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THE QUANTUM THEORY OF QUASI-UNIMOLECULAR GAS REACTIONS

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Assuming activation by collision Rice and Ramsperger² developed the following general formula for the way in which reaction rate, K (at the beginning of the reaction, i.e., with a pure gas), falls off with pressure, p , in the case of gas reactions which are unimolecular at high pressures, but whose rates deviate from the unimolecular law at low pressures:

$$K = \int_{\epsilon_0}^{\infty} \frac{W_e b_e d\epsilon}{1 + b_e kT/(ap)}. \quad (1)$$

In this formula $W_e d\epsilon$ is the fraction of the molecules in the energy range ϵ to $\epsilon + d\epsilon$, while b_e is the fraction of these which will react in unit time, ϵ_0 is the minimum energy necessary for reaction, k is the gas constant, T is the absolute temperature and a is a constant from the kinetic theory of gases involved in calculating the number of collisions.

$$a = 4s^2\sqrt{\pi kT/m'} \quad (2)$$

where s is the molecular diameter and m' the mass of a molecule.

In the discussion of (1) they assumed that the energy expression for the molecule consisted of a sum of squares of coördinates and momenta, and treated the problem by the methods of classical statistical mechanics. In this paper the former assumption is retained, but we will attempt to indicate the nature of the modifications which must be made when the motions of the molecule are quantized.

In theory II of Rice and Ramsperger, which seems the more important of their two theories³ and which alone will be considered here, it was assumed that b_e was proportional to the fraction of molecules of energy ϵ in which a certain squared term in the energy expression for the molecule exceeded the value ϵ_0 . This fraction was calculated by the use of classical statistical mechanics, and the expression for b_e thus obtained may be written conveniently for our present purposes in the form

$$b_\epsilon = K_\infty C \frac{e^{\epsilon_0/(kT)}}{(kT)^{1/2}} \frac{(\epsilon - \epsilon_0)^{\frac{n-1}{2}}}{\epsilon^{\frac{n-2}{2}}} \quad (3)$$

n is the number of squared terms in the energy expression (counting both coördinates and momenta). The essential parts of the formula are the parts containing ϵ . C , a constant as far as ϵ is concerned, was evaluated (for a given temperature) in the course of their calculations, by means of the limiting form which (1) takes at high pressures:

$$K_\infty = \int_{\epsilon_0}^{\infty} W_\epsilon b_\epsilon d\epsilon. \quad (4)$$

For W_ϵ they used the classical expression:

$$W_\epsilon = \frac{1}{kT\Gamma(n/2)} \left(\frac{\epsilon}{kT} \right)^{\frac{n-2}{2}} e^{-\frac{\epsilon}{kT}}. \quad (5)$$

We now inquire into the changes in b_ϵ and W_ϵ made necessary by quantum considerations.

b_ϵ we shall leave unchanged, except for the value of C . We do this in spite of the fact that the fraction of the molecules in which a certain specified energy term has a greater value than ϵ_0 under equilibrium conditions is considerably altered in the quantum theory. Since we assume that decomposition takes place the instant the particular squared term gets the requisite energy, it is not necessary for the fraction which decomposes to be proportional to the fraction which, under equilibrium conditions, has its energy in the proper place. The rate at which the term gets energy would be balanced at equilibrium by the rate at which energy is lost by it, and some assumption must be made to calculate either rate. Whether our assumption is the best or not can hardly be told from a priori grounds, but we may anticipate a little and say that it seems to be experimentally allowable in the case of azomethane. We may soon have some knowledge of the effect of other assumptions from work now being done by Dr. L. S. Kassel.

A word must be said as to the evaluation of n . Unless some of the degrees of freedom are completely frozen in, n should be determined by the number of atoms in the molecule, as follows: Multiply that number by six (since each atom has three coördinates and three momenta) and subtract nine (six, because the coördinates determining the position and orientation of the molecule as a whole do not affect the total energy, and three more because the translational energy of the molecule as a whole cannot affect its chance of reaction²). Rice and Ramsperger evaluated n empirically so as to best fit the rate of reaction data, supposing that, if n came out smaller than would be expected from the above calculation,

it was due to some of the degrees of freedom being wholly or partially unexcited. But, as intimated in the preceding paragraph, we shall assume provisionally, at any rate, that in calculating b_ϵ , n is to be given the value found in the above manner.

