PHOTOELECTRIC OBSERVATION OF THE RATE OF DISSOCIATION OF DINITROGEN TETROXIDE BEHIND A SHOCK WAVE

Thesis by

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ABSTRACT

An experimental method has been developed in which a shock wave is used to heat a gas by a definite amount in a time short compared to the rate of adjustment of the gas to the new temperature. The rate of attainment of the new thermal equilibrium is then followed photoelectrically. The apparatus described here can be used to study reactions with half times as short as 10^{-5} seconds.

By this method the rate of dissociation of dinitrogen tetroxide in the presence of a large excess of nitrogen has been studied over a 48 degree temperature range and with an eight fold variation in total pressure. The results indicate that dissociation is a unimolecular reaction, near its second order limit at one atmosphere pressure, and approaching a first order limit at higher pressures.

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I INTRODUCTION

This thesis describes a new method for the direct measurement of the rates of very fast gas reactions. Interest in this field is not principally derived from the desire to observe a reaction faster than any previously studied. Fast reactions are often single elementary processes, and as such are the simplest reactions from the standpoint of theory, and the most fundamental in chemical kinetics.

In chemical kinetics, as in most branches of chemistry, progress has come in spurts, stimulated by the appearance of some new theoretical concept or the development of an experimental technique which extends the accuracy or range of kinetic measurements. This has been especially true of fast reactions. The Polanyi diffusion flame technique and the Paneth mirror removal method were responsible for most of the early work in fast reactions. Einstein's treatment of the dispersion of the velocity of sound in a dissociating gas started a great deal of work on the rate of dissociation of N_2O_4, which up to then had been altogether beyond measurement. Dickinson's intermittent light method has proved very useful for studying fast reactions in photochemical systems. Recently, two techniques for the direct observation of fast reactions have been developed. A shift in the equilibrium must be produced much faster than the reaction can respond to this change in conditions. The return to equilibrium may then be followed by fast photoelectric observing techniques. An intense flash lamp has been used in this way by Davidson et.al.(1). It is the purpose of this thesis to describe a new method in which a gas is suddenly heated by the passage of a shock wave through it, and photoelectric methods are used to follow its rate of adjustment to the new temperature.

It was thought that a first test of this method should be made with a reaction that is fairly simple kinetically and experimentally. The dissociation of N_2O_4 to NO_2 is such a reaction. It has been of interest in chemical kinetics for many years, but its rate and kinetic behavior were only approximately known. This reaction was therefore chosen for the first trial of the shock wave method. A report of the preliminary results has already appeared(2).

The development by Einstein of the theory of the dispersion of the velocity of sound in a dissociating gas led to a great deal of work on this effect in N_2O_4. The method, at first sight very attractive, actually suffers from several major disadvantages. The maximum dispersion is only 4% and the change which may be practically observed is often only 1%. The interpretation of the results is complicated by the simultaneous absorption of sound, and by the fact that dispersion is to be expected from vibrational heat capacity lag, altogether apart from dissociation. The best results obtained with the sound dispersion method seem to be those of Richards and Reid(4), who claim an accuracy of 10%.

Brass and Tolman(5) were able to estimate only the order of magnitude of the rate constant in their experiments, in which they measured the cooling of an NO_2 - N_2O_4 mixture after it had flowed through a set of orifices.

A study of the rate of dissociation of N_2O_4 by a completely independent method is clearly needed, and has been undertaken here.

II GENERAL METHOD AND RESULTS

1. Shock Waves in a Perfect Gas

If a plane compression wave is started in a column of gas, for example by moving a piston into one end of the column, the pressure profile will undergo the changes in time indicated in Fig. 1.

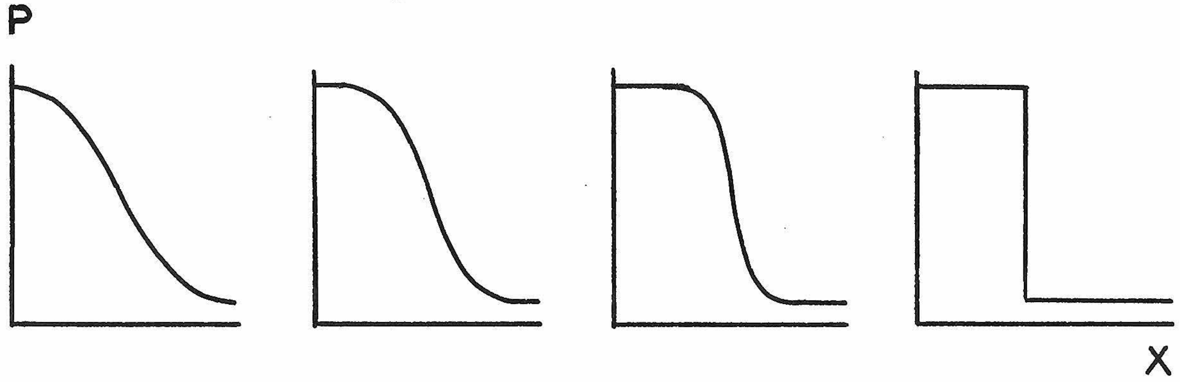

Fig. 1. Progressive Steepening of a Compression Wave

The disturbance at each position in the wave is propagated with the velocity of sound at that particular pressure and temperature. Since the density and temperature are higher in the rear of the wave, the velocity of sound, $a = \sqrt{\frac{C_p R T}{C M}}$, is greater there, and the back of the wave tends to catch up with the front. This causes the progressive steepening illustrated in Fig. 1. Ideally, this leads to a discontinuity in pressure, density, and temperature, a shock wave, whose velocity relative to the flow in front of it is supersonic, but subsonic relative to the flow behind it. Since a gas is not ultimately a homogeneous fluid, the discontinuity is not perfect. The thickness of a shock wave is of the order of a mean free path of the molecules in it, about 10^{-5} cm. for the present work.

In agreement with this qualitative picture, the (nonlinear) differential equations for the flow of a homogeneous fluid do require that a compression wave build up into a shock, and by inclusion of viscosity and heat conduction, the thickness may be approximately calculated(6).

Equations for the temperature and density changes across a shock wave may be derived simply by applying the conditions of conservation of mass, momentum, and energy across a discontinuity. These conservation equations are, respectively,

(1) $\rho u = n$ ρ, density; u, flow velocity; n, mass flux

(2) $P + nu = nV$ P, pressure; V, constant (not volume)

(3) $En + \frac{1}{2}nu^2 + Pu = \text{const.}$ E, internal energy/gram

These equations are written in a coordinate system moving with the shock wave. The situation may be pictured as a discontinuity, stationary in space, with low pressure gas flowing into it with supersonic velocity, and gas at higher density and temperature flowing away from it at subsonic velocity. These equations apply only to plane, one dimensional flow. The last states that the total flux of energy, internal plus kinetic plus mechanical, through any surface perpendicular to the flow, is constant. The form of these equations is that used by Bethe and Teller(7). Applying these results to a perfect gas with constant heat capacity gives for the ratios of specific volumes and temperatures across the shock:

(4) $v = \dfrac{1 + \dfrac{2\beta}{\gamma M^2}}{2\beta - 1}$ $\qquad\qquad \gamma = C_p/C_v$

(5) $\tau = v[1 + \gamma M^2 (1 - v)]$

where $v = \rho_\ell/\rho$, $\tau = T/T_\ell$, and $M = u_\ell/a_\ell$ is the Mach number, which is, in the laboratory coordinate system, the ratio of the shock velocity to the velocity of sound in the low pressure gas. Subscript ℓ denotes conditions in front of the shock wave, quantities without subscript refer to conditions after it. β is defined by

(6) $\beta = C_p/R = \dfrac{\gamma}{\gamma - 1}$

The ideal equations (4) and (5) hold strictly only for a perfect gas with constant heat capacity. In particular, the situation is more complicated if the heat capacity depends on temperature, as of course it does in NO_2 - N_2O_4 mixtures. The gas mixture used in the present work, nitrogen plus 1% N_2O_4, obeys the perfect gas law to a good approximation. It will be shown in Part III that the change in its heat capacity with temperature is a significant but small effect, so that equations (4) and (5) are still approximately valid, and may be used as a basis for a more exact treatment.

2. The Generation of Shock Waves

The best way to make uniform shock waves which do not gradually decay is to use a shock tube(8),(9). The tube used in the present work is shown schematically in

Fig. 2a. The pressure configuration at various times is indicated in Fig. 2b.

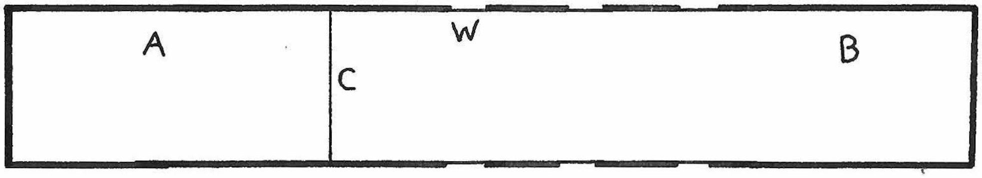

Fig. 2a. Schematic Diagram of Shock Tube. A, high pressure section; B, low pressure section; C, diaphragm; W, quartz windows.

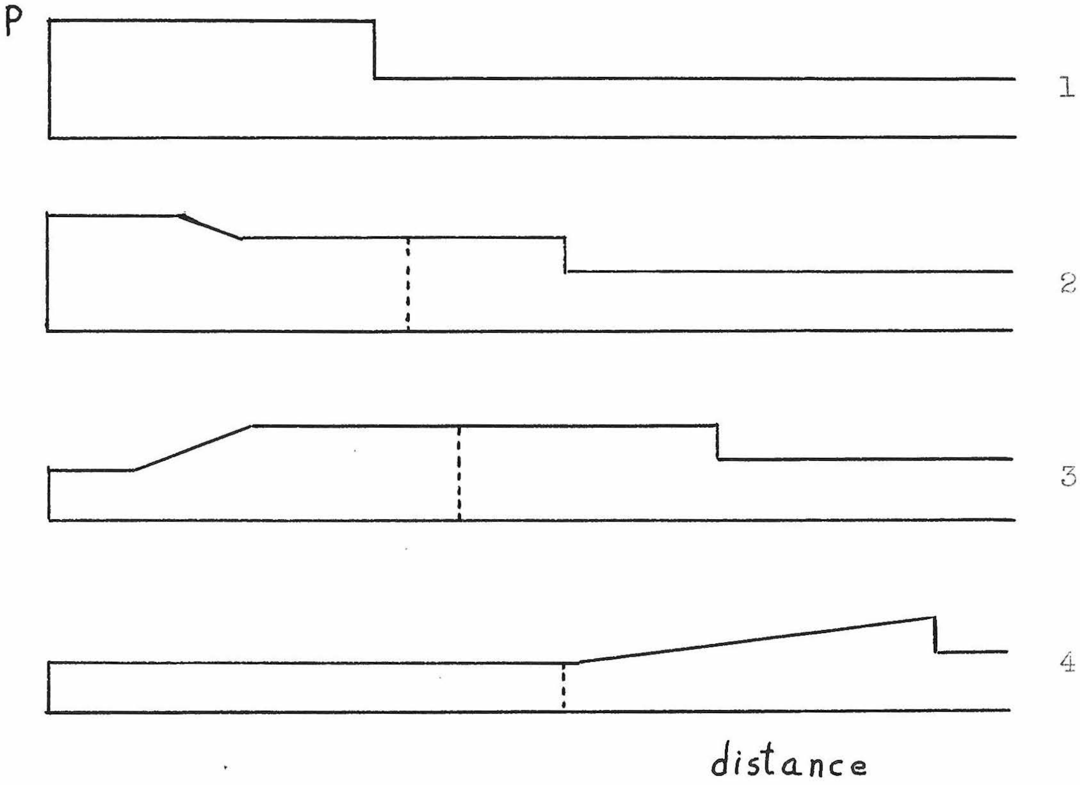

Fig. 2b. Pressure configuration in the shock tube: (1)Before diaphragm bursts, (2)Before reflection of rarefaction wave. (3)After reflection of rarefaction wave. (4)When the rarefaction has caught up with the shock wave. The dotted line represents the coldfront.

