

We have thus shown how to evaluate all our quantities in terms of the thermal properties of the decomposing molecules. The application of these considerations to a specific case, and comparison with the classical theory, will be undertaken in another paper.

In conclusion the writer wishes to acknowledge his indebtedness to various members of Gates Chemical Laboratory, especially to Dr. L. S. Kassel who is attacking the same problem from another angle. He is also indebted to Dr. H. C. Ramsperger of Stanford University.

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² Rice and Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1617 (1927).

³ Kassel, *J. Phys. Chem.* (in print). Rice and Ramsperger, *J. Am. Chem. Soc.* (in print).

⁴ Tolman, *Statistical Mechanics*, Chemical Catalog Co., 1927, p. 261.

⁵ This equation and its consequences will be considered in detail in another article.

THE THEORY OF THE DECOMPOSITION OF AZOMETHANE

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In this paper we intend to use the considerations of a previous article² in a study of the decomposition of azomethane, a homogeneous gas-phase reaction which is unimolecular at high pressures. Equations referred to are in that article and the nomenclature is the same as used there.

Our first task consists in the determination of n , m , and ϵ_0 . Later we shall consider B and C .

To get the various quantities we need to consider the thermal properties of azomethane, in particular we need to know the average energy at the temperature of reaction and higher temperatures. We have to get at this indirectly by considering first the specific heat, and it is necessary to estimate the specific heat itself by comparison with a similar compound, acetone. Acetone, for the range 129°C. to 233°C. has a specific heat (C_p) of 24 calories per mole.³ We subtract 2 to change C_p to C_v , and 3 more to get the "internal" specific heat, whose maximum possible value, as in the case of azomethane, is 51 calories per mole. We assume that at the temperature at which azomethane reacts, about 600°C. abs. it is slightly more excited, and estimate the specific heat at 0.5, the classical value. Let us assume for the moment that the oscillators are all equally excited. (We treat the rotational terms as if they were due to oscillators since they are small in number and hence relatively unimportant.)

Now from Einstein's formulas⁴ for the specific heat and energy of a harmonic oscillator it will be found that an oscillator which is 0.5 excited as regards specific heat has an energy 0.15 the classical value. This would make the average energy at 600°C. abs. equal to about 4500 calories. From the work of Ramsperger⁵ we may take $\bar{\epsilon} - \bar{\epsilon}$ (Eq. (7)) to be about 52,000 calories per mole, and this would make the average energy of the reacting molecule 56,500 calories per mole. 56,500 will be the average energy at about 1900°C., abs., and it will be close enough to consider that W_ϵ has a maximum at $\epsilon = 56,500$ calories per mole at 1900°. Then, from (10) we find m equal to 31 or 32.

We may investigate how m varies as we change ϵ_1 in equation (10) and this will give us some idea of the error we make by setting m constant in (6). It will be found that, in the neighborhood of 56,000, m varies about 2 per 10,000 calories, increasing with ϵ_1 . The effect of this is to spread the curve $W_\epsilon b_\epsilon$ against ϵ slightly, on both sides of the maximum, but the effect on the final results is inconsiderable. It may also be stated that the curves for $W_\epsilon b_\epsilon$ at different temperatures of reaction in the range in which we shall be interested (290°C. to 330°C.) come near enough to having their maxima at the same value of ϵ so that we do not need to worry about any difference in m between them.

On the other hand, had we supposed that the specific heat of 0.5 the classical value was due to half the oscillators being fully excited, with the other half completely frozen in (6) would become simply a classical formula with m equal to 25 or 26. The value of $\bar{\epsilon}$ at 600°C. abs. would be about 15,000 calories.

We have not yet found B and C , but as stated B is of no interest in itself and C only determines the pressure at which the rate has fallen to a certain fraction of its high-pressure value. If we plot $\log K/K_\infty$ against $\log p$, the curve for given values of n , m , and ϵ_3 is invariable in shape with changes of C , such a change merely shifting it along the pressure axis; and in such a plot the distance between any two points on two curves for different temperatures (with the same values of n , m , and ϵ_0) is invariant under changes of C , and definitely determined, since the temperature coefficients of all quantities involved are known. Now the experimental points lie at fixed positions along the $\log p$ axis, but may be shifted vertically, since K_∞ is not exactly known. Taking C as unknown, for the time, we may, by suitable horizontal shifting of the theoretical points and vertical shifting of the experimental points, bring them into coincidence, provided our theory gives the right dependence of relative rate and relative pressure. The results of such a comparison, taking $m = 31$ and $\epsilon_0 = 34,000$ calories per mole (found as explained in the preceding paper from the above value of m and assuming $\bar{\epsilon} = 6000$ calories per mole at 330°C.—actually it makes $\bar{\epsilon} = 7000$) is exhibited in figure 1. It is seen that the

agreement is satisfactory. Though the theory holds strictly for initial rate constants, we have used Ramsperger's average rates, the error caused by this being small.

