i_1 i_2 g_1 g_2} \frac{(2\pi m^* kT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 (8\pi^3 A^* B^* C^*)^{\frac{1}{2}} (kT)^{\frac{3}{2}}}{2h^3} \prod_{i=1}^{2} (1 - \exp(-h\nu_i^*/kT))^{-1}$$

$$\cdot e^{-E_0/kT} \frac{kT}{h} \left(\frac{(2\pi m_1 kT)^{\frac{3}{2}}}{h^3} \frac{(2\pi m_2 kT)^{\frac{3}{2}}}{h^3} (1 - \exp(-h\nu_2/kT))^{-1} \frac{8\pi^2 I_2 kT}{2h^2} \right)^{-1}. \quad (9)$$

By neglecting the frequencies which are high this gives

$$k' = (\kappa/g_1)(m^*/m_1 m_2)^{\frac{3}{2}} h(A^* B^* C^*)^{\frac{1}{2}} I_2^{-1} e^{-E_0/kT}$$

$$= \kappa 1.83 \times 10^{-11} e^{-E_0/kT} \text{ cm}^3 \text{ mol.}^{-1} \text{ sec.}^{-1} \qquad (10)$$

$$= \kappa 1.11 \times 10^{13} e^{-E_0/kT} \text{ cm}^3 \text{ mole}^{-1} \text{ sec.}^{-1} \qquad (11)$$

The subscript 1 refers to 0 and 2 to H_2 and the activated complex is indicated by an asterisk. m and ν are the masses and frequencies, respectively, while i and g refer, respectively, to the statistical weights due to the nuclear spin and to the electronic states. g_1 is readily found to be 6.76 at 300°K; the product of the three moments of inertia, $(A^* B^* C^*)$, is 1.91×10^{-119} according

to the dimensions given by Bear and Eyring,[18] while $I_2 = 4.56 \times 10^{-41}$. Taking $E_0 = 8$ kg. cal. according to these last authors, and $\kappa = 1.5 \times 10^{-5}$, we find that k', from Eq. (11), is 269, a very slow atomic reaction. Thus oxygen atoms in the presence of hydrogen undoubtedly disappear by some mechanism other than (8), as for example $H_2 + O = OH + H$, in which the multiplicity change can be avoided.

PRESSURE EFFECTS IN THE N_2O REACTION

It is interesting to consider briefly Hunter's results[3c] on the effect of pressure on the rate of reaction. Since we may write for the specific reaction rate[19]

[17] Bethe, *Handbuch der Physik*, Vol. 24, No. 1 (Berlin, Julius Springer, 1933).

[18] Bear and Eyring, J. Am. Chem. Soc. **56**, 2020 (1934).
[19] Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935).

$$k' = K^* \frac{kT}{h} = \exp -\frac{[\Delta E^* + \Delta(pV)^*]}{RT} \exp\left[\frac{\Delta S^*}{R}\right]\frac{kT}{h} \qquad (12)$$
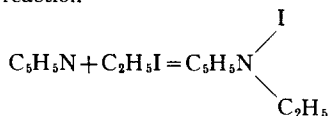
we may, of course, apply the usual thermodynamic considerations. Evans and Polanyi[20] have discussed the effect of pressure on reaction rates from a similar point of view. The process of taking partial derivatives gives

$$\left(\frac{\partial \log k}{\partial T}\right)_V = \left(\frac{\partial \log k}{\partial T}\right)_p - \left(\frac{\partial \log k}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p. \qquad (13)$$

Because of a misprint in their article they have a positive sign before the last term in (13). This does not affect their final results since, of course $(\partial p/\partial V)_T$ is a negative quantity so that they find

$$((d \log k)/dT)_V \gtreqqless 1.12((\partial \log k)/\partial T)_p \qquad (14)$$

for the reaction

$$C_5H_5N + C_2H_5I = C_5H_5N\begin{matrix} I \\ \diagup \\ \diagdown \\ C_2H_5 \end{matrix}$$

in acetone. Now Hunter measured $((\partial \log k)/\partial T)_p$, so that we cannot invoke (12) to explain his high activation energies as we might had he measured $((\partial \log k)/\partial T)_V$.

There is still another pressure effect also considered by Evans and Polanyi. From (12) we obtain at once

$$\left(\frac{d \log k'}{dT}\right)_p = \frac{\Delta H^* + RT}{RT^2} = \frac{\Delta E^* + RT}{RT^2} + \frac{p\Delta V^*}{RT^2}. \quad (15)$$

We assume that the N₂O molecule excludes other molecules from a prolate spheroid formed by the

[20] Evans and Polanyi, Trans. Faraday Soc. **31**, 875 (1935).

rotation of an ellipse about the molecule's major axis $a = b + r_3$ where b is the minor axis and r_3, as before, is the distance between the O and the far nitrogen atom. This volume is then $(\pi/6)(b+r_3)b^2$. Now the molal volume of liquid N₂O is 36 cc, and $r_3 = 2.32$A in the normal molecule so that we have $b = 4.16$A. Thus by increasing r_3 to 2.83A, as in the activated state, the molal volume is increased by only 2.8 cc. Consequently at a pressure of 40 atmospheres the quantity $p\Delta V$ increases the activation energy by only 2.7 small calories. We must therefore conclude that if Hunter's interpretation of his experimental results is correct, then at high pressures the decomposition goes by some new mechanism, as he suggests.

Although the picture of the nonadiabatic unimolecular decomposition of N₂O at moderate pressures with an activation energy of approximately 53,000 calories seems very satisfactory, an explanation of Hunter's high pressure results is not given.