When the diaphragm separating the high and low pressure gases is burst, a sharp, plane shock wave quickly forms, since the shock velocity relative to the gas behind it is subsonic, so that any disturbances there catch up and merge with the shock. The shock wave will be uniform, the conditions behind it being given by equations (4) and (5), until the rarefaction wave which starts backwards from the diaphragm as soon as it bursts is reflected from the end of the tube and catches up with the shock front (4 in Fig. 2b). The boundary separating gases originally on different sides of the diaphragm remains fairly sharp during the flow. This boundary is called the coldfront, since there is a temperature difference across it arising from the fact that gas on one side is part of the shock wave, while gas on the other side has expanded from the high pressure section.

The equation relating the pressure ratio across the shock to the initial ratio across the diaphragm is(8):

$$(7)\quad B^{1/2\beta} = \frac{\pi^{1/2\beta}}{1 - \frac{\pi - 1}{\sqrt{2\beta(1+\pi(2\beta-1))}}}$$

for a perfect gas with constant heat capacity. B is the initial pressure ratio across the diaphragm, and π is the ratio across the resulting shock wave. This is the equation to be used in making approximate predictions of the performance of a shock tube. For example, one might have $B = 550$, $\pi = 10$, $\tau = 2.6$ or $B = 2$, $\pi = 1.4$, $\tau = 1.1$ for shock waves in pure nitrogen. Thus, at high pressures B must be much greater than π, but it is still practical to produce high temperatures in this way. It must be remembered of course that the gas will not have constant heat capacity at temperatures at which vibration and dissociation become excited. For the highly dilute N_2O_4 mixture used here, equation (7) holds fairly well, but was used only as a qualitative guide. Most of the work was done with $B = 2$.

3. Description of the Apparatus

The set up is shown schematically in Fig. 3, page 10. The gas handling system with which the two sections of the tube were filled to known pressures of nitrogen and N_2O_4 - nitrogen mixture is not shown. This and the arrangement for cooling the tube to low temperatures are discussed in Part III. The tube used is steel, 5 cm. square in cross section, with a one meter high pressure section A separated from a two meter low pressure section B by a Cellophane diaphragm C. Light beams from the sources D and E are collimated by the 1 mm. slits S and pass through quartz windows which are flush with the inner surface of the tube to minimize turbulence. In the schlieren triggering system, the beam from D, when intersected by the shock wave, is refracted into the denser medium, and hence clears the knife edge F and reaches the photomultiplier G. The resulting photoelectric signal, after being amplified, triggers a thyratron which in turn triggers the delayed sweep of the Tektronix Type 512 oscilloscope, and the external delay circuit K. The beams from the two a.c.

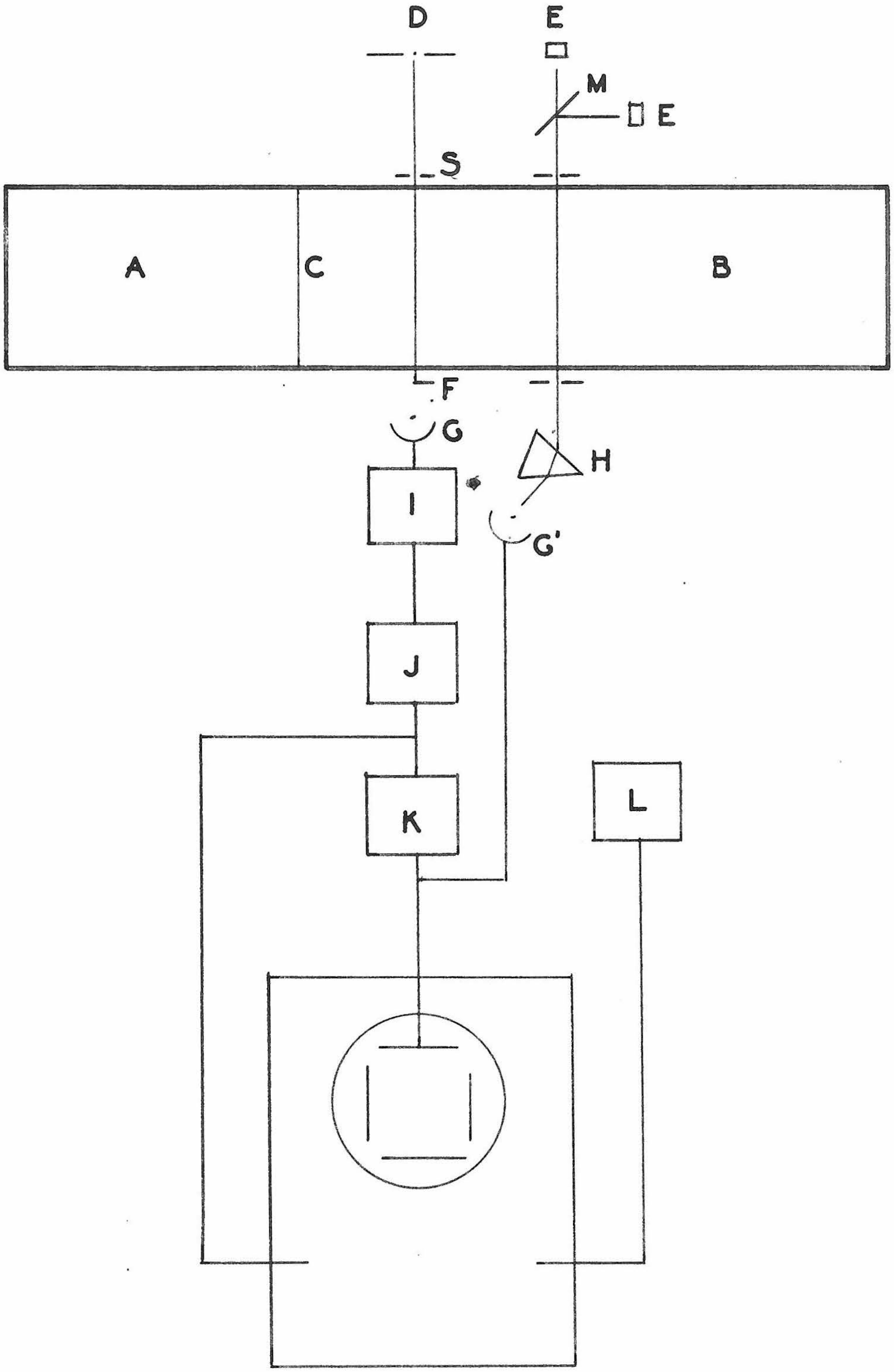

Fig.3 . Block diagram of the apparatus. See page 9.

mercury arcs E, which were run 90° out of phase to average out the a.c. variation, are combined by the half silvered mirror M, and passed through the second window, 12 cm. downstream from the first. The spectrograph H transmits to the photomultiplier G' only light absorbed by NO_2. The output of this photomultiplier is connected directly to the oscilloscope. The internal delay in the oscilloscope is so adjusted that the sweep starts just before the shock wave passes the observing light beam from the arcs E. Also the delay circuit K puts a small positive signal on the trace just before the shock wave appears. This comes at a known time after the delay was triggered by the shock wave passing the first window. This delay time, plus the time, measured from the sweep, between this mark and the appearance of the shock front at the second window, gives the time of flight of the shock wave between the two windows, and hence the shock velocity. This quantity, expressed as the Mach number, determines the temperature and density behind the shock (see equations (4) and (5)).

After the sweep starts and the time mark from the delay has appeared, the shock gets to the second window, where it refracts the light beam so as to produce a sharp spike on the trace, which lasts 3 or 4 microseconds, and obscures this much of the reaction. After this, the trace gives a record of the intensity of the light transmitted by the gas behind the shock front. As the dissociation proceeds and the NO_2 concentration rises to its new equilibrium value, the light intensity falls, at a gradually decreasing rate, which is indicated by a corresponding fall in the trace. Figs. 4 and 5 show typical records of shock waves in nitrogen, and in nitrogen containing 1% N_2O_4 respectively. The sharpness of the spike in these pictures means that the shock wave is sharp and well defined. By measuring the time of travel of the shock wave between the first two windows, and then between the second and third, no evidence for decay could be found. The apparatus used here is capable of measuring the rate of a reaction having a half time as short as 10^{-5} sec.

The sweep of the oscilloscope beam is photographed and the picture carefully measured. The vertical deflection is proportional to the voltage change, hence to the change in light intensity. The horizontal deflection, calibrated by "pips" from a 100 k.c. oscillator, gives the time scale. The method by which the rate constant is obtained from these data is explained in Part III. It is found essentially from the slope of a plot of the logarithm of the concentration of NO_2 against time, but the treatment is complicated by the deviation of shock waves in a dissociating gas from the ideal behavior characteristic of constant heat capacity, and by the fact that a fairly large shift in equilibrium is involved. The major

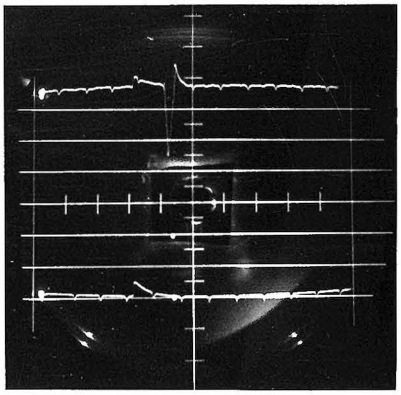

Fig. 4. Oscilloscope record of photocurrent for a shock wave in pure nitrogen. The small negative "pips" are time marks 10 μsec. apart. On the upper trace, moving from left to right, the first positive signal is a timemark from the external delay circuit. The sharp negative and positive spikes are schlieren effects as the shock front passes through the light beam. The lower trace is for purposes of calibration.

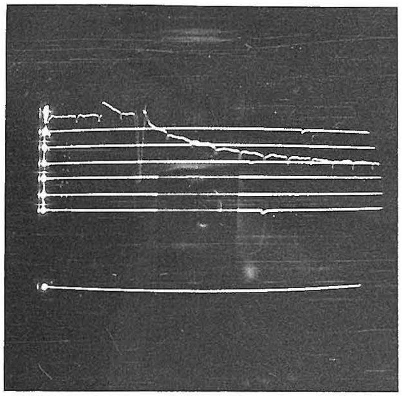

Fig. 5. Oscilloscope record of photocurrent for a shock wave in nitrogen containing 1% N_2O_4. After the shock front passes through the light beam (after the sharp negative spike), the photocurrent falls as dissociation proceeds, and levels off as the new equilibrium is reached. The smooth horizontal sweeps are voltage calibrations.

problem is to calculate the density and temperature, which are not constant, behind the shock front. The treatment of shock waves in a dissociating gas which has been used in these calculations is given in Part III.

4. Experimental Results.

The results of this study of the rate of dissociation of N_2O_4 in the presence of a large excess of nitrogen are given in Table I, page 15, and in Figs. 6,7, and 8 follow- the table. The results for the dependence of the rate on total concentration are rather poor, but the logarithmic plot of Fig. 6 indicates that the rate is approximately second order (first order with respect to nitrogen as well as with respect to N_2O_4) below concentrations of 0.05 m/l., where the slope of the curve is nearly 1. At high concentrations, the curve tends to level off, implying that the rate becomes first order (independent of nitrogen concentration). This is the behavior to be expected of a unimolecular reaction. The values in column 4 of Table I were calculated to .055 m/l. from the experimental values of column 2 by assuming a second order rate law. Most of the concentrations were close to this value, so that some deviation of the concentration dependence from second order will not have a large effect. The constants in column 4 are plotted against 1/T in Fig. 7. The mean deviation from the line is 15%. Systematic errors are discussed below and in Part III. At 25° C and a total concentration of 0.055 m/l. (99% nitrogen), the rate constant is $(8.3 \pm 1.3) \times 10^4$ sec^{-1}, interpolated from Fig. 7. The value given by Richards and Reid(4) at this

TABLE I The Rate Constant for the Dissociation of N_2O_4 as a Function of Temperature and Total Concentration.