The effect of changing m and $\bar{\epsilon}$ is shown by figure 2. Here the curves have been brought into the closest correspondence possible, by shifting along the $\log p$ axis. Curves IV are the result of applying the classical theory as originally developed by Rice and Ramsperger.⁶ It is seen that the curves have much the same shape, over what may be called reasonable variations of m and $\bar{\epsilon}$, and the comparison with the classical

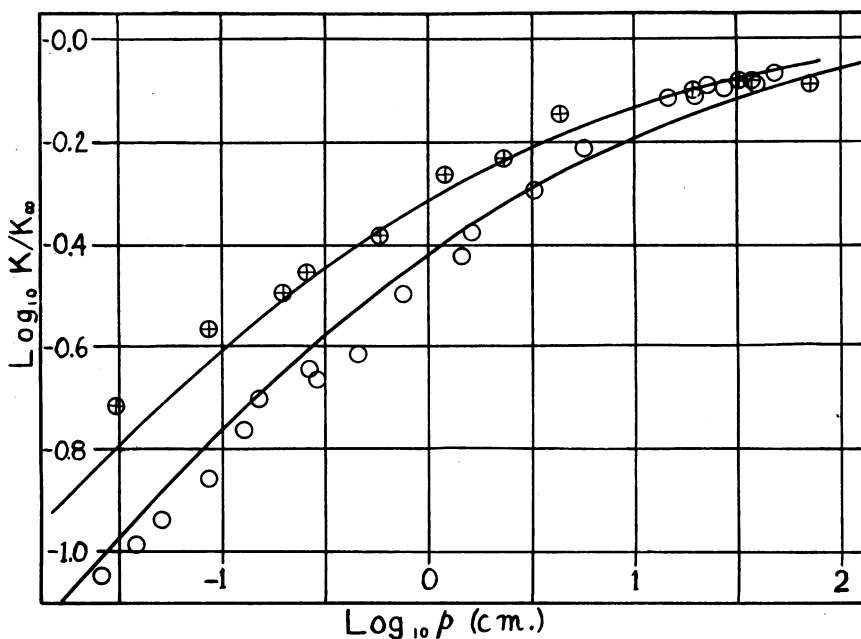


FIGURE 1

⊕, upper curve, 290°C.; ○, lower curve, 330°C.

curves seems to indicate that the same is true with respect to variation in n . All the curves can be fitted to the data about equally well. Deviations between the various curves would probably appear over a wider pressure range and if we used still a smaller value of n than was used in the classical case, we would reach a point where the rate would fall off relatively more rapidly with pressure, as was the case when the classical theory was applied to propionic aldehyde.^{6a}

But the point to be emphasized is the invariability of the shape of the curve over a considerable pressure, when the constants involved are varied through a reasonable range. This makes the agreement with experiment

much more significant, since it means that, though our determination of these constants was admittedly rough, what we have done could not be construed as a fixing of the shape of the curve by manipulation of arbitrary quantities.

By use of equations (3), (4), (6) and (14) we may find C in terms of I , which is defined in equation (13). Since I can only be approximately determined, and since small differences in I make large differences in C , it is best to first note that from equations (3), (4) and (5), and figure 1 (taking $s = 6 \times 10^{-8}$ cm.) the value of C (a dimensionless constant) which

