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On the Activation Energy of Unimolecular Reactions¹

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By using the principle of microscopic reversibility, unimolecular decompositions are considered from the point of view of the reverse reaction, which is a bimolecular association. In cases where the immediate product of the decomposition is a pair of free radicals, it is assumed that the probability of these free radicals recombining upon collision is independent of their energy. An explicit expression for the activation energy in terms of the energy of reaction and the thermal properties of the molecules involved is thus obtained. From this one may calculate

the energy of activation at absolute zero and the energy necessary to break the bond which falls apart in the reaction, quantities which may differ considerably from each other and from the energy of activation at the temperature of reaction. The results are applied to several cases of interest, and are critically compared with those of the earlier theories of Rice and Ramsperger, Kassel and Rice. A brief discussion is given of the calculation of the rate constant as a function of pressure, and its modification according to the point of view of the present paper.

I. INTRODUCTION

OF the theories that have been put forth to explain the experimental data on homogeneous first order gas reactions, those that give best agreement with the data are theory II of Rice and Ramsperger, the classical and quantum theories of Kassel and the quantum theory of Rice.³ All these involve arbitrary assumptions about the nature and mechanism of dissociation. It is assumed that a necessary (but not sufficient) condition for reaction is that the total energy of the molecule be equal to or greater than a constant quantity ϵ_0 . A second necessary condition is that this energy be localized in the molecule. According to the theory of Kassel, the energy must be localized in a bond (two energy terms), that is, the bond that breaks. This permits an identification of ϵ_0 with the energy of the bond.⁴ It can be shown that the translational energy of

the molecule does not contribute to the energy necessary for dissociation, while usually rotational energy contributes a trivial amount, so that only those molecules that have vibrational energy greater than or equal to ϵ_0 can react. Sometimes, to get agreement with experiment, it is necessary to assume that only a few of the vibrational degrees of freedom take part.

A consequence of the classical theories of Rice and Ramsperger and of Kassel, and of the quantum theory of Kassel, as well, is that for high pressures the energy of activation, as determined by the temperature coefficient of the rate constant, is equal (or at least very approximately equal) to ϵ_0 ; and it has been more or less customary to consider that the energy of activation gives an experimental determination of ϵ_0 . According to the quantum theory of Rice, however, ϵ_0 may be very considerably less than the energy of activation, and hitherto there has been no satisfactory way of determining which of the quantum theories gives the most nearly correct extension of the classical theories.⁵

The difference between the theories is due to different arbitrary assumptions made in calculating the probability that in a molecule having energy $\epsilon > \epsilon_0$, ϵ_0 or more will be localized in a given part of the molecule. It would, therefore,

¹ Presented, in part, at the Boston meeting of the American Association for the Advancement of Science, December, 1933.

² Thayer Fellow.

³ (a) O. K. Rice and Ramsperger, *J. Am. Chem. Soc.* **40**, 1617 (1928). (b) Kassel, *J. Phys. Chem.* **32**, 225, 1065 (1928). (c) O. K. Rice, *Proc. Nat. Acad. Sci.* **14**, 114, 118 (1928). For a more detailed analysis of these theories than will be given in this paper and for a more complete list of references to original papers, see (d) Kassel, *Kinetics of Homogeneous Gas Reactions*, Chem. Cat. Co., 1932, especially Chapter V.

⁴ More exact definition of the various energy quantities will be given below.

⁵ O. K. Rice, *L'Activation et la Structure des Molecules*, Réunion Internationale de Chimie Physique, Paris, 1928, p. 309. Kassel, reference 3 (d), pp. 105-6.

be of great advantage if we could replace these assumptions by some of a more rational character. We believe that we have been able to do this by making use of the principle of microscopic reversibility and considering the reverse reaction, for decompositions in which the reverse reaction has no activation energy or in which the activation energy of the reverse reaction consists only of the mutual translational energy of the recombining parts; and on the basis of more careful definitions of the various quantities involved we have considered the calculation of the energy of the bond and the energy of activation at absolute zero from the observed activation energy.

Recently, with a different goal in view, Rodebush⁶ has given a quasithermodynamic derivation of the rate of reaction for a simple type of unimolecular reaction by a somewhat similar use of the reverse reaction. In this paper we shall go more deeply into the statistics involved in the treatment of the direct and reverse reactions, and shall at first restrict our discussion to the energy of activation at high pressures, where the Maxwell-Boltzmann distribution is maintained.

II. GENERAL CONSIDERATIONS

According to the principle of microscopic reversibility the reaction in equilibrium with a unimolecular decomposition is a bimolecular association.⁷ Let us consider the reaction $AB \rightleftharpoons A + B$. At equilibrium the number of molecules AB that are dissociating is equal to the number of molecules AB that are being formed by the bimolecular association of A and B . Furthermore, the average energy of the molecules AB that are dissociating is equal to the average energy of those being formed. Therefore we have the relation

$$\bar{\epsilon}_{AB} + \epsilon_{AB}^{\circ} = \bar{\epsilon}_A + \epsilon_A^{\circ} + \bar{\epsilon}_B + \epsilon_B^{\circ} + \mathfrak{E} \quad (1)$$

where $\bar{\epsilon}_{AB} + \epsilon_{AB}^{\circ}$, $\bar{\epsilon}_A + \epsilon_A^{\circ}$, and $\bar{\epsilon}_B + \epsilon_B^{\circ}$ are respectively the average energies of the molecules

of AB , A and B that actually react,⁸ and \mathfrak{E} is the energy of the bond that is formed.⁹ The quantities ϵ_{AB}° , ϵ_A° and ϵ_B° are the respective zero point vibrational energies, while the other symbol designates the average energy of those molecules which *react*, in excess of the zero point energy.