Temp. °C	k sec.$^{-1}$ x10^{-4}	Total Conc. m/l. x10^{2}	k at .055 m/l. sec.$^{-1}$ x10^{-4}
-20	.346	6.13	.310
-20	.258	6.13	.232
-20	.303	6.32	.263
-15	1.10	26.2	
-15	.975	26.2	
-14	1.03	26.7	
-9	.795	5.99	.729
-9	.795	5.99	.729
-9	.675	5.99	.621
-7	.836	6.04	.761
-6	.492	3.18	.850
-6	.400	3.18	.690
-5	.665	3.14	1.16
-5	.634	3.14	1.11
-4	1.45	5.72	1.39
-3	1.36	5.72	1.31
-3	1.13	5.86	1.06
1	3.72	16.0	
2	4.32	16.0	
2	3.42	16.0	
2	3.98	16.0	
5	2.45	5.92	2.26
7	2.62	5.65	2.55
8	2.82	5.65	2.75
10	2.94	5.55	2.91
11	4.21	5.52	4.18
11	4.48	5.52	4.44
17	3.34	5.48	3.35
17	3.28	5.48	3.29
26	8.59	5.44	9.69
27	8.76	5.47	8.81
28	7.75	5.49	7.75
28	10.3	5.49	10.3

temperature and a total concentration of 0.036 m/l. (all NO_2 and N_2O_4) is $(6.6 \pm 0.7) \times 10^4$ sec.$^{-1}$. They found a smaller

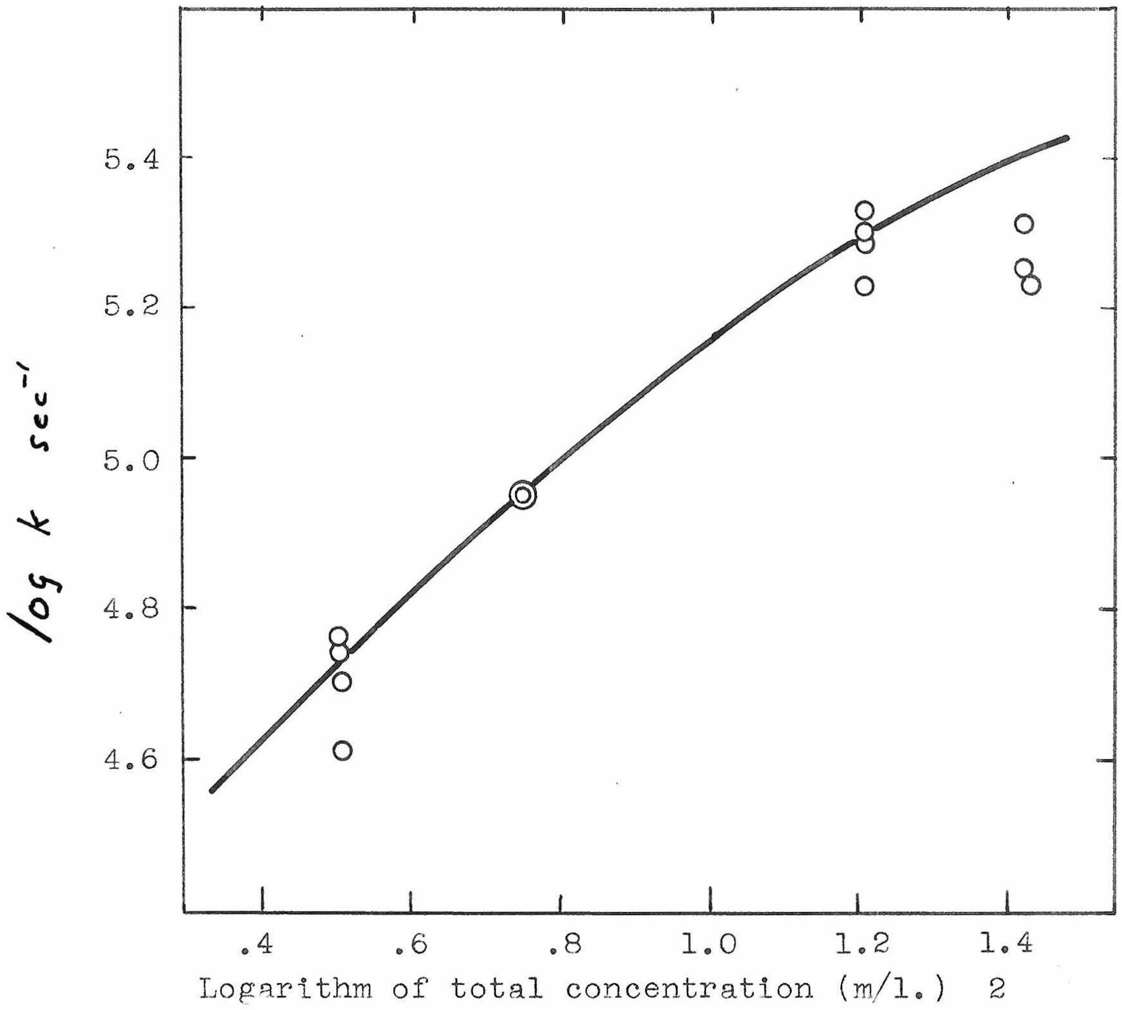

Fig. 6. Logarithm of rate constant at 298° K. ◎ denotes a point interpolated from the plot in Fig. 7.

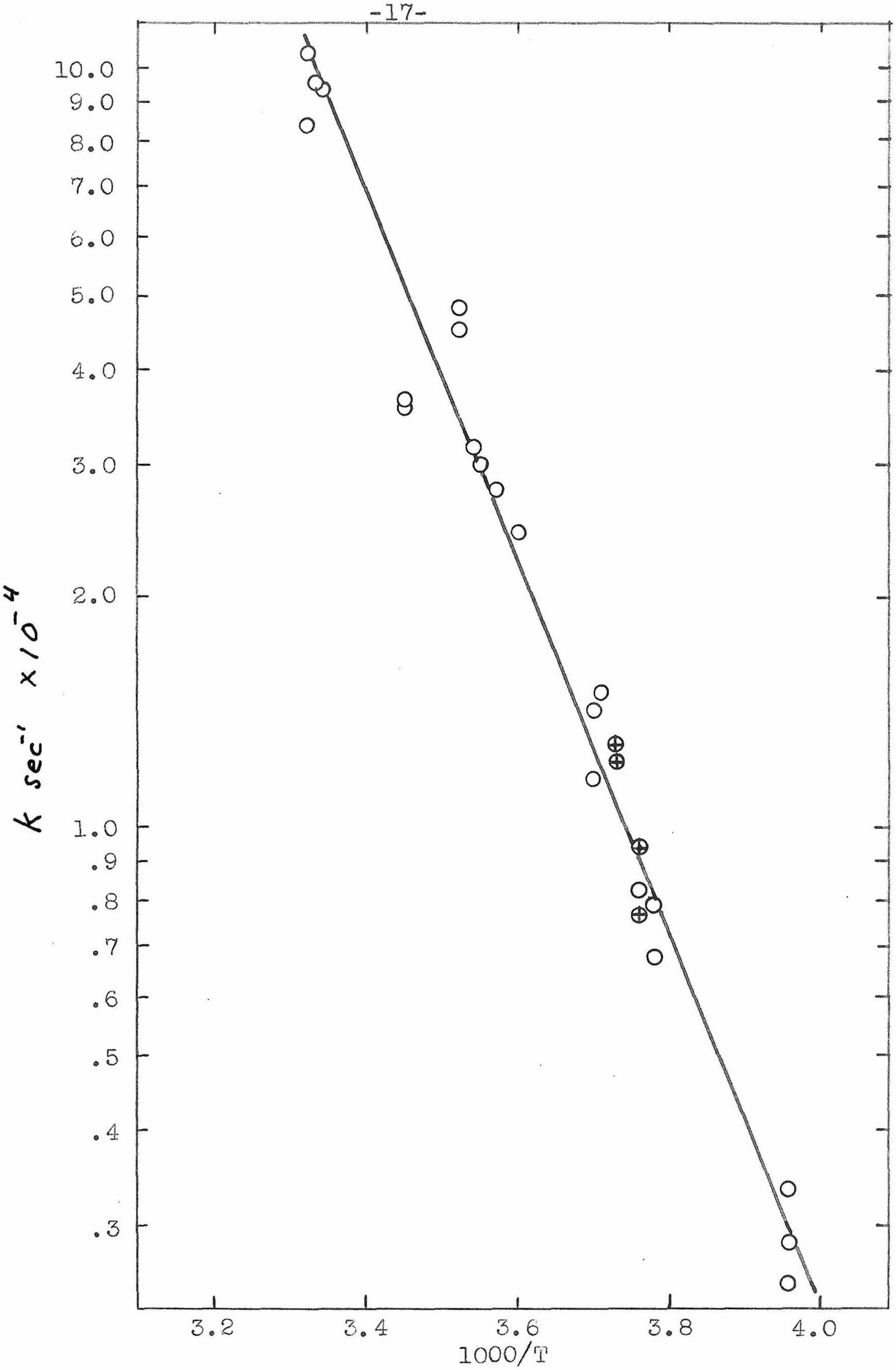

Fig. 7. First order rate constant at total concentration .055 m/l. ○ data taken near .055 m/l. ⊕ data taken at .03 m/l.

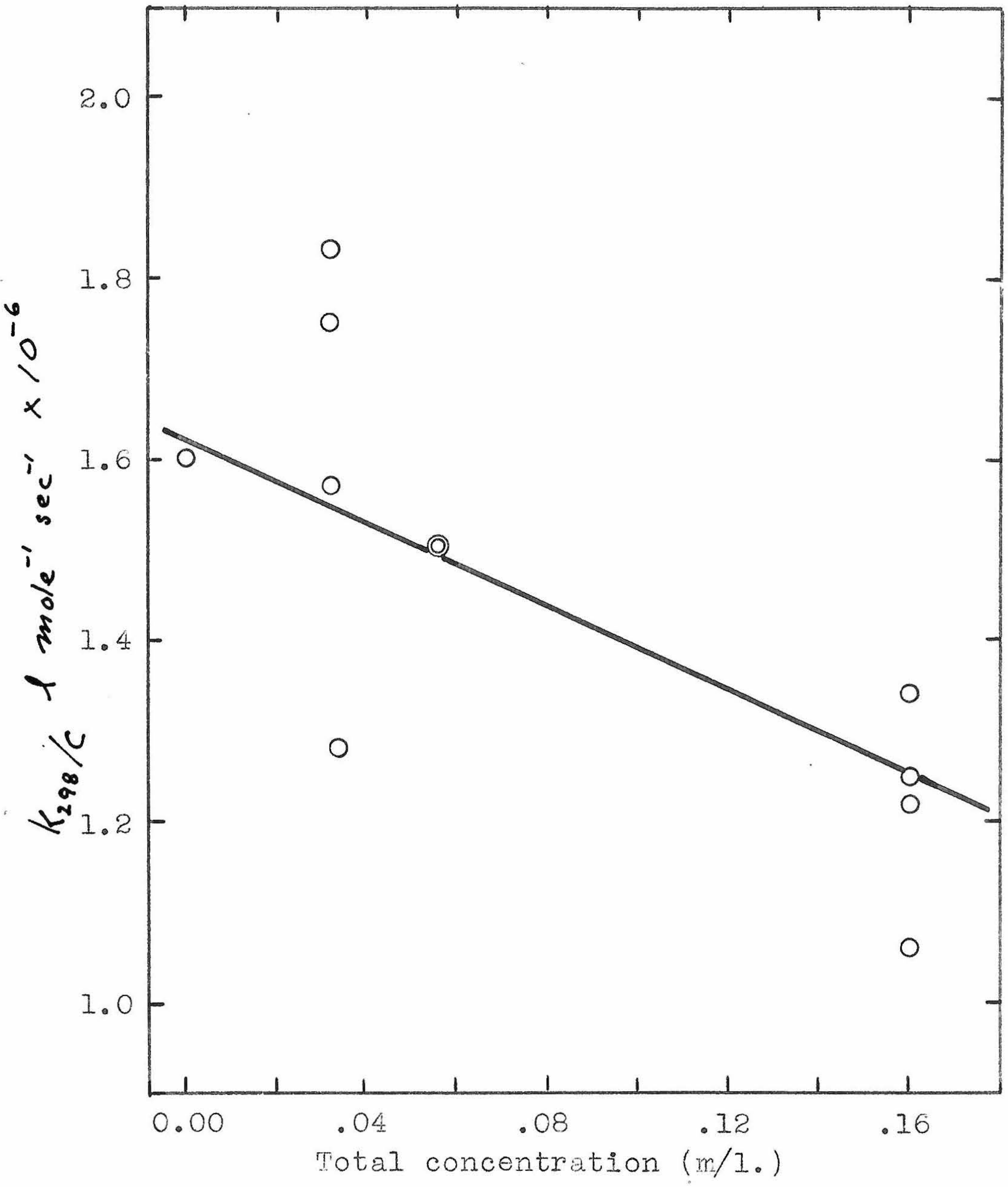

Fig. 8. Second order rate constant at 298°K.

effect of total concentration than that suggested by the present work, but comparison is difficult because of the different efficiencies of nitrogen and NO_2 - N_2O_4 in holding up the first order rate constant. The activation energy from Fig. 7 is 11.0 ± 0.6 kcal/m over a 48° temperature range. Richards and Reid found an activation energy of 13.9 ± 0.9 kcal/m over a 30° temperature range. Giauque and Kemp(10) give 13.1 kcal/m for the enrgy of dissociation.

