[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE MECHANISM OF HOMOGENEOUS GAS REACTIONS. I. THE EFFECT OF BLACK BODY RADIATION ON A MOLECULAR BEAM OF NITROGEN PENTOXIDE[1]

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The homogeneous unimolecular character of the decomposition of nitrogen pentoxide first studied by Daniels and Johnston[3] has now been thoroughly established by a large number of investigations.[4] However, in spite of a large amount of theoretical work,[5] the mechanism of the reaction cannot be regarded as well understood. The attempts to explain the mechanism of the nitrogen pentoxide decomposition in common with other reactions are based upon the Arrhenius hypothesis of active and inactive molecules. There is only one exception to this, namely, the form of the radiation hypothesis in which it is assumed that the molecule absorbs a quantum of light and decomposes in a single act. The velocity of the reaction would therefore be proportional to the density of radiation capable of decomposing the molecule. Since the density of this radiation increases exponentially with the reciprocal of the absolute temperature, the temperature coefficient of the reaction is satisfactorily explained. On the basis of all other hypotheses it seems necessary to assume a process of activation in order to account for the temperature coefficient. Our difficulties arise when we attempt to devise a process of activation, for this must be much more rapid than the observed chemical reaction. We may conveniently summarize the various proposals that have been made, as follows.

1. The Simple Radiation Hypothesis.—This can be represented by

$$AB + h\nu \longrightarrow A + B$$

Or we may have a process of activation of the type

$$AB + h\nu \longrightarrow AB'$$

followed by the reaction

$$AB' \longrightarrow A + B$$

or

$$AB' + AB \longrightarrow A + B + AB$$

or

$$AB' + AB \longrightarrow 2A + 2B$$

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[1] This paper is an abstract of the thesis of R. N. Washburne submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Du Pont Fellow in Chemistry.

[3] Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921).

[4] A summary of these is given by Rice and Getz, *J. Phys. Chem.*, **31**, 1572 (1927).

[5] Most of these references are included in a review of the radiation hypothesis, Daniels, *Chem. Reviews*, **5**, 39 (1928).

In the last two examples the velocity of the reaction will fall with decreasing pressure.

It should be pointed out, however, that nitrogen pentoxide does not absorb in the region such that $Nh\nu$ is equal to the heat of activation as calculated from the temperature coefficient of the reaction.

2. **The Elaborated Radiation Hypothesis.**—On the basis of this hypothesis nitrogen pentoxide for example is supposed to absorb successive quanta such that the total is equal to the heat of activation. Nitrogen pentoxide has a very strong absorption band at 5.81 μ such that absorption of five of these quanta would give the heat of activation. It should be pointed out, however, that the coefficient of absorption of compounds (including nitrogen pentoxide) would have to be many orders higher than ever observed to account for the observed rates of chemical reactions. It must also be noted that infra-red radiation does not increase the rate of chemical reactions.[6]

3. **Radiation Hypothesis with a Chain Mechanism.**—On the basis of this hypothesis it is assumed that the molecule of nitrogen pentoxide activated by radiation starts a chain of successive reactions which results in the final decomposition of many molecules. This suggestion will not explain the decomposition of nitrogen pentoxide for reasons given under (2) and in addition any chain mechanism appears to be improbable because the energy change for the entire reaction is very small; it would be necessary to assume that one of the products of a decomposing nitrogen pentoxide molecule carried all the energy of activation and others none and farther that this energy would be completely transferred to another nitrogen pentoxide molecule and not to any other molecules. This appears to be very improbable.

4. **Sir J. J. Thomson Hypothesis.**—On the basis of this hypothesis[7] it is assumed that a molecule of nitrogen pentoxide may acquire energy of activation from the surrounding medium by some other means than radiation or collisions with other molecules. He postulates that the amount of energy possessed by a molecule may fluctuate with the time and that only on the average is energy conserved. He assumes that the probability that a molecule will acquire a certain energy is an exponential function of its internal energy. Our experiment throws no light on this hypothesis.

5. **Activation by Molecular Collisions.**—On the basis of this hypothesis, a molecule of nitrogen pentoxide is assumed to obtain its energy of activation by collision with another molecule. In this case the rate of activation is proportional to the number of collisions and should therefore

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[6] Hibben, THIS JOURNAL, **50**, 937 (1928). The paper contains the references to previous work.