We wish now to consider the activation energy of the direct and reverse reactions. Activation energy has been defined in many ways by previous investigators.¹⁰ For cases in which the Maxwell-Boltzmann quota of activated molecules is maintained, i.e., the cases in which equilibrium statistics can be applied, the most rigorous definition of activation energy is that given by Tolman,⁸ as the difference between the average energy of the molecules that react and the average energy of all the molecules. Therefore for the activation energy of a unimolecular reaction we have

$$\epsilon_a = \bar{\epsilon}_{AB} - \bar{\epsilon}_{AB}, \quad (2)$$

where $\bar{\epsilon}_{AB}$ is the average energy of all the

⁸ See Tolman, *Statistical Mechanics*, pp. 261-2, Chem. Cat. Co., 1927. Our definitions of $\bar{\epsilon}_{AB}$, $\bar{\epsilon}_A$, and $\bar{\epsilon}_B$ are the same as Tolman's definition of the corresponding quantities.* But see reference 11.

All average energies include the translational energy.

* In previous published work the symbol ϵ with two bars above it has been used for this quantity. Throughout this paper the symbol $\bar{\epsilon}$ is being substituted.

⁹ The exact significance of the quantity \mathfrak{E} is perhaps best understood by considering the corresponding quantity for diatomic molecules, namely, the energy from the minimum of the lowest potential energy curve representing the bond to its asymptote (if potential energy curves cross, to the lowest asymptote). It is therefore identical with the quantity that spectroscopists call D_e (Jevons, *Report on Band Spectra*, Chap. IX, Cambridge University Press, 1932). It must be distinguished from D_0 , the quantity that is experimentally determined spectroscopically, and which differs from it by the amount of the zero point energy. In this paper we shall call \mathfrak{E} the energy of the bond, and distinguish it from ΔE_0 , the energy change of the reaction at absolute zero, which gives the difference between the energy of the associated molecule in its lowest energy state and the energy of the dissociated particles in their lowest energy states. The difference between \mathfrak{E} and ΔE_0 will be given by the difference between the zero point energy of the associated molecule and the sum of the zero point energies of the dissociated particles. In the literature the concept of bonding energy for the case of polyatomic molecules has not been unequivocally defined.

¹⁰ See for example Rice and Ramsperger, *J. Am. Chem. Soc.* **49**, 1618 (1927); and Kassel, reference 3 (d), p. 21.

⁶ Rodebush, *J. Chem. Phys.* **1**, 440 (1933). La Mer (*J. Chem. Phys.* **1**, 289 (1933)) has also considered energy of activation as a function of temperature but has applied his results only to reactions in solution.

⁷ The possibility of bimolecular association has been discussed by Kassel, *J. Am. Chem. Soc.* **53**, 2143 (1931).

molecules AB in excess of their zero point energy. Similarly, for the bimolecular reaction the activation energy will be given by¹¹

$$\epsilon_a' = \bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_A - \bar{\epsilon}_B. \quad (3)$$

Combining Eqs. (1), (2) and (3),

$$\epsilon_a = \bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} + \epsilon_a' + \mathcal{E} + \epsilon_A^0 + \epsilon_B^0 - \epsilon_{AB}^0. \quad (4)$$

If now we let ΔE be the energy of reaction and ΔE_0 the energy of reaction at absolute zero,¹² then according to the usual definitions of these quantities

$$\epsilon_a = \bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} + \epsilon_a' + \Delta E_0, \quad (5a)$$

$$\epsilon_a = \epsilon_a' + \Delta E. \quad (5b)$$

We shall need a special symbol for the activation energies of the unimolecular and bimolecular reactions at absolute zero; they will be denoted respectively by $\epsilon_{a,0}$ and $\epsilon'_{a,0}$.

In many recombinations that involve heavy

¹¹ In the case of the bimolecular reaction our definition differs slightly from that of Tolman. He defines the energy of activation as the average energy of all pairs of reacting molecules minus the average energy of all pairs of *colliding* molecules. This is not very clearly brought out in his book, but is clearly stated by Kassel, reference 3 (d), p. 26. We define the activation energy as the average energy of all pairs of reacting molecules minus the average energy of *all* pairs of molecules. The latter quantity is $\frac{1}{2}kT$ less than the average energy of the colliding pairs (i.e. we have an "energy of activation of collision"), so that in this way we avoid the term $\frac{1}{2}T$ which appears in Tolman's Eq. (614). If we write N_A , N_B , and N_{AB} for the concentrations of the respective molecules and define K' by the equation $dN_{AB}/dt = K'N_A N_B$, where dN_{AB}/dt represents the rate of increase of N_{AB} due to reaction between A and B , we have simply

$$kT^2 d \log K'/dT = \bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_A - \bar{\epsilon}_B.$$

If we combine this with the equation

$$kT^2 d \log K/dT = \bar{\epsilon}_{AB} - \bar{\epsilon}_A - \bar{\epsilon}_B$$

for the unimolecular reaction, it is readily seen from the immediately following development of this paper that we get the correction thermodynamic relation for the temperature dependence of the equilibrium constant K'/K . It must be noted, however, that if the bimolecular rate constants are defined in terms of partial pressures rather than concentrations a slight correction must be made. Such a correction has in fact been applied in the case of the data on the association of ethylene and hydrogen discussed below.

¹² For thermodynamic quantities we use the notation of Lewis and Randall, *Thermodynamics* (McGraw-Hill, 1923).

free radicals it seems very probable that no activation energy will be required (we neglect the "energy of activation of collision"¹¹). This is the case that will be considered first. For this special case Eq. (5b) reduces to

$$\epsilon_a = \Delta E \quad (6a)$$

and we also have

$$\epsilon_{a,0} = \Delta E_0. \quad (6b)$$

The equations of this section are not new in themselves,¹³ but the terms which enter into them do not seem to have been carefully defined; when this is done their range of applicability is much increased.