5. Principal Sources of Error

The density and temperature behind the shock front are very sensitive functions of the shock velocity. An error of 0.6% in the measurement of the shock velocity means an error of 1.5° in the calculated temperature, and an error of 15% in the rate constant. This is just the average deviation from the straight line in Fig. 7. It is believed that 0.6% is the probable error in the velocity measurements, and that this is the principal reason that the rate constants are reproducible to only 15%. These errors should be random, and subject to averaging out.

It is possible that the nitrogen - N_2O_4 mixture in the shock tube may sometimes have contained as much as 1 or 2% of air. This could have no significant effect on the ratio of the specific heats, or on the mean molecular weight of the gas, and it seems very unlikely that a reaction that goes as fast as the N_2O_4 dissociation would be greatly accelerated by a small amount of another inert gas, in addition to the large excess of nitrogen. The presence of other impurities is thought to be unlikely. This, and other sources of error, will be discussed in more detail in Part III. As a result of these considerations, it is thought that the absolute error in constants obtained from the line in Fig. 7 is not more than 15%.

6. Summary of the Lindemann Mechanism of Unimolecular Reactions

A unimolecular reaction is the result of spontaneous decomposition or rearrangement of single molecules. In general each quantum state of a given molecule will have a different transition probability for this decomposition. The rate of the overall reaction is then the sum of the rates at which each state reacts:

$$(8) \qquad -\frac{dN}{dt} = \sum k_E N_E \qquad N = \sum N_E$$

E is a set of quantum numbers defining the state of the molecule, N_E is the number of molecules actually in that state, and k_E is the rate of decomposition of that state. Suppose that during the course of the reaction the various quantum states of the reacting molecules all remain effectively in thermal equilibrium with one another. This will be the case if the rates of transitions among the various states due to collisions are all much greater than the spontaneous decomposition rates k_E. Then the number of molecules in a given state depends only on the temperature and the total number of molecules. Each term in equation (8) will be proportional to the total number N of molecules of the reacting species, and the first order rate constant for the unimolecular reaction, defined by

(9) $-\frac{dN}{dt} = kN$

will really be independent of N. In arriving at equations (8) and (9), it has been considered that only molecules of the reacting species were present. These equations hold equally well when an inert gas is present. Collisions between molecules of the inert gas and those of the reacting species will tend to maintain the latter in their thermal equilibrium energy distribution. If the distribution of the reacting molecules among their quantum states is not one of equilibrium, the steady state concentration of each state is determined by the balance between processes such as collisions feeding molecules into that state, and processes such as collision and spontaneous reaction depleting the state.

It is assumed, since there is no definite information to the contrary, that the transition probabilities k_E depend only on the energy of the state. Furthermore, it is reasonable to assume that a molecule must have a certain minimum amount of energy, called the critical energy, before it can react at all, that is, k_E is zero for all $E < E_0$. It will then be approximately all right to consider all molecules having energy below this critical value as being in a single class, that of normal molecules. Depending on the degree of approximation, the other molecules may be distinguished according to their energy, or all taken together as energized molecules. If there is no reaction, and thermal equilibrium is maintained by collisions, the rate of collisional energization of normal molecules to the state E equals the rate at which E molecules are de-energized by collisions. The critical energy is usually much higher than thermal energies, so that the energized molecule is in a very improbable state. It is expected theoretically and confirmed experimentally that nearly every collision between an energized and a normal molecule results in two normal molecules. If a large excess of inert gas is present, so that its concentration M is much greater than N, the the total concentration of the reacting species, the thermal equilibrium rate of de-energization of E molecules is the rate of collision between these and inert gas molecules, $ZMN_E(eq)$, where Z is the kinetic theory collision number, and $N_E(eq)$ is the equilibrium concentration of E molecules. This rate of de-energization must, by microscopic reversibility, be the rate of energization at equilibrium, and we assume that it is the rate of energization in any case. Then equating the rate of energization to the rate of removal of energized molecules in the non-equilibrium steady state:

$$N_E = \frac{Z M N_E(eq)}{Z M + k_E} \tag{10}$$

This is the value of N_E to be used in equation 8 in general.

When collisions are so infrequent (when the total concentration is so low) that every energized molecule has time to react spontaneously, the over-all rate of reaction is the rate of energization, a second order process. Thus the rate can change with total concentration (which may include inert gas) from first order to second order although the basic unimolecular mechanism is the same.

The various theories of unimolecular reactions differ in the forms chosen for the functional dependence of k_E and $N_E(eq)$ on energy. It is to be expected that k_E will increase strongly with energy, since the more energy the molecule has, the easier it is for a given amount E_0 to get into the bond to be broken. The classical forms will treat E as a continuous variable, which should be fairly good for molecules with a large amount of vibrational energy. Some theories will find the rate constant as a product of an average k_E and an average N_E, instead of averaging the product $k_E N_E$ as is implied by equations ([illegible]) and (9). For reference in future discussion, the basis and results of several theories will be presented here.

Several theories are based on the model of a polyatomic molecule as a system of s weakly coupled harmonic oscillators(11). The classical results for this model are:

(11) $k_E = A\left(\frac{E-E_0}{E}\right)^{s-1}$ $\qquad N_E(eq)/N = \frac{E^{s-1}\exp(-E/RT)}{(s-1)!\,(RT)^s}$

(12) $k_\infty = A\exp(-E_0/RT)$

(13) $k_\ell = ZM\exp(-E_0/RT)\left\{\left(\frac{E_0}{RT}\right)^{s-1}\frac{1}{(s-1)!} + \left(\frac{E_0}{RT}\right)^{s-2}\frac{1}{(s-2)!} + \cdots 1\right]$

in which E_o is the critical energy, and M the total concentration. If no single molecular species is in great excess, an average Z must be used, both here and in equation (10). k_∞ and k_ℓ are first order rate constants at the high and low concentration limits, respectively. A is of the order of vibrational frequencies, being the frequency of the average fluctuations of energy among the oscillators. The expression for the rate constant at intermediate values of M can not be integrated. However, if instead of equation (11), is be assumed that all the k_E have the constant value B, one can easily obtain

$$\frac{k_\infty}{k_M} = 1 + \frac{B}{ZM} \tag{14}$$

where k_M is the apparent first order rate constant at the total concentration M. B is expected to be much smaller than A, since it represents the rate at which a large amount of energy accumulates in one bond, rather than the frequency of the average energy fluctuations.

If the oscillators in the model whose classical treatment gives equations (11),(12),(13), are considered to be quantized, the result for the high concentration rate is the same. The results for intermediate and low concentrations are analogous to the classical results, but not so easily useful.

When these theories are compared with experiment, it is usually found that the best fit is obtained when the number of oscillators s is taken to be considerably less than the actual number of vibrations in the molecule. This is because some oscillators will have smaller efficiency than others in exchanging energy with the bond to be broken, and because the vibrations may not all be excited, even in the energized molecule. Rice(12),(13),(14), has suggested taking this latter factor into account by calculating the temperature T_{en} at which the average energy of all the molecules equals that of the energized molecules at the temperature of the reaction. The effective s would then be $s' = E/RT_{en}$ where E is the average energy of the energized molecules.

Eyring's statistical theory applied to a unimolecular dissociation gives

$$k = \frac{ZM}{kT/h + ZM} \, \frac{kT}{h} \, K^{\ddagger} \tag{15}$$

$K^{\ddagger}$ is an equilibrium constant between activated and normal molecules.* An activated molecule is an energized molecule which has the required amount of energy E_0 in the bond to be broken. The k_E introduced above is the rate at which energized molecules attain this energy configuration characteristic of activated molecules. Activated molecules are assumed to decompose in a time of the order of a vibrational period. Equation (15) is considered to give the rate constant as a product of an average rate of decomposition of activated molecules, kT/h, corresponding to the quantity A introduced above, and an average concentration of

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* However, $K^{\ddagger}$ does not contain the partition function for translation of the activated molecule along the "reaction co-ordinate".

activated molecules, derived from the equilibrium constant.

The only real advance in the theory of unimolecular reactions in the past 20 years is the recent work of N.B. Slater(15). He considers a polyatomic molecule as a system of s non-interacting normal modes, and calculates the frequency with which their contributions to a particular bond length get sufficiently into phase to give that bond the critical energy. This rate constant is then averaged over molecules of all energies to give the total rate constant. The treatment has only been applied to the high concentration case, where it gives the same result as equation 12. Its most important contribution is that it gives an explicit expression for the rate of the average energy fluctuations (A of equation 12) in terms of the masses and force constants in the molecule, or alternatively as an average of the frequencies of the normal modes.

7. The Significance of the Activation Energy.

More important than the numerical value of a rate constant are its activation energy, pre-exponential factor, and concentration dependence, for it is these that give information about the physical and chemical processes taking place in the reaction.

In any discussion of activation energy, four quantities must be distinguished. (1) The only tie with reality is the experimental activation energy, found from the slope of a plot of the logarithm of the experimental rate constant against reciprocal temperature. (2) The theoretical activation energy is correspondingly obtained by differentiation of a particular theoretical expression for the rate constant. (3) The critical energy is the minimum amount of energy which a molecule must have before it can decompose. (4) The thermodynamic ΔE of the activation process. When "the activation energy" is mentioned without further qualification, the result of perfect experiments, or of a correct theoretical calculation of the temperature coefficient of the rate is meant. If concentration rather than pressure units are always used, these energy quantities correspond to the internal energy, not the enthalpy, of thermodynamics.

According to the principle of microscopic reversibility, the forward and reverse reactions in an equilibrium system must go through the same activated molecules. Hence the difference between the ΔE of activation for the forward and reverse reactions must be the over-all energy of reaction. Furthermore, since the concentration equilibrium constant is the ratio of concentration rate constants, the difference between forward and reverse activation energies must equal the energy of reaction. As will be seen below, the energy of activation may not always equal the ΔE of activation.

It is often assumed that the recombination of simple radicals requires no activation energy, so that the activation energy of the corresponding dissociation is the overall energy of dissociation. This assumption will be discussed later.

Tolman(16) has shown by general statistical mechanical arguments that the activation energy of a homogeneous gas reaction is always given by

$$E = \bar{\bar{E}} - \bar{E} + O(RT) \tag{16}$$

$\bar{\bar{E}}$ is an average energy of the reacting molecules, or an average energy of reactions, defined by

$$\bar{\bar{E}} = \sum E R_E \Big/ \sum R_E \tag{17}$$

where R_E is the rate of reaction of molecules having energy E. $\bar{E}$ is the concentration average energy of all the molecules,

$$\bar{E} = \sum \frac{E N_E}{N} \tag{18}$$

The reaction average (17) is equal to the concentration average energy of the activated molecules,

$$E^{\ddagger} = \sum E N_E^{\ddagger} \Big/ \sum N_E^{\ddagger} \tag{19}$$

if, in the unimolecular case, where $R_E = k_E N_E$, k_E has the form

$$k_E = A P_E \tag{20}$$

in which A is independent of energy and P_E is the probability that an energized molecule is in the activated state. The thermodynamic ΔE of activation is the difference between the averages of equations (19) and (18). The additional term in equation (16), of the order of RT, is strictly zero for a unimolecular reaction at its first order limit. At lower total concentrations, it approaches $\frac{1}{2}RT$, since the rate is determined by the collisional activation process. There is another, more important effect as the concentration decreases. Since energized molecules having appreciably more than the critical energy react much faster than those having just the critical energy, the concentration of the former will be relatively decreased, and so $\bar{\bar{E}}$ and hence the activation energy will decrease.