[7] Thomson, *Phil. Mag.*, [7] **3**, 241 (1927).

be proportional to the square of the concentration. In order that the reaction may be experimentally unimolecular it is necessary to assume that the rates of activation and deactivation are very rapid compared to the rate of the reaction and further that the rate of decomposition of the activated molecules is a truly unimolecular process which is independent of collisions of the activated molecules; thus the probability of decomposition of an activated molecule per unit time is no greater during collision than during the time between collisions. This last condition seems to be supported by the fact that nitrogen pentoxide decomposes at the normal rate when dissolved in liquids, with the exception of nitric acid.[4] This exception is due probably to the formation of a complex compound.

Attempts have been made to test this hypothesis by conducting experiments at low pressures which should at sufficiently low pressures change the order of the reaction from unimolecular to bimolecular and decrease the absolute rate. The experiments that have been published so far are contradictory.[8] We are unwilling to discuss these papers because some work in this Laboratory by Miss E. Wilson has yielded results differing from both these papers. Preliminary measurements show that the rate falls off even at pressures of several mm.

The difficulty of deciding the mechanism of the decomposition of nitrogen pentoxide or any other reaction lies perhaps in the fact there are three processes occuring simultaneously in reactions as ordinarily studied. These three processes are (*a*) absorption and emission of radiation, (*b*) intermolecular collisions and (*c*) collisions with the walls of the vessel. It is the purpose of this series of papers to separate these three effects and study them independently. The first effect may be isolated from the other two by allowing a molecular beam of nitrogen pentoxide to pass through a furnace, within which approximately black body radiation is maintained. Similar work has been done by Kröger[9] using iodine and by Lewis and Mayer, and Mayer[10] using pinene. They report no reaction in either case. The results of our investigation are in accord with these results; no detectable decomposition occurred.

The second effect may be isolated by allowing two beams to impinge as was done by Kröger for cadmium and iodine and cadmium and sulfur. Undoubtedly this is impractical in the case of nitrogen pentoxide because in the first place the total number of collisions is small and only a very minute fraction of these would result in active molecules.

The third factor may be isolated by allowing the beam to impinge

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[8] Hirst and Rideal, *Proc. Roy. Soc.* (London), **109A**, 526 (1925); Hibben, THIS JOURNAL, **50**, 940 (1928).

[9] Kröger, *Z. physik. Chem.*, **117**, 387 (1925).

[10] Lewis and Mayer, *Proc. Nat. Acad. Sci.*, **13**, 623 (1927); Mayer, THIS JOURNAL, **49**, 3033 (1927).

on a heated surface from which it is reflected to a surface cooled to liquid air temperatures. Mr. L. A. Staib has undertaken experiments of this character in this Laboratory. Such experiments offer the possibility of determining the life of excited molecules providing it happens to be of the order of magnitude of the time of flight from the activating to the collecting surfaces. This point, however, will be discussed in greater detail in a following paper.

Apparatus and Methods

Molecular Beam Apparatus.—The apparatus with which the final experimental work was done (see Fig. 1) was made of Pyrex glass. The nitrogen pentoxide evaporates from the storage reservoir (not shown) and enters the beam chamber, C, through the 3 mm. hole, a, in the end of the delivery tube, B; 9 millimeters above a is the rough defining hole, b, which is 4 mm. in diameter. The final defining hole, c, 1 mm. in diameter, is 10 millimeters above b. The holes b and c are in the center of glass disks which were sealed into the apparatus when it was constructed. This eliminates the possibility of any nitrogen pentoxide entering the furnace chamber other than through c. The beam of nitrogen pentoxide issuing from the chamber C passes through the furnace, D (described in detail below), and is condensed on the liquid-air cooled surface E. This surface is the base of the cylindrical tube, F, which is introduced into the apparatus by means of a ground-glass joint at G. This facilitates the removal of the sample for analysis at the completion of an experiment. The surface, E, which is 2.6 cm. in diameter, is surrounded by a collar 1.3 cm. high which serves as an auxiliary condenser to reduce losses that would occur if the molecules did not condense upon the first collision with E.