III. DISCUSSION OF THE ACTIVATION ENERGY IN SEVERAL SPECIAL CASES

The derivation of Eqs. (6a) and (6b) is almost on a thermodynamic basis. Nevertheless, it may not be entirely superfluous to mention several cases in which it may be shown that they are substantiated by the experimental facts.

An example in which (6b) is applicable is afforded by measurements recently made in this laboratory by Dr. R. A. Ogg, Jr., on the unimolecular decomposition of methyl iodide into methyl radicals and iodine atoms.¹⁴ The experimentally determined activation energy is equal to ΔE_0 for the C—I bond as calculated from thermochemical data. In this case the change of the vibrational energy (indeed, the whole vibrational energy) will be negligible.

All the information necessary to test (5b) is supplied by data available on the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$. The decomposition of ethane has been studied by Marek and McCluer¹⁵ who find it to be a first order reaction with an activation energy of 73.0 kg cal. per mole. The association has been studied by Pease¹⁶ and

¹³ For example, they have been used by Bodenstein and Jung (Zeits. f. physik. Chemie **121**, 129 (1926)), who got them from Trautz (Lehrbuch d. Chemie **1**, 406 (1922); **3**, 81 (1926), Berlin). The relation used here was not exact being $Q = \epsilon_a - \epsilon_a'$ where Q is the *heat of reaction*.

¹⁴ R. A. Ogg, Jr., J. Am. Chem. Soc. **56**, 526 (1934).

¹⁵ Marek and McCluer, Ind. Eng. Chem. **23**, 878 (1931).

¹⁶ Pease, J. Am. Chem. Soc. **54**, 1876 (1932). We have made our calculations for Pease' temperature, about 800°K. Marek and McCluer worked at slightly higher temperatures, but this difference can be neglected.

found to be bimolecular with an activation energy of 44.75 kg cal. per mole. (This has been corrected so that it applies to the rate constant expressed in terms of concentrations rather than pressures.¹¹) The heat of hydrogenation at room temperature (ΔH_{300}) has been determined by v. Wartenburg and Krause¹⁷ as 30.6 kg cal. per mole. ΔC_p as a function of temperature is given by the equation $6.5 - 0.004T$ cal. per mole per degree.¹⁸ If we make the approximation $\Delta C_v = \Delta C_p - R$ we may replace ΔE by $\Delta H - RT$. We have therefore

$$\begin{aligned}\epsilon_{a, 800} &= \Delta H_{800} - RT + \epsilon'_{a, 800} \\ &= \Delta H_{300} + \int_{300}^{800} \Delta C_p dT - R \cdot 800 + \epsilon'_{a, 800} \\ &= 76.0 \text{ kg cal. per mole,}\end{aligned}$$

the subscripts denoting the absolute temperatures at which the quantities are evaluated. This compares favorably with Marek and McCluer's value of 73.0 kg cal.

Pease has already made a calculation to show that the ratio of the reverse and direct reaction rates gives the equilibrium constant, which involves essentially the above calculation, except that it does not take account of the ΔC_v term. This term is small in this case, involving as it does only small molecules. Since (5b) differs from equations in common use only in that these terms involving the vibrational and other internal energy are explicitly taken into account, it would be of more interest if it could be verified for a case in which these are large, but data for this purpose are not available.

The real importance of the equations of Section II lies in the fact that they give us the possibility of calculating \mathcal{E} and $\epsilon_{a, 0}$ in various cases and comparing with the quantum theories of Kassel and Rice. This comparison is, however, rendered difficult by the fact that the zero point energy was not carefully considered in the earlier work. It was treated as a more or less non-distributable and constant residue of energy. On this basis it would seem that the quantity called E_0 by

Kassel^{3b} and ϵ_0 by Rice^{3c} corresponds more nearly to our $\epsilon_{a, 0}$ than to our \mathcal{E} . Accepting this identification, then according to the theory of Kassel $\epsilon_{a, 0}$ should always be just equal to the activation energy at the temperature at which it is measured, while according to the theory of Rice it should be less than the energy of activation at the temperature of reaction and increasingly so for larger molecules. We may thus consider $\epsilon_{a, 0}$ in attempting to form an opinion as to which of the older theories is the better approximation, but \mathcal{E} would seem to be intrinsically the more interesting quantity, and we shall consider how to calculate both of them from ϵ_a .

The calculation of $\epsilon_{a, 0}$ and \mathcal{E} rests upon our ability to find out something about the reverse reaction. In cases where dissociation is into free radicals it seems reasonable to assume that the bimolecular association requires no activation energy,¹⁹ which implies that the steric factor is essentially independent of the energy. This very important assumption will be shown in the next section to take the place of the assumption made in the previous theories of unimolecular decomposition that the rate of reaction of a molecule of a given energy is proportional to the fraction of such molecules which at equilibrium would have sufficient energy localized in a given bond. This latter assumption was purely *ad hoc*; the one which replaces it seems very natural, especially if a large number of degrees of freedom are involved in the reaction; for at the energy at which a molecule is activated the energy levels are fairly closely and uniformly spaced in an actual molecule.²⁰ The probability of two

¹⁹ A consideration of this assumption, and how our results would be affected if it does not hold, will be given later on in the paper. We should remark that there is some evidence that free methyl radicals do not combine in the gas phase (Ogg, reference 14; Bates and Spence, J. Am. Chem. Soc. **53**, 1689 (1931)). Since the recombination does not occur over a considerable temperature range it is unlikely that need of activation energy is the cause but rather some quantum-mechanical selection rule concerning rotation. Work is now being done on this problem.

²⁰ To verify this point the spectrum of the vibrational energy levels of the cyanogen molecule was plotted as far as the level representing 27.43 kg cal. per mole. Between 26.01 kg cal. and 27.43 kg cal. there are ten separate energy levels. As the total energy of the molecule increases the

¹⁷ v. Wartenburg and Krause, Zeits. f. physik. Chemie **151**, 105 (1930).