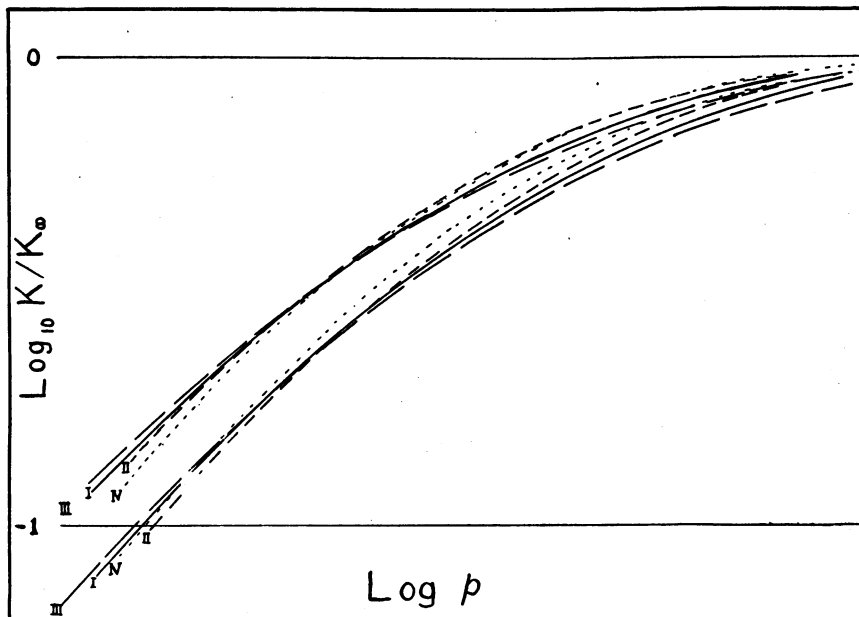


FIGURE 2

Curve	n	m	ϵ_0	$\bar{\epsilon}$ (330°C.)	Curve	n	m	ϵ_0	$\bar{\epsilon}$ (330°C.)
I	51	31	34,000	7,000	III	51	25	40,000	12,000
II	51	51	34,000	12,000	IV	25	25	51,000	15,000

makes the rate fall off at right pressure, is 3.0×10^7 at 290°C., and then attempt to discover whether the value of I corresponding to this is a reasonable value. Substituting (3) and (5) in (4), integrating approximately, and using (14) we find that the above value of C makes $I = -18.5$.

In order to find out whether this is a reasonable value or not we must consider equation (13). Now in the neighborhood of the lower limit the integrand of the first integral of (13) may be neglected compared with the second. For the average energy of molecules which have an energy greater than $\epsilon_{max.}$ will by either of the distributions (5) or (6) be close to

$\epsilon_{\max.} + kT$ at a low temperature and the difference between the classical and quantum molecules will be small compared to $\bar{\epsilon}_c - \bar{\epsilon}$, which we have previously estimated to be $0.8 nkT/2$ at 600°C ., abs. (since $\bar{\epsilon} = 6000$ calories per mole) and which could only be a little more than it is at 290°C . (The classical average energy $\bar{\epsilon}_c = nkT/2$.) On the other hand, if we go to a temperature, say, 2400°C ., abs., such that practically all the molecules have energy greater than $\epsilon_{\max.}$ (which is 58,000 calories per mole) it will be seen that the two integrals cancel each other. Hence we may write (for 290°C . or 563°C ., abs.)

$$I = \frac{n}{2} \int_{563}^{2400} \frac{R}{T} dT = \frac{n}{2} \bar{R} \log (2400/563).$$

R is determined to make the above identical with equation (13) and, from what we have said above, varies from about -0.8 to 0.0 , and \bar{R} is a sort of average in which the values at low temperatures are more heavily weighted. We might guess it to be about -0.55 . From the value of I , -18.5 , we get -0.50 , which is close enough considering the nature of the calculations. The above comparison is, of course, based on the values we have chosen for m and $\bar{\epsilon}$, but is not very sensitive to changes in these quantities.

A factor which we have heretofore neglected may now be considered briefly. We have shown previously that our considerations resulting in equation (1) do not hold unless almost all collisions of activated molecules result in such a way that neither molecule after collision shall find itself in an energy range in which the number of molecules is depleted appreciably due to reaction.^{6a} Let us consider a typical case. At the lowest pressure for which we have evaluated (1) in order to get the curve for 330°C ., in figure 1, we find that only about 22 per cent of the integral is contributed by molecules whose energy is greater than 54,000 calories per mole. Now let one of these collide with an average molecule of about 6000 calories per mole. What is the chance that after collision either one of the molecules should have an energy greater than 50,000, below which molecules are present practically in equilibrium numbers? The sum of the energy of the molecules being 60,000, this is equivalent to asking what is the chance that one of the molecules should have more than 50,000 or less than 10,000 calories. If it were just as likely to have one energy as another, the chance would be one-third, and might necessitate a serious correction of our theory. Let us try to estimate the chance that each of the molecules shall leave the collision with energy in some small interval near 30,000, as compared with the chance that one should have 50,000 and the other 10,000. We shall assume that statistical equilibrium is established between the degrees of freedom of the two molecules at col-