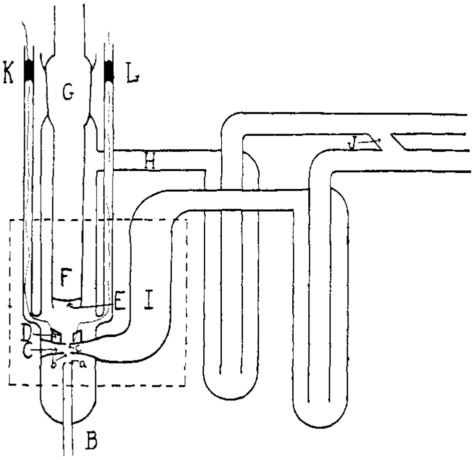

Fig. 1.—Molecular beam apparatus.

The apparatus is evacuated through H and I, which lead to separate liquid-air traps and Stimson two-stage diffusion pumps. The two branches are connected at J to eliminate any circulation of gases through the region C should the diffusion pumps not be working with equal efficiency. A single Nelson oil pump was used as a fore pump. Pressures were measured with a McLeod gage with which pressures of 10^{-5} mm. of mercury could be read accurately, and those in the 10^{-6} order were estimated within 10%.

Furnace.—The furnace D used as a source of black body radiation (see Fig. 2) was made from a piece of Pyrex tubing 1.2 cm. long with an inside diameter of 8.8 mm. It is suspended by three glass prongs, a, from platinum stirrups, b, fused in the glass collar D which rests upon the plate containing the final defining hole. The furnace is heated electrically with a platinum wire (0.14 mm. dia.) wound spirally about it in a groove made for that purpose. Electrical current is supplied through heavy platinum leads and tungsten seals at K and L (Fig. 1). The groove, which encircles the furnace ten times, was etched into the glass with hydrofluoric acid. The distance between successive spirals is 1 mm. The furnace was firmly mounted on a spool-like core which could be fitted into the chuck of a lathe. The glass was coated with a thin layer of wax in which a spiral was cut with a needle-like tool mounted in the tool carrier. By adjusting the latter for a screw pitch of 24 turns to the inch, a very uniform spiral was obtained. The furnace was then immersed in hydrofluoric acid for five minutes. Longer immersions were found to widen the groove too much. By repeating the above process five times a sharply defined groove about 0.2–0.3 mm. deep was obtained, a depth sufficient to prevent the wire from slipping off the furnace when heated. The furnace was then wired and in the finished furnace 8 complete winds (23.2 cm.) were effective in heating. Current input was measured by a milliammeter and voltmeter.

The portions of the apparatus which had to be at liquid-air temperatures are included within the dotted lines in Fig. 1. This cooling was finally effected by covering the glass with lead foil to increase thermal conduction and circulating liquid air from a container above the apparatus through a ten foot length of rubber tubing, which had been wound snugly about the two branches of the apparatus. The whole region was heavily insulated with asbestos and cotton to make the cooling more efficient. To maintain circulation of the liquid air through the rubber tubing a gentle suction was applied at the free end. If suction is not applied moisture condensing from the air soon plugs the tube with the result that the temperature of the apparatus rises. Tests made with a large test-tube wound with rubber tubing in this way showed that temperatures of about −170° could be maintained. The reservoir is heavily insulated with felt, the liquid air level being indicated by a wire attached to a cork float. A very fine wire gauze in the bottom of the reservoir prevents ice crystals from entering the rubber tube and plugging it. This method of cooling was found entirely satisfactory aside from the fact that about 700 cubic centimeters of liquid air was required per hour.

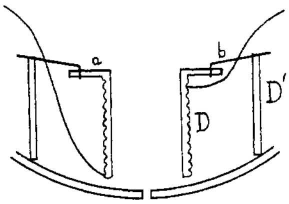

Fig. 2.—Furnace.

The final experiments were made with the supply of nitrogen pentoxide at a temperature of −60 ± 1°. This temperature was maintained by surrounding the reservoir with toluene contained in a Dewar flask. The Dewar flask was likewise surrounded by a larger one containing carbon dioxide snow and ether. As the inner Dewar was not very highly evacuated, heat was conducted from it nearly as fast as absorbed from the apparatus. The temperature of the toluene was measured with a pentane thermometer and controlled by the addition of small pieces of carbon dioxide snow or with a nichrome heating wire. Aside from frequent stirring, little attention was needed to maintain the desired temperature.