¹⁸ Parks and Huffman, *The Free Energies of Some Organic Compounds*, p. 80, Chem. Cat. Co., 1932.

radicals recombining also depends upon the amount the energy level, into which they are to go, is broadened. But all the energy levels are presumably equally broadened, since the broadening depends upon the lifetime of the molecule in the given state, and the latter quantity depends only upon the collision frequency, when the pressure is sufficiently high.

In order to see how our assumption works out it is desirable to treat a specific case which is as simple and exact as possible. To avoid arbitrary assignation of vibrational frequencies an actual molecule with known frequencies is preferable. For this purpose the cyanogen molecule was chosen. Although there are no data on the kinetics of the reaction, the equilibrium $\text{C}_2\text{N}_2 \rightleftharpoons 2\text{CN}$ had been studied by G. B. Kistiakowsky and one of us,²¹ and the vibrational frequencies are known. Hence it is possible to assume that the decomposition is unimolecular, and to calculate $\epsilon_{a,0}$ and $\bar{\epsilon}$ in terms of ϵ_a . Since we assume $\epsilon_a' = 0$, it follows that the average energy of the radicals that combine upon collision is equal to the average energy of all the radicals. We can, therefore, set up our equilibrium statistics and calculate the energy distribution at equilibrium.

The molecules CN and C_2N_2 each have, of course, three translational degrees of freedom, and since the molecules are linear they have only two degrees of rotational freedom. CN radicals have one vibrational frequency, while C_2N_2 has seven normal modes of vibration, only five of which are distinct, as due to the symmetry of the molecule the transverse vibrations are double. We thus get, for the average energies of CN and C_2N_2 , respectively,

$$\bar{\epsilon}_{\text{CN}} = (5/2)kT + h\nu_0 / [\exp(h\nu_0/kT) - 1] \quad (7)$$

where ν_0 is the vibration frequency of CN, and

$$\bar{\epsilon}_{\text{C}_2\text{N}_2} = (5/2)kT + \sum_{i=1}^{i=7} h\nu_i / [\exp(h\nu_i/kT) - 1] \quad (8)$$

where the ν_i are the vibrational frequencies of

energy levels become closer together. Since the energy of dissociation for this molecule is about 77 kg cal. the energy levels in this region will be exceedingly close together. See also, Kassel, reference 7.

²¹ Kistiakowsky and Gershinowitz, J. Chem. Phys. 1, 432 (1932).

C_2N_2 . If we now insert the necessary numerical values of the vibrational frequencies²² and let $T = 1500^\circ\text{K}$, the temperature at which the equilibrium was studied, we obtain

$$\bar{\epsilon}_{\text{CN}} = 8.47 \text{ kg cal. per mole} \quad (9a)$$

$$\bar{\epsilon}_{\text{C}_2\text{N}_2} = 19.87 \text{ kg cal. per mole.} \quad (9b)$$

Hence

$$\epsilon_{a,0} = \Delta E_0 = \epsilon_a + 2.9 \text{ kg cal. per mole.} \quad (10)$$

The zero point energy of cyanogen is 11.2 kg cal. per mole (being $1/2 h\nu$ for each oscillator) and that of cyanide radicals 2.9 kg cal./mole, so using Eqs. (4) and (10), we get

$$\bar{\epsilon} = \epsilon_a + 8.3 \text{ kg cal. per mole.} \quad (11)$$

Considering the high temperature involved it is seen that the effect of the internal energy is not large in this case which deals with a rather small molecule, though the difference between $\bar{\epsilon}$ and ϵ_a is nevertheless appreciable. For molecules of this small size neither the theory of Rice nor that of Kassel would demand much difference between $\epsilon_{a,0}$ and ϵ_a . Since, however, such deviation as exists is in the opposite direction to that predicted by the theory of Rice it would appear that as far as may be indicated by this specific case the theory of Kassel is to be favored.

Before considering the application of the equations of Section II to more complicated molecules it is desirable to examine more closely the relation between the concepts of "binding energy" and energy of dissociation of organic compounds as used in the literature. The calculations of Pauling²³ have shown that to each bond in an organic compound can be assigned an energy practically independent of the compound, such that the sum of all the "binding energies" gives the energy of formation of the compound from its component atoms. In the application of these binding energies to chemical data it has been assumed (at least implicitly) that they should be equal to the energy of breaking the molecule into two parts at that bond. Thus in order to explain the low dissociation energies of the highly substituted ethanes it has been necessary to assume that the bond is weakened, in the cases where phenyl groups are the substituents by resonance,²⁴ and in others by steric hindrance; more careful investigation, however, indicates that there is no reason

²² Reference 21, p. 436.

²³ Pauling, J. Am. Chem. Soc. 54, 3570 (1932).

²⁴ Pauling and Wheland, J. Chem. Phys. 1, 362 (1933).

to expect the dissociation energy to be equal to the bonding energy. The quantity measured in chemical reactions is ΔE_0 , the difference between energies of the products and the reactant, both with their zero point energies. Even though the energy of all the carbon-carbon bonds in heptane were the same we should expect that at absolute zero the energy required to break off an end CH_3 group would be different from that required to break the chain in the middle, simply because the products have different zero point energies in each case. In calculating energies of formation, however, the zero point energy is of a so much smaller magnitude than the total energy of formation that it can be neglected. But when we consider ordinary chemical decompositions, involving only one bond and try to compare the energy of dissociation with a so-called "binding energy" it is first necessary to investigate the ΔC_0 change in the reaction, as well as the change in zero point energy.