We next inquire into the changes that need to be made in W_ϵ . W_ϵ will retain its exponential character, and the part which will have to be changed is the factor containing ϵ outside the exponential. Now W_ϵ occurs in the formula (1) only multiplied by b_ϵ , and is important only insofar as it modifies the shape and position of the curve $W_\epsilon b_\epsilon$ against ϵ . Now the shape of this curve is chiefly determined by the factor $(\epsilon - \epsilon_0)^{\frac{n-1}{2}} e^{-\frac{\epsilon}{kT}}$ and is such that in the case of azomethane, for example, $W_\epsilon b_\epsilon$ has appreciable values over a range of values of ϵ which is about one-fourth of the average value of ϵ in that range, most of the area under the curve lying within a narrower range. These considerations make it seem reasonable to here set, for purposes of approximation,

$$W_\epsilon = \frac{B}{kT} \left(\frac{\epsilon}{kT} \right)^{\frac{m-2}{2}} e^{-\frac{\epsilon}{kT}} \quad (6)$$

where B is independent of ϵ and m is taken as constant within the range in which $W_\epsilon b_\epsilon$ has appreciable values. We expect that m will be less than n , but m will be determined later. It will be noted that we have assumed the distribution law to be continuous, which is justified because of the many frequencies in the complex molecules that decompose unimolecularly.

We now look to the methods of determining the constants ϵ_0 , m , B and C , which appear in our equations. The equation which Rice and Ramsperger used for the determination of ϵ_0 is not applicable in this case. We must make use of the more general formula of Tolman's:⁴

$$\frac{d \log K_\infty}{dT} = \frac{\bar{\epsilon} - \bar{\epsilon}}{kT^2}. \quad (7)$$

In this equation $\bar{\epsilon}$ is the average energy of the molecules which react (equal to $\frac{\int_{\epsilon_0}^{\infty} \epsilon W_\epsilon b_\epsilon d\epsilon}{\int_{\epsilon_0}^{\infty} W_\epsilon b_\epsilon d\epsilon}$) and $\bar{\epsilon}$ is the average energy of all the molecules. This is derived on the assumption that "the rate at which molecules can be activated is so high compared with the rate at which the molecules decompose...that the equilibrium concentration of molecules in the activated states is always maintained." Since it is consistent with Tolman's use of the term "activated state" to define an activated state as a state in which the molecule has energy in a certain range, this condition is certainly maintained at high pressures, for which case we have written the equation. In using this equation we must estimate $\bar{\epsilon}$ from the thermal properties of the molecule, and $\bar{\epsilon}$ can be taken with sufficient accuracy as the value of

ϵ for which $W_\epsilon b_\epsilon$ is a maximum. This cannot be found until ϵ_0 and m are known but m is determined independently later, and the amount by which it exceeds ϵ_0 is easily found approximately before ϵ_0 is determined, and if necessary a second approximation may be made later. The temperature coefficient of $\log K_\infty$ is known fairly well from experiment, therefore, $\bar{\epsilon} - \epsilon$ can be determined, and knowing how much $\bar{\epsilon}$ exceeds ϵ_0 and the value of ϵ it is possible to find ϵ_0 .

In order to determine m we need to make use of the following theorem. If W is the fraction of the molecules which lie in certain specified quantum states, for example, those states which lie in a certain energy range, then

$$\frac{d \log W}{dT} = \frac{\bar{\epsilon}_W - \bar{\epsilon}}{kT^2} \quad (8)$$

where $\bar{\epsilon}_W$ is the average energy of the molecules in the states W and $\bar{\epsilon}$ is the average energy of all the molecules. The proof of this is much like Tolman's proof of equation (7).

From it follows immediately

$$\frac{d \log (W_{\epsilon'} / W_\epsilon)}{dT} = \frac{\epsilon' - \epsilon}{kT^2} \quad (9)$$

where $W_{\epsilon'}$ refers to the energy ϵ' and W_ϵ to ϵ . Equation (9) shows us that the change of the distribution law with temperature is the same in any theory.⁵ Consider now a classical case in which (6) (which has the form of the classical distribution) holds for one temperature. We know from the classical law that it will hold at any temperature. But if this is true for classical theory it is true for any theory over the range of energies for which (6) holds (with a certain value of m). And it is seen that if (6) represents the situation with a certain degree of accuracy at one temperature, it will represent it with the same degree of accuracy at another. (B , however, may change with temperature, since it does not affect the distribution in the range over which (6) holds.)