In experiments in which the crystals were kept at the temperature of carbon dioxide snow and ether or liquid ammonia, the nitrogen pentoxide reservoir was merely immersed in a Dewar flask containing the desired substance. When liquid ammonia was used, the gas was kept from entering the room by bringing a metal funnel-like cap down over the flask. The funnel was connected to a suction pump and such a rapid flow of air maintained that no odor of ammonia could be detected.

The nitrogen pentoxide was prepared in the same manner as described by Rice and Getz.[4] Before distilling the crystals into the reservoir of the molecular beam apparatus they were raised to room temperature and all visible traces of nitrogen tetroxide removed by passing dried air over them. The use of ozone for purification of the nitrogen pentoxide was omitted to preclude the possibility that traces of it might be collected with the sample and subsequently oxidize the alkaline nitrite solution. The traces of nitrogen dioxide which were always present could be corrected for by the blank runs, that is, experiments in which the furnace was not heated.

Experimental Procedure

The experimental procedure can best be described by a brief outline of the steps involved in an actual determination. A phosphorus pentoxide tube is sealed to the projection of the storage bulb of the molecular beam apparatus. The main supply of nitrogen pentoxide is then connected to this tube and a third drying tube is sealed in at this junction and air drawn through it over the crystals, which are at room temperature, until visible traces of nitrogen dioxide are removed. The lower end of the reservoir is now surrounded with carbon dioxide snow and ether and about 3–4 g. of nitrogen pentoxide condensed by evacuating the system. The lower ends of the liquid-air traps are immersed in liquid air to prevent mercury vapor from distilling back into the reservoir during the process. The main supply of crystals and the drying tubes are then removed and the reservoir is immersed in the toluene bath described above. To remove the greater portion of the nitrogen dioxide formed in the above transfer the diffusion pumps are started and the toluene is kept at $-35°$ for about one and one-half hours. During this time the furnace is heated to 300–400° to drive off adsorbed gases. Finally the toluene is cooled to $-60°$ and liquid air is then introduced into the liquid-air reservoir and the collecting tube F. In about one and one-half hours the molecular beam apparatus comes to liquid-air temperature. The burners under the diffusion pumps are turned down and air, which passes through soda lime, calcium chloride and phosphorus pentoxide is admitted. The collecting tube is removed while a current of air is forced through the apparatus to prevent the diffusion of moisture into it. The opening is immediately closed with an inverted beaker having a rubber collar which fits tightly about G. The collecting tube is washed off and dried, by warming in a flame and wiping with a linen cloth before putting it back into the apparatus. The burners under the diffusion pumps are lighted, liquid air is poured into the collecting tube and the fore pump started. In four minutes the pressure in the apparatus drops to 1×10^{-5} mm. of mercury and in six minutes to less than 1×10^{-6}. Readings of the current input and the pressure are taken frequently during the runs. At the end of the desired time the sample is removed and dissolved in dilute potassium hydroxide (1 cc. of 0.001 N KOH made up to 20 cc.). The collecting surface and collar are thoroughly rinsed into the solution and the tube is dried as above before returning to the apparatus. The experiments were carried out in series of from five to nine runs each.

Analytical Methods.—The nitrite content was determined by a method described in a bulletin of the American Public Health Association[11] and the nitrate content by the method of Chamot, Pratt and Redfield.[12] These methods make it possible to determine 0.001 mg. of nitrite nitrogen and 0.1 mg. of nitrate nitrogen to within 2–3%.

Calculations

Before the experiments which have been described were undertaken, it was necessary to make preliminary calculations on the amounts of nitrogen pentoxide which would pass through the defining holes of our molecular beam apparatus, the time the molecules are in the furnace and the furnace temperature required to secure measurable decomposition.

[11] "Standard Methods of Examination of Water and Sewage," American Public Health Association, **1920.**

[12] Chamot, Pratt and Redfield, THIS JOURNAL, **33,** 366, 381 (1911).