Thus there are two distinct quantities that have been called binding energy in the literature, one of which corresponds to our ΔE_0 , the other to \mathcal{E} . The quantity calculated by quantum mechanics,²⁵ at least for diatomic molecules, is \mathcal{E} . This, therefore, is the quantity that might be expected to be constant for a given bond in various compounds if anything is. On the whole, however, there is little evidence either experimental or theoretical for the constancy of either quantity. Quantum-mechanical calculations by Eyring²⁶ show in fact that the hydrogens on ethane are bound less firmly than those on methane. A wave-mechanical analysis of methane using group theory indicates that it takes more energy to pull off the first hydrogen than the rest.²⁷ Heitler and Schuchowitzki,²⁸ investigating bonding energy in organic molecules, find no way of explaining why it should be constant to more than 20 percent at best. As we have stated above, these binding energies are not the same as those considered by Pauling.²³ The equations derived in this paper afford a means of computing energies of dissociation and bonding energies from activation energies, provided the mechanism of the reaction and something about the properties of the reactants and products is known.

Let us now consider the decomposition of the azo compounds. Azomethane,^{29a} methylazoisopropane^{29b} and isopropylazoisopropane^{29c} are

²⁵ We refer to calculations by the variation method which manipulate the electronic wave functions holding the distance between nuclei fixed.

²⁶ Eyring, J. Am. Chem. Soc. **54**, 3202 (1932).

²⁷ Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 783 (1933); also see Van Vleck, *ibid.* **2**, 24 (1934); Mulliken, *ibid.* **1**, 500 (1933).

²⁸ Heitler and Schuchowitzki, Phys. Zeits. d. Sow. **3**, 241 (1933).

²⁹ Ramsperger, (a) J. Am. Chem. Soc. **49**, 912, 1495 (1927); (b) **51**, 2134 (1929); (c) **50**, 714 (1928). The energies of activation used are those calculated by Kassel, reference 3 (d).

homologues that decompose unimolecularly with activation energies of 52,440 cal., 47,480 cal. and 40,900 cal., respectively. Recent investigations have shown that the most probable mechanism for these reactions involves the breaking of a C-N bond with the formation of free radicals,³⁰ so we assume that the reverse reaction requires no activation energy and Eqs. (6a, b) are applicable.

Although there are no data on the vibrational frequencies of the azo compounds, some estimate of the frequencies involved can be made by considering the frequencies in compounds containing equal numbers of heavy atoms. Examination of data obtained from Raman and infrared absorption spectra³¹ indicates that the larger the molecule the lower the frequency of the transverse vibrations, and hence the more temperature vibration and the less zero point energy per oscillation in the molecule. Since the reaction products are smaller than the decomposing molecule, it is seen that decomposition will necessarily be accompanied by a decrease in temperature vibration (more or less counterbalanced by the increase in translational and rotational energy) and an increase in vibrational energy.

As a rough first approximation we might assume that on decomposition all the frequencies remain unchanged except four transverse vibrations, one longitudinal vibration, and one free (classical) rotation that are converted into six classical degrees of freedom, three of translation and three of rotation. For a compound with four heavy atoms these frequencies will be on the order of 600 cm^{-1} as in cyanogen (or perhaps a little lower, since there are triple bonds in cyanogen), while for eight heavy atoms they may be as low as 200 cm^{-1} . Using these figures we will have for methylazomethane at 600°K ,

$$\begin{aligned}\bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} &\sim 0.3 \text{ kg cal. per mole,} \\ \epsilon_A^\circ + \epsilon_B^\circ - \epsilon_{AB}^\circ &\sim -4.3 \text{ kg cal. per mole,} \\ \epsilon_{a,0} = \Delta E_0 \sim \epsilon_a - 0.3 &= 52.1 \text{ kg cal. per mole,} \\ \mathcal{E} \sim \epsilon_a + 4.0 &= 56.4 \text{ kg cal. per mole,}\end{aligned}\quad (12a)$$

³⁰ Leermakers, J. Am. Chem. Soc. **55**, 3499 (1933); F. O. Rice and Evering, *ibid.* **55**, 3898 (1933).

³¹ Andrews, Phys. Rev. **36**, 548 (1930); Kohlrausch, *Der Smekal-Raman Effekt*, pp. 304 ff. Springer, 1931.

and for isopropylazoisopropane

$$\begin{aligned}\bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} &\sim -1.7 \text{ kg cal. per mole,} \\ \epsilon_A^\circ + \epsilon_B^\circ - \epsilon_{AB}^\circ &\sim -1.4 \text{ kg cal. per mole,} \\ \epsilon_{a,0} = \Delta E_0 \sim \epsilon_a + 1.7 &= 42.6 \text{ kg cal. per mole,} \\ \mathcal{E} \sim \epsilon_a + 3.1 &= 44.0 \text{ kg cal. per mole.}\end{aligned}\quad (12b)$$

It is thus seen that ΔE_0 and \mathcal{E} are different for the two azo compounds, and methylazoisopropane will be intermediate. It does not seem possible that any reasonable assumption as to the frequencies could bring the values of \mathcal{E} together. If, however, there is a somewhat more profound alteration of frequencies, i.e., a general shifting to higher values, when the molecule decomposes (which is not beyond the realm of possibility) the values of ΔE_0 may be closer together, as we shall show. We still assume that the longitudinal vibrations of the hydrogens are more or less independent of the size of the molecule. As to the rest of the vibrations, we assume in the case of azomethane that we have 18 vibrations of average frequency 1000 cm^{-1} (which may be taken to include the free rotations in this case) going into twelve vibrations of average frequency 1100 cm^{-1} and six classical degrees of freedom, which gives us $\bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} \sim 1.3 \text{ kg cal. per mole at } 600^\circ\text{K}$. If for isopropylazoisopropane we assume that we have 46 vibrations of average frequency 700 cm^{-1} going into 40 vibrations of average frequency 1000 cm^{-1} and 6 classical degrees of freedom we get $\bar{\epsilon}_A + \bar{\epsilon}_B - \bar{\epsilon}_{AB} \sim -6.3 \text{ kg cal. per mole}$. We get for methyl azomethane $\epsilon_A^\circ + \epsilon_B^\circ - \epsilon_{AB}^\circ \sim -6.8 \text{ kg cal. per mole}$ and for isopropylazoisopropane $\epsilon_A^\circ + \epsilon_B^\circ - \epsilon_{AB}^\circ \sim 11.1 \text{ kg cal. per mole}$; therefore for methylazomethane