The activation energy obtained by logarithmic differentiation of a particular theoretical rate constant will naturally depend on the model and approximations used in that theory. The predictions of several theories will be presented now.

The Slater theory, the classical theory of equation 12, and its quantum mechanical analog, all give the same form for the rate constant at the first order limit, and all agree that the activation energy should be the critical energy. By differentiation of equation (15), the high concentration activation energy predicted by the Eyring theory is

$$E_\infty = \Delta E^\ddagger - \tfrac{1}{2}RT + RT \tag{21}$$

where the second term on the right is due to the fact that $K^\ddagger$ in equation (15) is not the true equilibrium constant (see the footnote, p. 24). $\Delta E^\ddagger$ is the thermodynamic energy of activation. Using the classical model, equation (11), in equation (16) gives

$$E_\infty = E_0 + (s' - s'')RT \tag{22}$$

where empirical evaluation of the effective number of oscillators, as suggested by Rice, has been allowed for by distinguishing the s values of the normal and energized molecules by " and ' respectively. The term s" can be calculated statistically (s"RT can be looked up in tables). In general, s' will be greater than s", since in the energized molecules energy transfer among the vibrations will be easier, and more vibrations will be excited than in normal molecules. For the dissociation of N_2O_4, the critical energy is to be identified with the energy of dissociation at 0°K, which is given by Giauque and Kemp(10) as 12.875 kcal/m. The consensus of the theories, then, is that the activation energy for the decomposition at the first order limit should be at least this value.

From equation (13), the classical theory gives as the activation energy at the second order limit

(23) $E_l = E_0 - (s - \frac{3}{2})RT$

The Eyring theory gives in this limit

(24) $E_l = \Delta E^{\ddagger}$

predicting a change of only $\frac{1}{2}$RT from the high to the low concentration limit. The fact that this change is so small is due to the fact that this theory does not take into account the decrease in energy of the reacting molecules as the concentration is decreased. According to Tolman's result, equation (16), the second order activation energy is $\bar{\bar{E}} - \bar{E} + \frac{1}{2}RT$. It is reasonable to assume that the energized molecules have the average amount of rotational and translational energy. Since the relative energy along the line of centers of two molecules which have at least the energy E_0 in that direction is $E_0 + RT$, it seems reasonable to assume that $\bar{\bar{E}} = E_0 + RT$ plus 3RT for rotation and translation. The result is, for the low concentration limit activation energy,

$$E_\ell = E_0 + \frac{3}{2}RT - s''RT \tag{25}$$

For N_2O_4 the data of reference(17) give $s''RT = 2.8RT$ at 298°K, so that equation (25) predicts an activation energy of 12.1 kcal/m. Equation (23) gives for $s = 3$, $E = 12.1$, for $s = 4$, 11.5, and for $s = 5$, 10.9 kcal/m. The activation energy predicted for the high concentration limit was $\geqslant 12.8$. The experimental result obtained in the present work is 11.0 ± 0.6 kcal/m. at a total concentration of about 0.055 m/1, and over the temperature range -20°C to 27°C. This result is consistent with a unimolecular decomposition near its low concentration limit at 0.055 m/1. and characterized by 4 or 5 effective oscillators. This picture is also suggested by the concentration dependence of the rate, to be discussed in section 8.

The fact that the activation energy is less than the dissociation energy(13 kcal/m.) means that the activation energy for the association of two NO_2 molecules is negative under the above conditions. This is explained by the fact that the energized molecules (which are involved in both the forward and the reverse reactions) are not in thermal equilibrium in the low concentration region (as long as there is a finite departure from chemical equilibrium). On the average they have less energy than they would have at thermal equilibrium, so that only relatively cold NO_2 molecules can associate to form these energized molecules. The concentration of these cold NO_2 molecules will decrease, and so will the rate of association, as the temperature increases.

8. Dependence of the Rate on Total Concentration.

The data that have been obtained are shown in Fig. 6, page 16, as a plot of log k at 298°K against log of total concentration. The slope of this curve should approach 1 at the low concentration (second order) limit, and 0 at the high concentration (first order) limit. The slope in the region of 0.05 m/l. is 0.9, indicating that here the reaction is nearly second order. On the basis of this curve it is estimated that the limiting low concentration rate constant is 1.6×10^{6} $1\ \text{mole}^{-1}\ \text{sec.}^{-1}$ corresponding to an apparent first order rate constant of $6.4\times10^{4}\ \text{sec.}^{-1}$ at 0.04 m/l. The second order constant may be expressed as $k_1' = 2.0\times10^{14} \exp(-11000/RT)$ $1\ \text{mole}^{-1}\ \text{sec.}^{-1}$. The apparent first order rate constant calculated from equation (13), using $s = 5$, $E_0 = 12.9$ kcal/m., $M = 0.04$ m/l., and collision diameters 3.1 and 5.3 A for nitrogen and N_2O_4 is $2.4x10^4$ sec.$^{-1}$, in fair agreement with the experimental value $6.4x10^4$ sec.$^{-1}$.

Johnston(18) has developed a method by which the high concentration rate constant for a unimolecular reaction can be estimated from data taken only at the low concentration limit. The second order rate constant in the low concentration region is plotted against total concentration (Fig. 8). Then, according to Johnston, the high concentration limit of the first order constant is greater than or equal to the square of the low concentration limit of the second order constant, divided by the slope of this plot (which should be a straight line at low enough total concentrations). By comparison with the results in the case of unimolecular reactions which have been studied experimentally at both limits, it is possible to guess that the high concentration rate constant will exceed the lower bound set for it by about a factor of 3. This gives $k_\infty = 3x10^6$ sec.$^{-1}$, or $1x10^{16}$ exp(13000/RT), assuming that the high concentration activation energy is the energy of dissociation.

The pre-exponential factor in a unimolecular reaction is typically 10^{13} to 10^{14}, so that the unusually large value 10^{16} found here requires special explanation. It may be understood in terms of the Eyring theory and the entropy of activation.

From equation (15), the pre-exponential factor in the high concentration rate constant is $\frac{kT}{h}\frac{Q^\ddagger}{Q}$. Q is the partition function for normal N_2O_4. $Q^{\ddagger}$ is the partition function for the activated molecule, apart from the N - N stretching vibration, which is included in the kT/h term. At room temperature, kT/h is 6×10^{12} sec.$^{-1}$. $Q^{\ddagger}$ does not contain the factor $\exp(-E_o/RT)$. In what follows, it is shown that reasonable guesses give a $Q^{\ddagger}/Q$ which explains the high pre-exponential factor.

N_2O_4 in the solid has a planar structure(24), and this will be assumed for the gas too, in view of the strong evidence(10) that the NO_2 groups are not free to rotate about the axis through the N-N bond in the normal molecule. It is reasonable to assume that this free rotation does occur in the activated molecule. It does not seem unreasonable to estimate the N-N bond length in the activated molecule as the distance corresponding to an energy E_o - RT in the N-N stretching vibration, this distance being determined from a Morse function defined by the dissociation energy E_o, and the equilibrium frequency and internuclear distance of this vibration. Thus the N-N distance increases from 1.64 A (Ref. 24) to 3.1 A. Using this to calculate the ratio of the moments of inertia of activated and normal molecules about an axis perpendicular to the N-N axis, and calculating the moment of inertia about this axis from the data of Ref. 24, the ratio of the classical rotational partition functions, including free rotation for the activated molecule only, is 52. By analogy with ethane, the partition function for the torsional vibration about the N-N bond in the normal molecule is expected to be near unity. There remain to be considered only the bending vibrations of the N-N bond, since the other vibrations in the molecule will not contribute much to the partition function, and these contributions from activated and normal molecules will tend to cancel. The bending frequencies will not contribute much to the partition function of the normal molecule at room temperature, since most of them have energies appreciably greater than kT. In the activated molecule, on the other hand, these vibrations will be looser and of lower energy, because of the greater N-N bond length. Frequencies of approximately 100 cm.$^{-1}$ for these four vibrations would raise the total partition function ratio to 10^3, and hence account for a pre-exponential factor of 10^{16}.

Slater's theory of unimolecular reactions(15) can not explain a pre-exponential factor larger than the largest vibrational frequency in the molecule, which is $5x10^{13}$ sec.$^{-1}$ for N_2O_4.

Combining the rate of recombination of methyl radicals (25) with the equilibrium constant for the dissociation of ethane to methyl radicals(26) gives a pre-exponential factor of $1.5x10^{15}$ for the unimolecular dissociation of ethane into methyl radicals. This may be explained in the same way as the N_2O_4 value. The fact that it is smaller than the latter may be due to the smaller moment of inertia of the methyl radical about its three fold axis, which would reduce the entropy of the activated molecule relative to the case of N_2O_4.

The rate constant in equation (9) is an average, in the sense that it is a sum over energy of the rates at which molecules of a particular energy are reacting, divided by the total number of molecules considered to be reacting. If account is taken of the fact that all k_E are zero unless $E > E_0$, one may calculate in the same way an average rate constant for the decomposition of energized molecules:

$$(26) \quad \bar{k}_E = \sum k_E N_E \Big/ \sum_{E>E_0} N_E = A(s-1)! \left(\frac{RT}{E_0}\right)^{s-1}$$

which has been evaluated using equation (11), and hence holds strictly only in the high concentration limit. It is to be expected that the rate constant will fall off when the frequency of collisions becomes less than this average rate. The location of the transition range should be given approximately by

$$(27) \quad M = \bar{k}_E / Z$$

According to the classical theory, the quantity A is the pre-exponential factor in the high concentration rate constant. Using this, one finds that the region of transition should lie at 24 m/l. (s=4) while for s = 5 it is at 4 m/l. The same collision diameters were used in this calculation as on page 31. Actually, it is more reasonable to take A as 10^{13} or 10^{14}, since the entropy factor should not greatly affect the lifetime of an energized molecule. Taking A as

10^{14} reduces the transition concentration by a factor of 100, giving 0.24 m/l. for s = 4.

Whenever an equilibrium constant and the corresponding rate constant in one direction are known, the rate of the reaction in the other direction can be found. Thus the rate constant for the bimolecular association of NO_2 molecules is calculated as 5.2×10^8 l mole^{-1} sec.$^{-1}$ at 298° K. This corresponds to a steric factor of about 6×10^{-3}, using as the collision diameter for NO_2 the value for CO_2, 4.2 A. This fairly low probability of association is explained by the fact that there is a considerable entropy decrease in this process, due to the ankylosis of two translational and four rotational degrees of freedom of the two NO_2 molecules when they combine to form the activated N_2O_4 molecule. If it were not for the free rotation about the N-N bond in the the activated molecule, the entropy decrease on association would be even greater. If recombination took place on every collision, the corresponding dissociation would be much too fast for the present apparatus to follow.

In summary it may be said that the dissociation of N_2O_4 in dilute mixture with nitrogen, has, at a total gas concentration of 0.055 m/l., an activation energy to be expected for a unimolecular reaction near its low concentration (second order) limit. The dependence of the first order rate constants on total concentration in this range supports this, and there is an indication that the rate approaches first order behavior at higher concentrations.

The activation energy and the value of the rate constant at the low concentration limit are consistent with the classical theory of unimolecular reactions, with 5 effective oscillators.

Richards and Reid(4) found an activation energy and pressure dependence much more typical of a first order reaction, even at concentrations below 0.04 m/l. Some of this discrepancy may be due to the fact that they used pure NO_2 - N_2O_4, which is probably more effective than nitrogen in maintaining the thermal equilibrium concentration of energized molecules. This would of course extend the first order behavior of the reaction to lower total concentrations.