Stern[13] in his work on molecular beams has used pressures in the high pressure chamber such that the mean free path of the molecules is of the same order of magnitude as the width of his slit. Kröger and Lewis and Mayer have used much more intense beams and Johnson[14] has studied the intensities and sharpness of such beams as functions of the pressure. We found in this work that higher pressures than those used by Stern resulted in the freezing up of the defining holes. Since nitrogen pentoxide and nitrogen dioxide can be determined quantitatively in very small amounts, it was unnecessary to use beams of high intensity. It was found empirically that when the nitrogen pentoxide chamber was held at a temperature of −60°, a satisfactory beam was secured. The calculated vapor pressure at this temperature is 0.042 mm. using the formula of Russ and Pokorny;[15] assuming that the nitrogen pentoxide molecule has the same diameter as the benzene molecule, the mean free path would be 0.3 mm., which is only one-tenth of the diameter of the first defining hole. The amount of nitrogen pentoxide passing through the last defining hole can easily be shown to be

$$p\sqrt{\frac{M}{2\pi RT}} \times \frac{2A_1A_2}{d^2} \tag{1}$$

where A_1 and A_2 are the areas of the defining holes, d is the distance between the holes and p is the pressure in dynes per sq. cm. The calculated amounts of nitrogen pentoxide passing the slit system per hour is 1–2 mg., which is about ten times the amount actually secured. This discrepancy may be due to a considerable error in calculating the vapor pressure of nitrogen pentoxide, to the fall in pressure along the tube leading from the storage chamber to the first defining hole and to a considerable time lag in the warming up of this tube from liquid air temperature to −60°.

We shall now calculate the fraction of the nitrogen pentoxide molecules which should decompose during their flight through the furnace, assuming that the probability of decomposition per unit time is the same in the beam as that observed when the gas decomposes in bulk. In making this calculation we shall use the following symbols: T = temperature of furnace; T' = temperature of N_2O_5 chamber; $K(T)$ = probability of decomposition per unit time at temperature T, that is, the velocity constant of the reaction; n_v = number of molecules having velocities lying between v and v + dv; n = total number of molecules of all velocities; x = coördinate along the axis of the furnace.

The number of molecules having velocities lying between v and v + dv which decompose during the time dt is

$$K(T)\, n_v\, \mathrm{d}t \tag{2}$$

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[13] Stern, *Z. Physik*, **39**, 751 (1926).

[14] Johnson, *Phys. Rev.*, **31**, 103 (1928).

[15] Russ and Pokorny, *Monatsh.*, **34**, 1027 (1913).

Now

$$n_v = 4\pi \left(\frac{M}{2KT'\pi}\right)^{3/2} e^{-\frac{mv^2}{2KT'}} v^2\,\mathrm{d}v \tag{3}$$

and changing to the variable x instead of t by the relation $\mathrm{d}x = v\mathrm{d}t$ we have

$$\mathrm{d}n = -K(T)n4\pi \left(\frac{M}{2KT'\pi}\right)^{3/2} e^{-\frac{mv^2}{2KT'}} v^2\,\mathrm{d}v\,\frac{\mathrm{d}x}{v} \tag{4}$$

Integrating and remembering that $K(T)$ is a function of x, the position in the furnace, we have

$$\int \frac{\mathrm{d}n}{n} = 4\pi \left(\frac{m}{2KT'\pi}\right)^{3/2} \int e^{-\frac{mv^2}{2KT'}} v\,\mathrm{d}v \int -K(T)\mathrm{d}x \tag{5}$$

This gives

$$\ln \frac{n}{n_0} = \frac{\sqrt{2m}}{\sqrt{KT'\pi}} \int_0^l -K(T)\mathrm{d}x \tag{6}$$

Since we have taken x to be the coördinate along the axis of the furnace, this calculation applies only to those molecules passing directly along the axis. Molecules passing at an angle traverse a longer path and pass through a part of the furnace having a higher temperature. Since the results are negative, we shall assume that all the molecules pass along the axis; this approximation would merely reduce somewhat the theoretical decomposition. The last integration has been made graphically by calculating temperatures along the axis of the furnace; the velocity constants corresponding to these temperatures were then calculated from the formula $k = 4.98 \times 10^{13}\, e^{-\frac{24{,}700}{RT}}$ and plotted against corresponding values of x.