$$\begin{aligned}\epsilon_{a,0} = \Delta E_0 \sim \epsilon_a - 1.3 &= 51.1 \text{ kg cal. per mole} \\ \mathcal{E} \sim \epsilon_a + 5.5 &= 57.9 \text{ kg cal. per mole}\end{aligned}\quad (13a)$$

while for isopropylazoisopropane

$$\begin{aligned}\epsilon_{a,0} = \Delta E_0 \sim \epsilon_a + 6.3 &= 47.2 \text{ kg cal. per mole.} \\ \mathcal{E} \sim \epsilon_a - 4.8 &= 36.1 \text{ kg cal. per mole.}\end{aligned}\quad (13b)$$

So with these assumptions we have made ΔE_0 the same for the two compounds, almost within the limits of experimental error, while the difference in the \mathcal{E} values is much increased.

We feel, however, that the assumptions made, though by no means out of the question, may be a little extreme in the direction of making the average frequencies change too much on reaction. The assumptions resulting in Eqs. (12a, b) may also be too extreme, but tending in the opposite direction. We may thus feel reasonably certain that the true values for ΔE_0 and \mathcal{E} lie between those we have obtained, provided the reaction mechanism we have taken is correct.

The matter of the reaction mechanism is one of some importance, and, unfortunately, one that cannot be definitely settled at the present time. We might, for example, have the azo compounds breaking into three pieces—a nitrogen molecule and two alkyl radicals—in one step. The reverse reaction would then be trimolecular, but in this case the method of calculation would not be substantially affected. On the other hand, we might suppose one bond to break, as we have hitherto assumed, but with a simultaneous rearrangement of some kind in the fragments.³² Such a rearrangement might well differ as between a methyl and an isopropyl compound, and one might perhaps invoke something of this sort to explain the difference in the \mathcal{E} values we have found. And if, in addition, some of the energy of activation is thrown back into the molecule in the process of this rearrangement, and left localized at or near the place which breaks, then of course our calculations would not be justified. For then the recombining radicals would, by the principle of microscopic reversibility, also require an energy of activation and we should be barred from making any very effective calculation by the same difficulty which arose in connection with the earlier theories, namely the difficulty of calculating the fraction of molecules with a given total energy which have a certain amount of energy localized in some particular way.

Be that as it may it seems reasonable to conclude from the examples we have given that, in cases where a bond is broken and other complications do not come in, the quantum theory of Kassel is to be preferred as a first

³² Such a rearrangement is postulated in theories of chemical binding advanced by Heitler and Schuchowitzki, reference 26.

approximation over that of Rice, and we may judge the order of magnitude of the correction (to get $\epsilon_{a,0}$ from ϵ_a) which is needed, it being much smaller than demanded by Rice's theory. Furthermore, in cases where the activation energy of the reverse reaction is small or negligible, we see how to calculate the important quantity \mathcal{E} , which was not considered at all in the older theories.

Though difficulties might arise similar in nature to the possibilities discussed in the last paragraph but one, we nevertheless believe that it is very probable that considerations like those applied to the azo compounds may be used in discussing the decompositions of hydrocarbons into hydrogen and an unsaturated compound, in spite of the fact that it obviously does not involve simply the breaking of a single bond, but rather the splitting off in one step of a hydrogen molecule. In this case, of course, the reverse reaction requires an activation energy but this is probably largely the relative translational energy necessary to get the hydrogen molecule over a potential energy hill. It may also involve an excitation of the vibrational energy of the hydrogen, but if it does not involve any localization of energy in the unsaturated molecule in order for the hydrogen to unite with it, it seems very reasonable to suppose that the probability that the hydrogen will stick will be very nearly independent of the amount of energy the system may have, provided only that the relative translational energy and the vibrational energy of the hydrogen be at least equal to the minimum. Since no carbon atoms split off in this reaction, it is probable that the average vibrational frequency is in this case the same before and after the reaction, and it is very probable that $\epsilon_{a,0}$ and \mathcal{E} are both essentially equal to the value of ϵ_a at the temperature of reaction. Thus in this case, Kassel's quantum theory would be correct. The values of ϵ_a for the dehydrogenation of propane and *n*-pentane have been determined by Marek and McCluer to be 61.8 and 46.5 kg cal. per mole, respectively, which are to be compared to 73.0 for ethane. In this case while \mathcal{E} varies from one compound to another, it is seen from the heats of combustion, which are known, that ΔE_0 is constant from compound to compound.³³ Thus, though the activation energies of the forward and reverse processes in the hydrogenation of the hydrocarbons differ from one compound to another, their differences remain constant. Just why this should be the case is not at present clear.