lision. Then the ratio of the probabilities is $P_{30}^2/(P_{50}P_{10})$ where P_{30} is the probability, according to the distribution law, that a molecule shall have energy 30,000, P_{50} that a molecule shall have 50,000, P_{10} that a molecule shall have 10,000 calories per mole.⁷ This quotient is independent of temperature, and we may take P 's at the temperature at which 30,000 is the average energy (and about the energy, therefore, at which W_e is a maximum). Let us attempt to calculate P_{30}/P_{50} . If the oscillators were all equally excited to give a specific heat 0.5 the classical value at 600°C., abs., this temperature would be 1300; if half of them were completely excited it would be 1200. Let us use the former figure to be sure we will not overestimate P_{30}/P_{50} . Then we find from (10) that we should use a value of m equal to 25 in the neighborhood of 30,000. If we used this value of m in a classical formula we would get $P_{30}/P_{50} = 6.2$. If we used instead a value of 31 for m (which seems to be at least high enough for 50,000) we would get $P_{30}/P_{50} = 1.3$. Actually it will be between these values. As P_{30}/P_{10} will also be greater than 1, it is seen that there is considerably more chance that the molecules should have about equal, rather than widely different energies, and as the molecule we originally considered had somewhat more than the energy of the average reacting molecule at that pressure, it would seem that the effect may be neglected, although the treatment cannot be made so satisfactory⁸ as in the classical case.^{6b} The error caused is in the opposite direction to that caused by using a constant value of m in (6) for the evaluation of (1).

The question still remains as to whether other satisfactory interpretations of the decomposition of azomethane could be made. Of the various hypotheses regarding activation in unimolecular reactions, the only one which occurs to us as likely to offer a possible alternative hypothesis is the chain reaction of Christiansen and Kramers. This is a possibility in the case of azomethane, since the decomposition is undoubtedly strongly exothermic. It is hard to see how to construct a theory to take this into account, but it must produce some disturbance. However, if some kind of chain is an important means of activation at low pressures, and unless the mechanism of transfer of energy is very specific, we would expect the reaction rate to fall off during the course of a run as the reaction products accumulate, but actually this takes place to only a very slight extent. Certain photochemical considerations also indicate indirectly that a chain reaction does not play a very important part in the thermal case.⁹

At present the evidence seems strongly in favor of the view that in the decomposition of azomethane activation is by collision, and that the chance of reaction of an activated molecule depends upon the energy in about the way that one would expect if reaction is due to the energy becoming localized in a particular place in the molecule.

The writer wishes to acknowledge the collaboration of Dr. H. C. Rams-

perger of Stanford University in the calculations for the classical case, and in the discussion applicable to that case.

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² Rice, these PROCEEDINGS, **14**, 113 (1928). A joint paper treating this case will soon appear.^{6b}

³ Landolt, Börnstein, *Tabellen*, **1923**, p. 1275.

⁴ See, e.g., Reiche, *Quantum Theory*, E. P. Dutton & Co., New York, p. 31. Zero point energy does not concern us.

⁵ Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1495 (1927).

⁶ (a) Rice and Ramsperger, *J. Amer. Chem. Soc.*, **49**, 1617 (1927); (b) *Ibid.* (in press).

⁷ We are using *P*'s in this place instead of *W*'s in order to avoid confusion.

⁸ In later work it has been made more satisfactory. This calculation and the similar one made for the classical case (Ref. 6b) represent extreme differences in the assumptions as to the nature of the molecule, so it seems very probable that equation (1) needs no sensible modification.

⁹ Ramsperger, *J. Amer. Chem. Soc.*, **50**, 131 (1928); *Proc. Nat. Acad. Sci.*, **13**, 849 (1927).

FUNDAMENTAL FREQUENCIES, INTERATOMIC FORCES AND MOLECULAR PROPERTIES

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During the past three or four years the study of the spectra of molecules has brought to light a large number of facts which have to do with the properties of the individual molecules as contrasted with the facts of chemistry which pertain to the properties of atoms and molecules in the aggregate. Of these specifically molecular properties, one of the most significant is the fundamental frequency, that is, the frequency of the vibration of an atom in the molecule when it moves with an amplitude which is small compared to its own dimensions. For this frequency there are now available quite accurate values covering a number of compounds. with the help of these values, we wish to point out some relations between the frequency and the force of binding on the one hand, and such macrochemical properties as heats of linkage, boiling points and directive influence on substitution.

In several fields different investigators have already met with considerable success in interpreting chemical behavior and physical properties with the help of the recently acquired knowledge of the behavior of individual atoms. Franck² has related the possibility of the photochemical decomposition of a molecule into atoms with the changes in binding and vibrational frequency which accompany electronic excitation. He and