The temperature of the furnace was determined by placing a thermocouple against its inner wall. This gave a temperature of 793°K., which is a minimum value since heat was conducted away from the wall through the lead wires. We also suspended the thermocouple in the center of the furnace. It registered a temperature of 523°K., but a calculation of the amount of radiant energy falling on the thermocouple and that conducted away through the lead wires shows that this temperature must be far too low. In calculating the temperatures along the axis we assume that Pyrex glass radiates 0.9 as much energy per second as a black body. This makes the effective wall temperature of the furnace $793 \times 0.9^{1/4} = 771$°K. The temperature of a point on the axis distant x cm. from one end of the furnace is equal to the effective temperature of the furnace wall multiplied by the fourth root of the fraction of the solid angle subtended by the furnace at this point, divided by 4π. This is

$$771 \left[\frac{l - x}{2\{(l - x)^2 + r^2\}^{1/2}} + \frac{x}{2(x^2 + r^2)^{1/2}}\right]^{1/4} \tag{7}$$

This gives a temperature of 718°K. and 634°K. for the center and ends of the furnace, respectively, and 10^6 for $\int_0^l K(T)\mathrm{d}x$; substituting the numerical values in Equation (6) we find for n/n_0 the value 10^{-27}, which means that only one molecule in 10^{27} should remain undecomposed. We performed additional experiments at higher temperatures which we estimated roughly from the relative power input; the effective wall temperatures were 806°K. and 846°K., that is, 35 and 75° higher than the temperature at which the detailed calculations have been made. We attempted to use the change of resistance with temperature of the furnace winding as a measure of its temperature but found this to be erratic. We attribute this to the conductivity of the Pyrex glass furnace, which was heated to its softening point.

In all these calculations we have used the least favorable assumptions and approximations so that the calculated decomposition should be less than if these assumptions and approximations were not made.

Experimental Results

The greater portion of this research was done with the furnace walls at 793°K. as determined by the thermocouple; this temperature is that used in the calculations given in the preceding section. Three runs were made at 806°K. and one at 846°K. as determined by the increased power input. These results are summarized in Table I. The percentages of nitrogen peroxide obtained are the same as in the original material, as shown by separate analysis. There is no indication of any decomposition whatsoever in the beam.

TABLE I

BLACK BODY RADIATION ON NITROGEN PENTOXIDE

Time of each expt. = 1.5 hours

Expt. no.	N_2O_5, mg.	NO_2 (as N_2O_5), mg.	NO_2 (as N_2O_5), %	T, °K.
1a	0.0639	0.0088	13.8	Cold
1b	.0713	.0086	12.1	793
1c	.0668	.0086	12.8	Cold
1d	.0631	.0102	16.0	793
1f	.0744	.0084	11.3	Cold
1g	.0697	.0096	13.7	793
1h	.0709	.0054	7.6	Cold
1k	.0634	.0068	10.7	793
1m	.0702	.0063	9.0	Cold
2a	.0995	.0034	3.4	Cold
2b	.0803	.0028	3.5	806
2c	.0631	.0029	4.6	Cold
2d	.0818	.0027	3.3	806
2e	.0665	.0026	3.9	Cold
2f	.0748	.0026	3.5	806
2g	.0670	.0023	3.4	Cold
3a	.0796	.0027	3.4	846

Discussion of Results

We have passed a beam of nitrogen pentoxide molecules through a furnace containing approximately black body radiation under such conditions that there was no intermolecular collision or collisions with the walls. The temperature of the furnace was such as to give practically complete decomposition if nitrogen pentoxide reacted at the rate secured by extrapolating the known experimental values obtained in the bulk decomposition to these higher temperatures. Since no decomposition occurred we have proved that infra-red radiation does not decompose nitrogen pentoxide molecules and there appears to be no special mechanism of absorption alone that can explain away this experiment. It may be pointed out that chains cannot occur in a molecular beam; consequently this experiment does not disprove the hypothesis which assumes a chain mechanism started by absorption of radiation.