In this connection two series of compounds studied by Coffin,³⁴ in which the activation energy ϵ_a seems to remain

constant from compound to compound, are of interest. To explain these data, Coffin has adopted the assumption made on different grounds by Rice and Ramsperger and by Rice³⁵ that a molecule may be divided into reactive and nonreactive sections (the latter having little or nothing to do with the part of the molecule which actually reacts) and he has offered a new definition of activation energy as "the difference between the average energy of the reactive sections which react and the average energy of all the reactive sections." This definition necessitates such a complete separation of the sections that absolutely no exchange of energy between reactive and nonreactive sections can take place; nor can the various sections affect each other's vibration frequencies. It seems doubtful to us whether as strict a separation as this can exist, and the parts still be tied together at all. Further, in view of the considerations of this paper, it is our feeling that the data do not warrant a reformulation of the definition of activation energy, for given this new definition it would again be necessary to go through an analysis such as has been given in Part I of this paper, treating the average energies of the reactive parts instead of the whole molecules, and $\epsilon_{a,0}$ and \mathcal{E} for the series of reactions would have to be calculated before any comparisons could be made. In the cases discussed by Coffin, for example the decompositions of butylidene diacetate and ethylidene diacetate, the fact that the absolute rates are different at the same temperatures, while the activation energy is the same, indicates to him that the respective homologues have different numbers of degrees of freedom in their active parts. If this were so the average energies of the reactive parts of the homologues would be different and it is difficult to see offhand why the differences between these quantities and the average energies of the activated parts of the molecules that actually react should be the same for the homologues. For these reasons it is our opinion that the data of Coffin should be treated on the same basis as the other reactions we have discussed. There is so little basis at present for estimating the vibrational frequencies of these molecules that we have made no attempt to find $\epsilon_{a,0}$ and \mathcal{E} , but we feel that ultimately this must be done to establish the validity of any interpretation of the constancy of the observed activation energy. It seems very likely, however, in these cases, in which the group of atoms added as one goes from one member of a homologous series to the next member is small compared with the whole molecule, that the values of $\epsilon_{a,0} - \epsilon_a$ and $\mathcal{E} - \epsilon_a$ will not differ much from one member of the series to the next, so that the fact that ϵ_a remains constant is really significant. In fact, it seems more likely to be significant if we disregard Coffin's suggestion that the molecules are so completely divided into separate portions, than if we take it into consideration.

These examples of the application of the equations of Section II, will serve to illustrate what we hope may be done with much better success when more experimental data become available. As our knowledge of vibrational frequencies and specific heats of complex molecules grows,

³³ From the data of Kharasch, Bur. Standards J. Research 2, 359 (1929), the heats of hydrogenation of both propylene and butylene can be calculated to be 32 kg cal. as compared with the 31 kg cal. experimentally determined for ethylene.

³⁴ Coffin, J. Chem. Phys. 2, 48 (1934); Can. J. Research 6, 417 (1932).

³⁵ (a) Rice and Ramsperger, J. Am. Chem. Soc. 50, 619 (1928); (b) Rice, Zeits. f. physik. Chemie B7, 226 (1930).

the usefulness of our equations will continually increase. It is to be noted that in the derivation of Eqs. (6a) and (6b) no assumptions have been made regarding the mechanism of energy exchange within the molecule or the number of degrees of freedom involved in the reaction. It is hoped, therefore, that these equations may serve as testing blocks for theories of unimolecular reaction based upon the statistics of the dissociating molecule, and perhaps suggest new approaches to the solution of this important problem.

IV. DEPENDENCE OF THE RATE CONSTANT ON THE PRESSURE

In the foregoing portions of the paper we have confined ourselves to considerations involving only the *average* energy of the reacting molecules. The theories of Rice and Ramsperger, Kassel and Rice were, however, chiefly concerned with determining the change of the rate constant with pressure, and this involves a detailed consideration of the energy distribution in those molecules which react, and the determination of the probability $b(\epsilon)$ that a molecule of given energy, ϵ (or ϵ_{AB} , but we will omit the subscript for simplicity), will react. To determine $b(\epsilon)$ it was necessary, as we have noted, to make some rather artificial assumptions; we shall now show how the considerations of this paper allow $b(\epsilon)$ to be determined if recombination of the parts in the reverse bimolecular reaction is independent of the total energy of those parts. This last condition is equivalent to the assumption that ϵ_a' is zero (but if it is necessary for the colliding particles to have a certain relative kinetic energy to get over a potential hill, and once they have this energy the probability of their recombining is independent of the excess energy, the indicated modification is readily made). With $\epsilon_a', 0$ equal to zero, if a molecule of energy ϵ decomposes (ϵ , of course, does *not* include the zero point energy) it will go over into a pair of molecules whose total energy, above their zero point energy, is $\epsilon - \epsilon_{a, 0}$. Now we let the equilibrium fraction of all undissociated molecules with energy between ϵ and $\epsilon + d\epsilon$ (i.e., the distribution function of the molecules) be $W(\epsilon)d\epsilon$, and we let the corresponding equilibrium fraction of such pairs of the colliding dissociated molecules as have a combined energy between $\epsilon - \epsilon_{a, 0}$ and $\epsilon - \epsilon_{a, 0} + d\epsilon$ be $F(\epsilon - \epsilon_{a, 0})d\epsilon$. Then by the assumptions we have made and the principle of micro-

scopic reversibility, we must have

$$b(\epsilon)W(\epsilon) = k_1 F(\epsilon - \epsilon_{a, 0}), \quad (14)$$

where k_1 is a constant which contains a steric factor and a collision number. From this $b(\epsilon)$ may be calculated and the result may then be inserted into the general equation of Rice and Ramsperger.³⁶

This differs from the result of the old theories only in the nature of the distribution function on the right. According to Kassel's classical and quantum theories $W(\epsilon - \epsilon_{a, 0})$ would replace $F(\epsilon - \epsilon_{a, 0})$. This is also approximately true of the classical theory of Rice and Ramsperger, while the quantum theory of Rice would demand quite a different distribution function.