III DETAILS OF THE EXPERIMENTAL AND THEORETICAL METHODS

1. Operation of the Shock Tube.

The principles and operation of the apparatus have been described in a general way in Part II. A more thorough description of the physical set up will now be given.

The shock tube was of the type frequently used in hydrodynamic investigations(8),(9). Each window was fitted into a carefully machined seat so that the inner surfaces of quartz and steel were flush. O-rings here and in the flanges joining sections of the tube made the apparatus vacuum and pressure tight. The diaphragm could be burst at a definite pressure by pricking it with a needle moving on the end of a shaft which was sealed through the side of the tube with another O-ring. A screen just downstream from the needle assembly served to catch the larger pieces of the burst diaphragm, preventing them from flying down the tube. Diaphragms are required that will not burst spontaneously at the desired pressure difference between sections A and B, Fig. 3, but will be sufficiently strained at that pressure so as to burst catastrophically when pricked. Most of the runs were made with the gas in B at one atmosphere, and a bursting pressure ratio of 2. The laminated Cellophane (zip tape) of the Dobeckmun Company was found most satisfactory for the required 15 p.s.i. pressure difference. It was used in double thickness. For pressure differences of 30 or 40 p.s.i. a single thickness of Visking sausage casing was satisfactory.

In the high pressure chamber, Linde Pure Dry nitrogen was used. The NO_2 which was used in the low pressure section was taken from a Matheson cylinder, and passed through P_2O_5. This gas invariably gave a green liquid on condensation. This was allowed to stand in the presence of dry oxygen until all trace of the green color had disappeared and the material on freezing gave a pure white solid. The NO_2 thus purified was used to fill a small commercial oxygen cylinder (which had been carefuly cleaned and outgassed) to a pressure of about one half an atmosphere. Dry nitrogen was then run in to dilute the NO_2 to a concentration of about 1%. Usually a full day was allowed for the two gases to diffuse into one another in the cylinder.

The mixture so obtained was analysed as follows. A 1 liter vessel with a narrow neck was filled with the gas mixture to a pressure of 1 atmosphere. Then 25 ml. of standard base was added and the vessel capped until all the NO_2 had been absorbed, as judged by the disappearance of its color. The excess base was then titrated with standard acid. Results obtained in this way were reproducible to 2%, which was good enough.

The gases were admitted to the shock tube through copper tubing, on which the dry NO_2 - nitrogen mixture seemed to have little effect. There were inevitably small air leaks in the system. Oxygen from this source would certainly oxidize any NO formed by reaction of NO_2 with the copper. It is hard to see how a few mm. of air (perhaps $\frac{1}{2}$ mm. of oxygen) could significantly effect the rate of dissociation of N_2O4 already mixed with a hundred fold excess of nitrogen. A reaction which goes so fast is hardly likely to be subject to marked catalytic effects. Pressures, other than atmospheric, in the low pressure section were measured with a mercury manometer. The mercury was slowly attacked by the gas, but since 1 mm. accuracy was sufficient, the method was satisfactory. Pressures on the high pressure side were measured on a Marshalltown Permagage, which was protected from the sudden change in pressure resulting from the bursting of the diaphragm by a length of capillary bore copper tubing. Bursting pressures and shock velocities were reproducible to 1% or better.

The dissociation of N_2O_4 at temperatures above 30 °C is too fast to be measured conveniently in the present apparatus. In order to study the reaction over a range of temperature, the shock tube had to be cooled. Four lengths of copper tubing were soldered lengthwise to the low pressure section. A centrifugal pump circulated alcohol (or trichloroethylene, for the lowest temperatures) through these, and through a coil immersed in a trichloroethylene - dry ice mixture. In this way the tube could be cooled to temperatures as low as -35° C, with a dry ice expenditure of about 5 lb. per hour. The temperature was read from two copper-constantan thermocouples placed near the observing windows. The thermocouples were calibrated against a National Bureau of Standards calibrated thermometer. The temperature could be approximately regulated by controlling the speed of the centrifugal pump.

When the shock wave passed the first window, it was detected by a schlieren optical system and photomultiplier. Light from a Western Union zirconium arc lamp (effectively a point source) was collimated by a 1 mm. slit and passed through the tube at the first window. On the other side it was nearly cut off by a knife edge. When the shock front intersected the light beam, the light was refracted into the shock, away from the knife edge, so that there was a sharp increase in light intensity reaching the photomultiplier. This sudden signal set other electronic circuits in action, and located the shock at the first window.

Two General Electric a.c. mercury arcs (type AH4) were the sources of the light whose absorption by the NO_2 formed in the reaction was directly observed by the photomultiplier at the second window. In order to get sufficient intensity, commercial a.c. arcs had to be used, and in order to partially eliminate the 120 cycle modulation in the light from such a source, two arcs were run 90° out of phase. This was accomplished by running each arc between ground and one of the leads of the three phase power line. Light from the two sources was combined with a half silvered mirror. As it traversed the shock tube, it passed through 1 mm. slits on either side, and through a small quartz prism spectrograph which selected wavelengths 4047 and 4358 A for the photomultiplier. The 120 cycle component in the resulting light was about 15%. This was not objectionable, since the time of observation was always much shorter than the period of this variation. For a given observation, the light was essentially constant, and never less than 85% of full intensity. The resolving time of the apparatus, about 4 μsec., is determined by the time required for the shock front to cross the observing light beam. This could be reduced by using narrower slits if light sources of sufficient intensity were available.

2. The Electronic Instrumentation.

R.C.A. 1P28 photomultipliers were used in the schlieren trigger system and at the observation window. They were operated at 50 to 100 volts per stage with a conventional filtered power supply. In typical operation the voltage was increased until the photocurrents reached 100 μa. with the gas mixture in the shock tube and the schlieren light beam almost cut off by the knife edge.

100 μa. is the maximum current that can be drawn from the tubes without fatiguing them.

The signal from the schlieren photomultiplier was amplified by a 6AK5 pentode and then used to trigger a thyratron(2D21). This gave a 150v. pulse which was used to trigger the oscilloscope and the external delay circuit which was used to measure the shock velocity.

The univibrator delay circuit K (in Fig. 3) has been described elsewhere(19). Its reproducibility was somewhat improved by putting two germanium diodes in the input to filter out irregularities in the output of the thyratron. The delay was calibrated by displaying its input and delayed output on the oscilloscope, with time marks from a 100 kc. oscillator superimposed. A calibration to 2 μsec. (out of about 300 μsec.) could be obtained in this way. The variation among various calibrations of the same delay on the same day were never more than 2 μsec. One of the problems which must be met in order to get more accurate determinations of the shock velocity is the need for a better delay calibration.

The time mark generator was a 100 kc. quartz crystal oscillator. The crystal and the circuit in which it was used were obtained from Monitor Piezo Products Co. The oscillator was calibrated against a frequency meter which had itself been calibrated against Station WWV. It was found to be 100 kc. to within the 0.5% accuracy required.

The output of the oscillator was put in through the time mark terminal at the rear of the oscilloscope, so as not to interfere with the other circuits.

The delay circuit K (Fig. 3) was isolated from the photoelectric signal by a frequency compensated attenuator.

The d.c. coupling of the oscilloscope was used, and only single triggered sweeps were photographed. The magnified sweep feature of the oscilloscope was used as an internal delay circuit. The signal from the schlieren circuit triggered a slow sweep when the shock front passed the first window. This does not actually appear on the cathode ray tube face, but any 20% of its length can be selected for observation, and the writing rate is automatically increased by a factor of 5 so that this part of the sweep covers the whole tube face. The instrument was adjusted so that the magnified sweep, usually writing at 10 μsec. per cm., appeared on the screen just before the shock reached the observing window. The external delay circuit, which was also triggered by the schlieren pulse, was used to put a sharp "pip" on the trace just after it started. This, coming at a known time after the shock passed the first window, served to determine the position of the magnified sweep in time relative to that event. Just after this signal from the external delay, the shock front reached the observing window and the changing photocurrent was displayed on the trace.

The oscilloscope was adjusted so that the level of the sweep corresponding to zero light intensity was near the top of the tube face, while for 100 μa. of photocurrent it was near the bottom. The trace rises toward the center of the tube as the reaction proceeds. The vertical deflection sensitivity was calibrated for these conditions by a series of known voltage ratios obtained from a dry cell by using a voltage divider made from precision(1%) resistors.

The oscilloscope trace was photographed with a Mercury II camera on Eastman Linagraph Pan 35 mm. film. After the sweep with the information from the shock wave on it, individual sweeps at several calibrating voltages were triggered externally, everything being recorded on the same time exposure. Thus a series of horizontal lines of known relative voltage were superimposed on the original picture. The time scale of the picture was calibrated by the 100 kc. oscillator, as described above. In order to measure the pictures, the negatives were projected in a microfilm reader and the image traced onto graph paper. From this, voltage - time values were tabulated and plotted in the way described in section 4.

3. The Absorption Coefficients of Nitrogen Dioxide.

When an absorption spectrum is discrete, the absorption coefficient, in addition to depending sensitively on wavelength, will in general depend on pressure, path length, and temperature of the absorbing substance, and on the nature and amount of inert, nonabsorbing gas that may be present. It will also depend markedly on the spectral nature of the light whose absorption is being observed. If the light source emits a single line, the apparent absorption coefficient will depend on the relative position and width of this line and the absorption line or lines which it overlaps.

The discrete adsorption of blue light by NO_2 has been investigated by Dixon(20). His absorption coefficients, obtained with light from a tungsten lamp monochromatized to a band width of 40 Å, show a regular, almost sinusoidal intensity variation, with a period of about 100 Å, superimposed on a steady increase in absorption towards the violet. In these experiments he found Beer's law to be valid, and there was no effect of temperature up to 85° C. Low pressure and high pressure mercury arcs as light sources gave the same absorption coefficient as the tungsten lamp at 4047 Å, but both arcs gave a value 15% higher than the tungsten value at 4358 Å. Absorption coefficients for lines from a high pressure mercury arc have been determined by Holmes and Daniels(21). Absorption coefficients have been determined in the present work, using the mercury arcs which were used for the observation of the dissociation. Hall and Blacet(22) have determined the absorption coefficients with a 2 Å band width in the region of interest. All these values, taken over a range of band widths from 2 to 40 A°, agree to within 10 or 15%. This surprising agreement makes it appear likely that Beer's law is approximately valid for the mercury lines 4047 A° and 4358 A°, but more satisfying evidence is clearly needed. Beer's law has always been assumed in previous work with NO_2. In this work on the dissociation of N_2O_4, the optical densities were about 0.4 and the total change was less than 0.1. Under these conditions, a small deviation from Beer's law will not be too important. Furthermore, in the approximation that the reaction is close to equilibrium (see section 4) the plot from which the rate constant is obtained (Fig. 10) does not depend on the absorption coefficient, which in general enters only as a fairly small correction.

The absorption coefficients of a typical NO_2 - nitrogen mixture were determined for the two mercury lines and a tungsten source, using a Beckman Model DU spectrophotometer and a 10 A° band width. Concentrations were determined by the method of analysis previously described (section 1) and the equilibrium constants of Verhoek and Daniels(23) were used. N_2O_4 does not absorb in this wave length region (4047 to 4358 A°). The extinction coefficients for the mercury lines 4047 and 4358 A°. were found to be equal, to 1%, being 150 l mole^{-1} cm^{-1}. Hence the relative intensities of the two lines need not be known. The absorption was found to be independent of nitrogen pressure up to 1 atmosphere. In working with the tungsten lamp, it is important to have reproducible wave length settings, since the absorption coefficient changes rapidly with wave length. The spectrophotometer was set on the absorption minimum at 4375 Å and the absorption coefficient determined as 113 l mole^{-1} cm^{-1}, with a band width of 10 Å. After each series of runs in the shock tube, the composition of the NO_2 - nitrogen mixture was checked with the spectrophotometer, setting the wave length scale in this way.

4. Calculation of the Rate Constant.

The differential equation for the isothermal rate of change of the NO_2 concentration following an arbitrary displacement from equilibrium will now be derived and integrated, taking into account the variation in density due to the departure from ideal behavior of a shock wave in a gas with dissociation heat capacity.