It is convenient at this point to consider the probability of absorption of a quantum of light by a molecule passing through the furnace. This calculation is not essentially different from previous considerations showing that the coefficient of absorption of nitrogen pentoxide or other molecules would have to be very much larger than the observed values in order to account for the observed rate of decomposition. An approximate value for this coefficient for nitrogen pentoxide may be calculated from observations made by Warburg and Leithäuser;[16] for the region of the strongest absorption band, namely, 5.81μ, they find that the intensity is decreased to 0.7 of its initial value by passing through a column 30 cm. long containing nitrogen pentoxide at 0.5 mm. of mercury. This gives approximately 6.7×10^{-19} for the coefficient of absorption per molecule, α_ν. This is related to the Einstein probability coefficient, $B_{i \longrightarrow j}$, for a transition from a state i of lower energy to a state j of higher energy by the absorption of light of frequency ν under the influence of unit energy density lying between the frequencies ν and $\nu + d\nu$ by the approximate formula,[17] $B_{i \longrightarrow j} = c/h\nu \int \alpha_\nu \mathrm{d}\nu$, where the integral is to be extended over the whole range of absorption. As a further approximation we take the coefficient α_ν as constant over the region of the half width of the line; from Warburg's curve this half width is about 0.3μ. The $\int \alpha_\nu \mathrm{d}\nu$ then becomes $c\alpha_\nu \Delta\lambda/\lambda^2$ and $B_{i \longrightarrow j}$ is 1.6×10^{17}. We have then for the rate of absorption of energy $\mathrm{d}N/\mathrm{d}t = -Nu_\nu B_{i \longrightarrow j}$; now assuming that each absorption results in decomposition we have $\ln (N_0/N) = u_\nu B_{i \longrightarrow j} t$. The mean life of the molecules is, therefore, $1/B_{i \longrightarrow j} u_\nu$; substituting the numerical value for $B_{i \longrightarrow j}$ and for u_ν the density of black body radiation of frequency ν at a temperature of 900°K., we secure the value 9 seconds for the mean life. Since the molecules in this experiment are in the furnace for about 4×10^{-5} secs., only a negligible fraction could even absorb radiation of this strongest absorption band. Similar calculations

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[16] Warburg and Leithäuser, *Ann. Physik*, **28**, 313 (1909).

[17] See Tolman, "Statistical Mechanics," The Chemical Catalog Co., Inc., New York, **1927**, p. 175.

using the absorption coefficients where an electron transition is involved, such as in the dissociation of bromine into a normal and an excited bromine atom, show that such dissociations could not be effected in a molecular beam using the most intense sources of light available. Thus the experiments of Kröger, Lewis and Mayer, Mayer and the present investigation are in entire agreement with the theoretical expectations.

Summary

1. In reactions as ordinarily studied there are three factors influencing the decomposition, namely, the absorption and emission of radiation, intermolecular collisions and collisions with the walls. Methods have been discussed for separating these three factors and studying them independently.
2. We have completed experiments on the effect of radiation alone on nitrogen pentoxide by passing a molecular beam of this substance through a furnace containing approximately black body radiation. Even at the lowest temperature only one molecule in 10^{27} should have escaped decomposition if black body radiation alone caused the decomposition under ordinary conditions. We could detect no decomposition in any experiment.
3. We have calculated the probability of absorption of radiation by the nitrogen pentoxide molecule and find the experimental result in agreement with theory.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

TRANSFERENCE NUMBERS OF IONS IN SOLID SODIUM CHLORIDE AT HIGH TEMPERATURES

BY T. E. PHIPPS AND R. T. LESLIE

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For a large number of solid salts it has been shown that the relation between the electrical conductance and the absolute temperature may be represented by an equation of the form:

$$\ln k = A/RT + C \qquad (1)$$

where k is the specific conductance, A is a heat quantity designated as the heat of liberation of the ions from the lattice, and R is the gas constant. It has been found, however, that this relation is not linear over the whole temperature range for sodium and potassium chlorides, bromides and iodides. Ussataja and Hochberg[1] have observed this deviation for sodium chloride above 500° and have attempted to apply an equation of the form

$$\ln k = AT + C \qquad (2)$$

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[1] Ussataja and Hochberg, *Z. Physik*, **46**, 88 (1927).