There is some evidence, however, as mentioned in the last section, for the supposition that in certain cases only a limited number of degrees of freedom are directly concerned in the reaction,³⁶ that is only these particular degrees of freedom transmit energy freely to the bond which is to break in the reaction, and the rest of the molecule exchanges energy only slowly with this which may be called the active part of the molecule. At first sight then it might appear that the characteristics of the reaction, at reasonably high pressures (so long as only a negligible portion of the activation of the active part is due to the slow transfer of energy from the inactive part), would depend only on the properties of the active part. That this cannot be strictly true, however, is evident from the fact that the general equations of this paper contain only quantities which refer to the whole molecule. That nevertheless no contradiction can arise will appear from the following calculation.

In the case under consideration it will be seen that the quantity $b(\epsilon)W(\epsilon)d\epsilon$ will be replaced by

$$d\epsilon \int_0^\epsilon W^i(\epsilon - \epsilon_c) W^c(\epsilon_c) b(\epsilon_c) d\epsilon_c, \quad (15)$$

where $W^c(\epsilon_c)d\epsilon_c$ is the probability that the active part of the molecule contain an energy between ϵ_c and $\epsilon_c + d\epsilon_c$, while $W^i(\epsilon - \epsilon_c)d\epsilon$ is the probability that the inactive part of the molecule have an energy between $\epsilon - \epsilon_c$ and $\epsilon - \epsilon_c + d\epsilon$, and $b(\epsilon_c)$ is the probability that the molecule react provided the energy of the active part

³⁶ Reference 3a, p. 1622, Eq. (8).

is ϵ_c . (This last quantity, it will be observed, is entirely independent of the condition of the inactive part of the molecule which is of course the important characteristic of any theory which distinguishes between an active and an inactive part.) That the above expression is the one which should replace $W(\epsilon)b(\epsilon)d\epsilon$ is readily seen from the fact that $W^i(\epsilon-\epsilon_c)W^c(\epsilon_c)d\epsilon_c d\epsilon$ can be shown³⁷ to be the probability that the active part have energy between ϵ_c and $\epsilon_c+d\epsilon_c$ and the whole molecule have energy between ϵ and $\epsilon+d\epsilon$. The integral will therefore give the entire contribution to the reaction which comes from molecules whose total energy lies between ϵ and $\epsilon+d\epsilon$. The expression (15) therefore may be set equal to $k_1 F(\epsilon-\epsilon_{a,0})d\epsilon$, and $b(\epsilon_c)$ may be obtained by solution of the integral equation thus set up.

Let us now compare this with what would be expected from the simplest of the older theories, namely the classical or the quantum theory of Kassel, on the assumption that in the calculation of $b(\epsilon_c)$ the inactive part is to be treated as though it were non-existent, and the calculation made on the assumption that the active part of the molecule is the whole thing. According to these theories of Kassel we should have on this basis

$$b(\epsilon_c) = k_2 W^c(\epsilon_c - \epsilon_{a,0}) / W^c(\epsilon_c), \quad \text{if } \epsilon_c > \epsilon_{a,0} \\ = 0, \quad \text{if } \epsilon_c < \epsilon_{a,0} \quad (16)$$

where k_2 is a constant.

Substituting (16) into (15) we get

$$k_2 d\epsilon \int_0^{\epsilon-\epsilon_{a,0}} W^c(\epsilon_c - \epsilon_{a,0}) W^i(\epsilon - \epsilon_c) d\epsilon_c. \quad (17)$$

But since $W^c(\epsilon_c - \epsilon_{a,0})$ is zero for $\epsilon_c < \epsilon_{a,0}$ we have from (17), if we let $\epsilon_c = \epsilon_{a,0} + x$,

$$k_2 d\epsilon \int_0^{\epsilon-\epsilon_{a,0}} W^c(x) W^i(\epsilon - x - \epsilon_{a,0}) dx. \quad (18)$$

This can be seen to be equal to $k_2 W(\epsilon - \epsilon_{a,0})d\epsilon$, for the integrand (if we include the factor $d\epsilon$) is equal³⁷ to the probability that the active part of the molecule have energy between x and $x+dx$ and the whole molecule have energy be-

tween $\epsilon - \epsilon_{a,0}$ and $\epsilon - \epsilon_{a,0} + d\epsilon$. Therefore, if the two theories were to agree, we should have

$$k_2 W(\epsilon - \epsilon_{a,0}) = k_1 F(\epsilon - \epsilon_{a,0}). \quad (19)$$

This shows that the amount by which the results of the two theories will differ will depend only upon the difference in the energy distribution for the direct and the reverse reactions, as before, and that it is the entire energy of the molecule, not of any part, which comes into consideration, and insofar as (19) is a good approximation, (16) may also be taken as a good approximation. This conclusion has an application in forthcoming work by Rice and Sickman, for their work is based on an assumption equivalent to (16).

The above deductions are, as stated above, based on the assumption that activation and deactivation of the active part is by collision with other molecules, rather than due to the slow leakage of energy from or to the inactive part. At very low pressures, however, the latter mode of activation will be dominant, and may cause a second apparently unimolecular stage of the reaction to appear at pressures so low that the true high pressure unimolecular rate constant has already dropped off. This has been discussed by Rice^{35b} and will be discussed by Rice and Sickman in more detail. What we wish to note at this place is that a very peculiar effect comes into play in this low pressure region. If two free radicals unite, the active part becomes deactivated by leakage of energy to the inactive part (from which it is eventually removed by collision). But if the energy of the two free radicals is high we may expect that enough energy will find its way back to the bond which breaks in the reaction *before* it is removed from the inactive part by collision, so that the molecule will decompose again. Such a molecule cannot truly be said to have been formed, and should not be counted when we reckon the rate of recombination. Thus the probability will depend, and depend strongly on the energy of the colliding molecules, i.e., k_1 will not be independent of ϵ , and the considerations of the preceding paragraphs will not hold. Thus we can draw no conclusion here about the temperature coefficient of the low pressure unimolecular stage.

³⁷ For the treatment of a similar problem see reference 3a, p. 1622.