In all that follows, subscripts have the following meaning. 1 refers to NO_2, 2 refers to N_2O_4, and o denotes formal quantities, calculated as though all the N_2O_4 were present as NO_2. The superscript ℓ refers to the low pressure region (undisturbed region) and f refers to values just behind the shock front, where no reaction has taken place. These quantities are calculated using the constant heat capacity relations presented in Part II. Quantities without superscripts are evaluated at an arbitrary distance behind the shock front. The superscript ∞ refers to final, equilibrium conditions.

Define the degree of dissociation α by

(28) $C_1 = \alpha \frac{C_0}{v} \qquad C_0 \equiv C_0^{\ell}$

where C is concentration, $v = \rho^{\ell}/\rho$ and ρ is density. Differentiation gives

(29) $\frac{dC_1}{dt} = \frac{C_0}{v}\frac{d\alpha}{dt} + \alpha C_0 \frac{d\,1/v}{dt}$

The first term on the right is the algebraic sum of the rate of formation of NO_2 by dissociation of N_2O_4 and its rate of removal by association to form N_2O_4:

$$N_2O_4 \underset{k_1}{\overset{k_2}{\rightleftarrows}} 2\,NO_2$$

(30) $\frac{C_0}{v}\frac{d\alpha}{dt} = \left(\frac{dC_1}{dt}\right)_v = 2k_2C_2 - 2k_1C_1^2$

which defines the rate constants k_1 and k_2. The second term on the right of (29) gives

(31) $\alpha C_0 \frac{d\,1/v}{dt} = \left(\frac{dC_1}{dt}\right)_{\alpha} = -\frac{C_1 v}{v^2}\frac{dv}{dt} = C_1(1+\nu)\frac{d\nu}{dt}$

with the definition $\nu = 1 - v/v_f$. In section 5 a relation between ν and $\Delta g_2 = g_2^{\ell} - g_2$ (where g is weight fraction) will be derived. For the purposes of the present calculation, this can be approximated by $\nu = a\Delta g_2$ where a is about 10 in the cases of interest here. Using this and the fact that $g_1 + g_2 = g_0$ gives

(32) $C_1 = \frac{g_1\rho}{m_1} = \frac{\left(g_0 - (g_2^{\ell} - \Delta g_2)\right)}{m_1}\frac{\rho^{\ell}}{v_f}(1+\nu) = \frac{(g_1^{\ell} + \nu/a)}{m_1}\frac{\rho^{\ell}}{v_f}(1+\nu)$

where m is molecular weight. Rearranging this gives

(33) $\frac{m_1 v_f C_1}{\rho_{\ell}} = g_1^{\ell} + (g_1^{\ell} + 1/a)\nu + \frac{\nu^2}{a} \; ; \; \nu = \frac{m_1 v_f C_1/\rho_{\ell} - g_1^{\ell}}{g_1^{\ell} + 1/a} \equiv AC_1 + B$

The term in ν^2 may be neglected, since ν is typically .05

or less and the g's are of the order 10^{-2}. Since ν is essentially a correction term for the departure of the shock wave from ideal (constant heat capacity) behavior, a 5% error in ν makes a much smaller error in the final result. It is convenient to use A in the form

$$(34)\quad \frac{C_0 A}{v_f} = \frac{g_0}{g_1^2 + 1/a}$$

Equation (31) may now be written

$$(35)\quad \alpha C_0 \frac{d\,1/v}{dt} = c_1(1+\nu)A\frac{dc_1}{dt} = (1+\nu)(\nu-B)\frac{dc_1}{dt}$$

Using the fact that $c_1 + 2c_2 = C_0/v$ gives from equation (30)

$$(36)\quad \frac{C_0}{v}\frac{d\alpha}{dt} = k_2\left(\frac{C_0}{v} - c_1\right) - 2k_1c_1^2 = k_2\left(\frac{C_0}{v}(1 + Ac_1 + B) - c_1\right) - 2k_1c_1^2$$

$$(37)\quad \frac{C_0}{v}\frac{d\alpha}{dt} = -2k_1c_1^2 + k_2\left(\frac{AC_0}{v_f} - 1\right)c_1 + k_2\frac{C_0(B+1)}{v_f} \equiv bc_1^2 + ec_1 + j$$

Combining equations (37) and (35) gives, according to (29),

$$(38)\quad \frac{dc_1}{dt} = \frac{bc_1^2 + ec_1 + j}{[1 - (1+\nu)(\nu-B)]}$$

Typically $\nu = .05$ and $B = -.05$, so that in the denominator the ν in the $(1+\nu)$ factor is a small correction to the 10% correction $(\nu - B)$, and hence may be neglected. In order to integrate (38), an average value of ν will be introduced as a constant. With any reasonable average value, $(1 + B - \nu)$ can only be in error by 2 or 3%. The smallness of ν and the resulting simplification in the treatment, is due to the fact that the large excess of inert gas is fairly effective in overbalancing the "chemical" heat capacity of N_2O_4. Equation (38) may now be integrated:

$$(39)\quad \frac{(1+B-\bar{\nu})}{-\sqrt{e^2-4bj}}\ln\left|\frac{\Delta}{\Delta + \frac{1}{\textcircled{a}}\sqrt{e^2-4bj}}\right| = t + \text{const} \qquad ; \Delta = c_1^{\infty} - c_1$$

ⓑ

According to equation (37) we have

$$(40) \quad \sqrt{e^2-4bj} = k_2\sqrt{\left(\frac{C_0A}{v_f}-1\right)^2+\frac{8C_0}{Kv_f}(1+B)} \equiv k_2 r$$

where use has been made of the equilibrium constant

$$(41) \quad K = \frac{(C_1^\infty)^2}{C_2^\infty} = \frac{k_2}{k_1}$$

The logarithm may be expanded to get a form more useful when Δ is small:

$$(42) \quad \ln\left|\frac{\Delta}{\Delta+\frac{1}{a}\sqrt{e^2-4bj}}\right| = -\ln\left|1-\frac{Kr}{2\Delta}\right| = -\ln\left[\frac{Kr}{2\Delta}\left(1-\frac{2\Delta}{Kr}\right)\right]$$

Since $\frac{2\Delta}{Kr}$ approaches zero as the reaction proceeds, we can make the expansion

$$(43) \quad \ln\left(1-\frac{2\Delta}{Kr}\right) = -\left[\frac{2\Delta}{Kr}+\frac{1}{2}\left(\frac{2\Delta}{Kr}\right)^2+\frac{1}{3}\left(\frac{2\Delta}{Kr}\right)^3+\cdots\right]$$

Equation (39) may now be written

$$(44) \quad \frac{1+B-\bar{\nu}}{-k_2 r}\left[-\ln\frac{Kr}{2\Delta}+\frac{2\Delta}{Kr}+\frac{1}{2}\left(\frac{2\Delta}{Kr}\right)^2+\cdots\cdots\right] = t+\text{const}$$

and the rate constant k_2 is determined from the slope of a plot of the quantity in brackets against time.

The quantities Δ and t must now be related to the measured voltage and time. Assuming Beer's law and linearity of the photomultiplier,

$$(45) \quad \Delta = \frac{1}{\epsilon d}\log_{10}\frac{v}{v_\infty}$$

where v is the voltage obtained from the oscilloscope trace and the calibrations. ϵ is the absorption coefficient determined in this work, and d is the optical path length, 5.3 cm.

The time t that appears above is of course the length of time that the gas being observed has been behind the shock front, which may be called the proper time, t_p. This is not equal to the time t_s, measured by an observer in the laboratory, between the arrival at the observation window of the shock wave and of the segment of gas being observed. This "relativistic" effect is due to the fact that when the shock wave reaches the observing window, the gas that will appear there at time t_s later is already behind the shock front and has begun to dissociate. If the mass flow velocity u were constant behind the shock front, one would have

$$t_p = t_s \frac{\overset{u^{\ell}}{u_0}}{u} = t_s \frac{\rho}{\underset{\rho^{\ell}}{\rho_0}} = \frac{t_s}{v} \tag{46}$$

since $u_0 t_s$ is the distance of the segment of gas behind the shock front and u is its velocity relative to the shock. The second equality in equation (46) follows from equation (1), p.5. Actually u and v are not constant behind the shock front. To find the t_p corresponding to a given t_s from equation (46), a v averaged between v_f and v at t_s must be used. Using the second of equations (33) and the approximate rate equation

$$\Delta = \Delta(t=0)\, \exp(-k_2 \surd\, t_s) \tag{47}$$

derived from (39) by setting $V = 0$, $B = 0$, and neglecting terms in Δ beyond the first, one can easily evaluate

$$t_p = \int_0^{t_s} \frac{dt}{v(t)} = \frac{1}{v_\infty}\left[t_s + \frac{\ln v/v_f}{k_2 \surd}\right] \;\xrightarrow[t_s \to 0]{}\; t_s/v_f \;\xrightarrow[t_s \to \infty]{}\; t_s/v_\infty \tag{48}$$

The various approximations used in deriving this are justifiable because the result is only a 10 or 15% correction. In equation (48) v has its value at time t_s. It is consistent with the approximations made in deriving equation (44), and sufficiently accurate for the present work to derive a linear relationship between t_p and t_s by introducing an average value of ν, independent of t_s, into equation (48). Substitution of this into equation (44) then merely changes the right hand side to t_s/ν_∞ + const., and the rate is obtained from the slope in the same way as before. If it were not for the large excess of nitrogen used with the N_2O_4 in this work, the change in ν behind the shock front would be much larger, and an average value could not be used. The treatment of this more complicated case is outlined at the end of the next section. The rather good straight lines, Fig. 9, obtained by plotting the data according to equation (44) indicate that the assumption of constant temperature, and the use of an average value for ν are justified. Of course this also confirms the assumption of a dissociation first order with respect to N_2O_4.

5. The Temperature and Density Behind Shock Waves in a Dissociating Gas.

In the previous section, a method of calculating a rate constant from the experimental data was explained, but nothing was said about the temperature to which this value corresponds. In this section a method is given for calculating the final (equilibrium) values of the density and temperature behind the shock. From these and the "frozen in" values just behind the shock front, one obtains the average ν and T used in the preceding section.

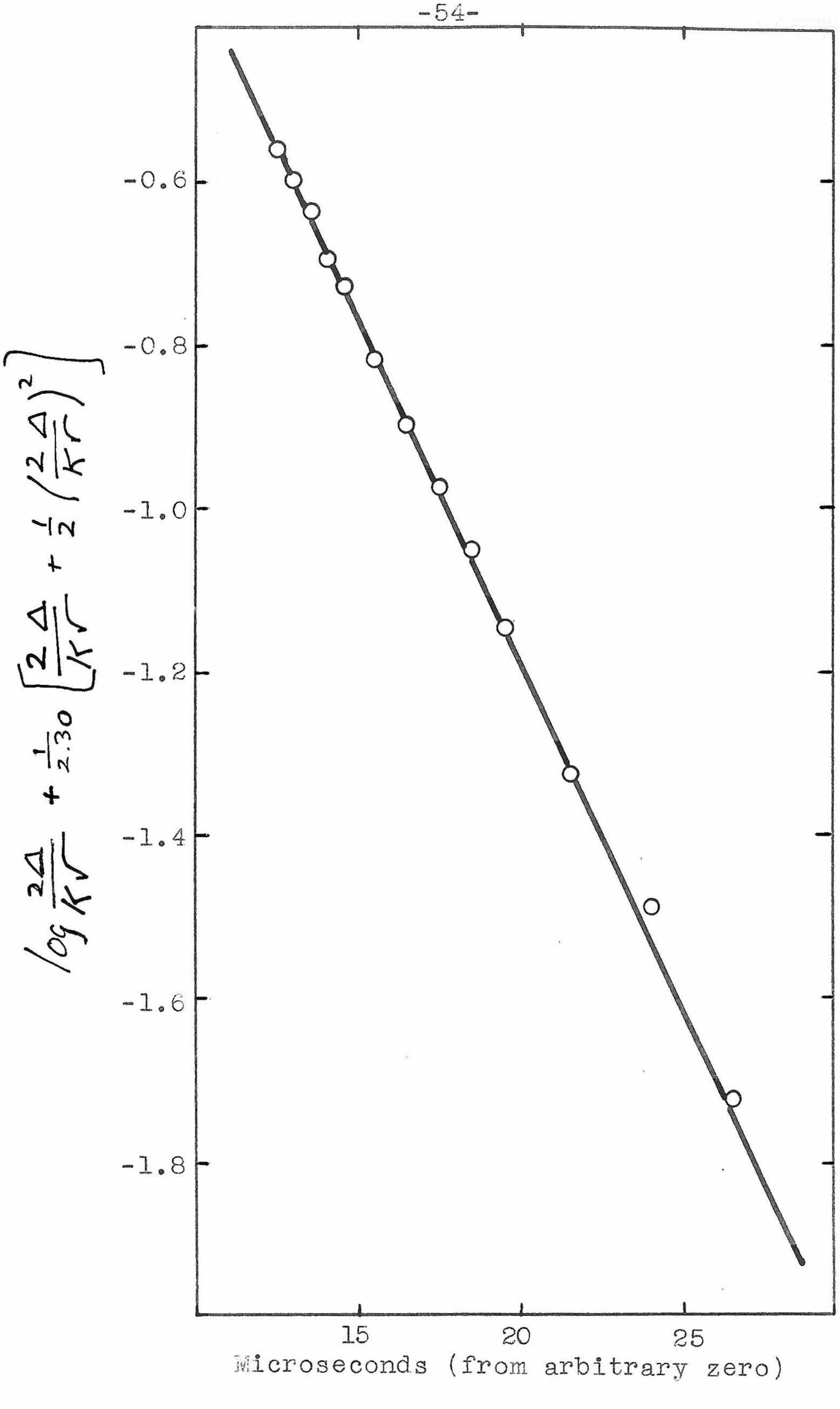

Fig. 9. Plot of experimental voltage - time data.