Now let ϵ_1 be a value of ϵ in the range in which (6) holds with some given value of m , and let T_1 be the temperature at which W_ϵ has a maximum when $\epsilon = \epsilon_1$. Then maximizing (6) we get the approximate relation

$$\epsilon_1 = (m-2)kT_1/2 \quad (10)$$

which enables us to find the appropriate value of m for the range of energies near ϵ_1 , provided we can find T_1 . In order to find the value of m for use in (6) for the evaluation of (1) or (4) we find the value of $\bar{\epsilon}$ and set this equal to ϵ_1 in (10), since $\bar{\epsilon}$ is practically in the middle of the range of values of ϵ which contribute appreciably to the integral in (1) or (4).

It now remains only to determine the proper value of B to use in equation (6), with the above value of m , over the range of energies in which we

are interested, and at the temperature of reaction. Then from B we find C , which determines the pressure at which the rate has fallen to a certain fraction of its high pressure value. B cancels out in the expression for K/K_∞ and so is of no interest except in the determination of C . (If we have data at more than one temperature, it is not necessary to make more than one calculation, since b_ϵ cannot vary with temperature, any variation in C simply cancelling the variation of the other quantities involved.)

Consider now $\int_{\epsilon_{\max.}}^{\infty} W_\epsilon d\epsilon$, where $\epsilon_{\max.}$ is the value of ϵ for which $W_\epsilon b_\epsilon$

has a maximum at the temperature of reaction. At the temperature of reaction W_ϵ is falling off rapidly with ϵ in the region of $\epsilon_{\max.}$, and most of the contribution to the integral takes place in the region where (6) holds with the value of m found from (10), and the value of B that we wish to determine. We may then assume m constant in the integration, and if $\epsilon_{\max.}$ is large with respect to $mkT/2$ as is usual (and is, in fact, the condition that W_ϵ should fall off rapidly with ϵ), we get

$$\int_{\epsilon_{\max.}}^{\infty} W_\epsilon d\epsilon = B \left(\frac{\epsilon_{\max.}}{kT} \right)^{\frac{m-2}{2}} e^{-\frac{\epsilon_{\max.}}{kT}}. \quad (11)$$

If we integrated (5) instead of (6) we should have obtained

$$\int_{\epsilon_{\max.}}^{\infty} W_\epsilon d\epsilon = \frac{1}{\Gamma(n/2)} \left(\frac{\epsilon_{\max.}}{kT} \right)^{\frac{n-2}{2}} e^{-\frac{\epsilon_{\max.}}{kT}}. \quad (12)$$

We can now use (8) to correct (12), and a comparison of the result with (11) will enable us to determine B . For we can let W in (8) be the fraction of molecules which have an energy greater than $\epsilon_{\max.}$. Then (8) holds for either a quantized or classical molecule, and subtracting the equation for the quantized molecule from the equation for the classical molecule we get, using the subscript c to distinguish the classical quantities,

$$\frac{d \log (W_c/W)}{dT} = \frac{\bar{\epsilon}_{Wc} - \bar{\epsilon}_W}{kT^2} - \frac{\bar{\epsilon}_c - \bar{\epsilon}}{kT^2}.$$

Integrating now from $T = \infty$ to the temperature of the reaction, and remembering that at high temperatures $W = W_c = 1$, we get

$$\log (W/W_c) = \int_T^{\infty} \frac{\bar{\epsilon}_{Wc} - \bar{\epsilon}_W}{kT^2} dT - \int_T^{\infty} \frac{\bar{\epsilon}_c - \bar{\epsilon}}{kT^2} dT = I. \quad (13)$$

Applying this correction to (12) and equating to (11) we get

$$B = \frac{1}{\Gamma(n/2)} \left(\frac{\epsilon_{\max.}}{kT} \right)^{\frac{n-m}{2}} e^I. \quad (14)$$

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.)