The development is motivated by the treatment of Bethe and Teller(7). It is based on the three conservation equations given on page 5. These state that the flux of mass, momentum, and energy across any surface perpendicular to the plane one dimensional flow is constant:

(49) $\rho u = n$ ρ,density; u,flow velocity; n,mass flux

(50) $P + nu = nV$ P,pressure; V,constant(not volume)

(51) $En + \frac{1}{2} nu^2 + Pu = const$ E,internal energy per gram.

By dividing the last equation by n, one has the equivalent form

(52) $E + \frac{1}{2}u^2 + \frac{P}{\rho} = H + \frac{1}{2}u^2 = const$ H,enthalpy per gram

The definition of v and equation (49) give

(53) $v = \frac{\rho^{l}}{\rho} = \frac{u}{u^{l}}$

Applying equation (52) across the shock wave gives

(54) $H - H^{l} = \frac{1}{2}(u^{l2} - u^2) = \frac{1}{2}u^{l2}(1 - v^2)$

This is a perfectly general hydrodynamic expression for the enthalpy change. Now a "chemical" expression for the enthalpy change will be equated to this:

(55) $H - H^{l} = \frac{\beta R T}{\mathfrak{m}} - \frac{g_2}{\mathfrak{m}_2}\mathcal{H} - \frac{\beta R T^{l}}{\mathfrak{m}} + \frac{g_2^{l}}{\mathfrak{m}_2}\mathcal{H}$

in which g is weight fraction, $\mathfrak{m}_2$ is molecular weight of N_2O_4, $\mathfrak{m}$ is the mean molecular weight, and $\mathcal{H}$ is the enthalpy of dissociation of N_2O_4 per mole. Here β is a mean "physical" heat capacity, apart from chemical reaction (see equation (6) page 6). It is a mole fraction average of the heat capacities of the component gases, considered as being independent:

(56) $$\beta = f_1\beta_1 + f_2\beta_2 + f_3\beta_3$$

where f is mole fraction, and subscript 3 refers to the inert gas nitrogen. The quantity Δh is defined from equation (55) by

(57) $$H - H^{\ell} = \frac{R\beta}{m}(T - T^{\ell}) + \Delta h$$

Equating (57) and (54) gives

(58) $$\frac{1}{2}u^{\ell 2}(1 - v^2) = \Delta h + \frac{R\beta}{m}(T - T^{\ell})$$

Now the temperature will be eliminated from this. Expressing the pressure in equation (50) in terms of the perfect gas law,

(59) $$\frac{RT}{m}\rho + nu = \frac{RT^{\ell}}{m}\rho^{\ell} + nu^{\ell}$$

Defining $\tau = T/T^{\ell}$ and rearranging gives

(60) $$\tau = \frac{n(u^{\ell} - u) + RT^{\ell}\rho^{\ell}/m}{RT^{\ell}\rho/m}$$

Introducing the downstream Mach number by

(61) $$\gamma M^2 = \frac{u^{\ell 2}}{RT/m} \qquad \gamma = C_p/C_v$$

gives the simple form

(62) $$\tau = \frac{1}{v}\left[1 + \gamma M^2(1 - v)\right]$$

Putting (62) and (61) into (58) gives

(63) $$\frac{1}{2}\gamma M^2(1 - v^2) = \frac{\Delta h}{RT/m} + \beta(1 - v)\left\{v\gamma M^2 - 1\right\}$$

Rearranging into quadratic form and dividing by $\frac{1}{2}\gamma M^2$ gives

(64) $$(2\beta - 1)v^2 - 2\beta\left(1 + \frac{1}{\gamma M^2}\right)v + \left(1 - \frac{2\Delta h}{u^{\ell 2}} + \frac{2\beta}{\gamma M^2}\right) = 0$$

The solution is

(65) $$v = \frac{1}{2\beta - 1}\left[\beta\left(1 + \frac{1}{\gamma M^2}\right) - \sqrt{\left[1 - \beta\left(1 - \frac{1}{\gamma M^2}\right)\right]^2 + \frac{2(2\beta - 1)}{u^{\ell 2}}\Delta h}\right]$$

Setting $\Delta h = 0$ gives

(66) $$v_f = \frac{1}{2\beta - 1}\left(1 + \frac{2\beta}{\gamma M^2}\right)$$

Equations (65) and (62) give the density and temperature at any point behind the shock front, as a function of the composition of the gas mixture (for given initial conditions and shock velocity).

Since β_2 (= 9.52) is approximately twice β_1 (= 4.57), equation (56) may be written

(67) $\beta = f_0 \beta_1 + (1 - f_0 + f_2)\beta_3$

since $f_1 + 2f_2 = f_0$. Since the f's are of the order 10^{-2}, β does not change appreciably as the gas dissociates. For most of the runs, $\beta = 3.51$ (β for nitrogen is 3.50). γ was always taken as 1.4, its value for nitrogen. Initial values of v and T may be calculated from equations (66) and (62). From these, with a little experience, it is easy to make a rather good guess of the final values v_{∞} and T_{∞}. These are then used with the equilibrium constant to calculate final concentrations. The agreement of the $\Delta(t=0)$ calculated from these with the observed was usually 10 - 15%. From these final concentrations Δh is calculated and a second approximation to v and T is derived. This process may be repeated, but this was usually not necessary. Typically, $T_{\infty} - T_f$ was 1 or 1.5 degree, and v/v_f was 0.95 or greater, corresponding to ν between 0 and 0.05. With such small changes from the frozen in to the equilibrium condition, it was not hard to decide on average values. $\bar{\nu}$ was arbitrarily taken as 2/3 of its final value, and T was taken as $T_f + 3/4\ (T_{\infty} - T_f)$ since the first part of the reaction was not observed. It is interesting that the temperature of the gas actually increases as a result of the endothermic reaction taking place in it. As the dissociation proceeds behind the shock wave, energy is supplied to it by a slowing down of the flow (with consequent increase in density) rather than by a decrease in temperature.

If the changes in v and T behind the shock front are too large to permit the use of average values, these quantities may be calculated at any point behind the shock front by using the observed values of Δ , and guessing a value of v , to find Δh and hence v and T. This may be repeated with the new v if the first guess was too far off. Alternatively, the formula

$$v = v_f \, A \, \Delta(t=0) \exp(-k_2 \Gamma t) + v_\infty \tag{68}$$

obtained from equation (47) and the second of equations (33), may be used as an interpolation formula between v_f and v_∞.

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PROPOSITIONS
Submitted by Tucker Carrington

1. The rate of excitation of vibration in nitrogen gas suddenly heated by passing a shock wave through it may be studied by following as a function of time the intensity of resonance radiation from a small amount of sodium mixed with the gas, since vibrational energy is much more efficient than translation in exciting sodium atoms.

2. The photolysis, using a high intensity flash lamp, of methyl iodide in the presence of excess radioactive iodine, when combined with a similar study of pure methyl iodide tagged with radioactive iodine, will make possible determination of the rates of the reactions $CH_3 + I \rightarrow CH_3I$ and $CH_3 + I_2 \rightarrow CH_3I + I$. The former will give information about the unimolecular thermal dissociation of methyl iodide.

Few unimolecular reactions have been studied over a large pressure range under conditions where the mechanism is simple and unquestionably known. This should be possible for the thermal decomposition of methyl iodide in the presence of radioactive iodine. Similar study of ethyl iodide will allow determination of the rates of the two competing modes of primary dissociation of the activated molecule.

3. The work of Rossler(1) on the effect of inert gases on the resonance fluorescence of iodine excited by monochromatic light should be reinterpreted, using the present value of the radiative lifetime of $I_2({}^3\Pi_{0u}^+)$, which was not known at the time of his work. The high efficiency which he found for vibrational energy transfer in collision is thus reduced.

Studies of the type made by Rossler(1) for I_2 and by Durand(2) for S_2 should be extended to a range of wavelengths and to other molecules whose electronic transition probabilities can be found, since these studies give information about vibrational energy transfer in collision which can not be obtained from sound dispersion or chemical kinetic studies.

The possibility of persistence of rotation of excited OH in low pressure flames could be investigated by studying monochromatically excited fluorescence from OH in the flame.

4. Direct evidence that the energy involved in the quenching of an electronically excited metal atom goes preferentially into translation rather than vibration of the quenching molecule could be obtained by looking for radiation of the D lines from sodium present in a system in which nitrogen is quenching excited thallium atoms.

5. The continuous flow isothermal crystallization apparatus of Garrels, Jones, and Howland(3) should be useful for studying the spontaneous resolution of a racemic mixture by crystallization under various conditions of temperature and pressure on suitable seeds.

The crystal structure of various metallic salts of dicarboxylic acids should be determined, with the purpose of understanding the widely differing yields in pyrolysis to cyclic ketones.

6. Spontaneous nucleation in a super-cooled gas could be studied in the products of pyrolysis behind a shock wave of molecules such as carbon suboxide or metal carbonyls. The "cobwebs" of carbon found by Norrish and Porter(4) in the flash photolysis of acetone should be investigated and the possibility of nucleation by cosmic rays considered.

7. In view of the fact that sodium is known to be "soluble" in compressed hydrogen(5), its "solubility" and absorption spectrum in compressed carbon monoxide would be of interest.

8. The additivity of indicator currents in the system Cu^{++}, Cu^{+}; Br_2, Br^- could be tested by buffering the system to constant Br_2 concentration with an organic solvent for Br_2, and then changing the Cu^{+} concentration independently of the Br_2.

9. A diffusion model similar to that used by Frenkel(6) in treating spontaneous nucleation in a super-cooled vapor indicates that the rate of energization in a quasi-unimolecular reaction is not strongly dependent on the stepwise nature of the process.

10. The poem "Waldgespräch" by Josef von Eichendorff is an allegory for seekers of truth.

WALDGESPRÄCH

"Es ist schon spät, es wird schon kalt,
Was reitst du einsam durch den Wald?
Der Wald is lang, du bist allein,
Du schöne Braut! Ich führ' dich heim!"

"Gross ist der Männer Trug und List,
Vor Schmerz mein Herz gebrochen ist,
Wohl irrt das Waldhorn her und hin,
O flieh! Du weisst nicht wer ich bin."

"So reich geschmückt ist Ross und Weib,
So wunderschön der junge Leib;
Jetzt kenn' ich dich - Gott steh' mir bei!
Du bist die Hexe Lorelei."

"Du kennst mich wohl - von hohem Stein
Schaut still mein Schloss tief in den Rhein.
Es ist schon spät, es wird schon kalt,
Kommst nimmermehr aus diesem Wald!"

- Eichendorff