known not to contain germanium, and since large quantities of copper are obtained from enargite, it is not impossible that at some stage of smelting or refining the germanium contained in the ore is concentrated in some waste product or by-product. We know that this happens in the case of certain zinc ores containing minute traces of germanium; these traces are increased to a very appreciable content in a by-product during the process of smelting.[7] It is our intention to extend the present investigation to copper smelter materials in hope of finding germanium in a form more concentrated than in the original enargite.

Summary

The arc spectral lines of germanium and the concentrations at which they appear were given.

The presence of traces of germanium in certain tin ores was noticed.

A method was given for the estimation of traces of germanium.

Germanium was found to be present in appreciable traces in certain varieties of enargite.

A method for the extraction of germanium from enargite was described.

ITHACA, NEW YORK

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

THE INFLUENCE OF RADIATION ON THERMAL UNIMOLECULAR REACTIONS

BY JOSEPH E. MAYER

RECEIVED AUGUST 12, 1927 PUBLISHED DECEMBER 10, 1927

Introduction[1]

The concept of molecules of high energy content as the reacting molecules in chemical reactions was first introduced by Arrhenius[2] primarily to explain the high temperature coefficient of most reactions. Although this theory has been generally accepted, there has been considerable dispute as to whether the mechanism of activation is by collisions between molecules or by the absorption of radiation. The radiation hypothesis, first suggested in a rather vague form by Trautz[3] and later elaborated by W. C. McC. Lewis[4] and by Perrin[5] appeared to be much strengthened by

---

[7] See Buchanan, *J. Ind. Eng. Chem.*, **8**, 585 (1916); Dennis and Papish, *Z. anorg. Chem.*, **120**, 1 (1921).

[1] A brief statement of the results of this investigation (excepting the last and most convincing experiment) has been published in a paper by G. N. Lewis and J. E. Mayer, *Proc. Nat. Acad. Sci.*, **13**, 623 (1927).

[2] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[3] Trautz, *Z. wiss. Phot.*, **4**, 160 (1906).

[4] W. C. McC. Lewis, *J. Chem. Soc.*, **109**, 796 (1916); **111**, 457 (1917); **113**, 471 (1918).

[5] Perrin, *Ann. phys.*, [9] **11**, 1 (1919).

investigations of Hirst and Rideal[6] who showed that the specific rate of the unimolecular decomposition of nitrogen pentoxide was as high or higher at very low pressures than at normal concentrations.

Various investigators[7] have pointed out that the observed reaction rate demands a higher rate of activation than seems likely to be afforded by radiation even under favorable circumstances. Lewis and Smith[8] showed that in the case of nitrogen pentoxide a high coefficient of absorption for radiation over a considerable range of the spectrum would account for the observed rate if the absorption of radiant energy alone were responsible for activation.

Later, measurements of absorption coefficients for nitrogen pentoxide in the infra red to wave lengths of about 7μ were published by Daniels.[9] These were much lower than the values found necessary by Lewis and Smith[8] to account for the observed decomposition rate. However, the absorption showed a noticeable trend, increasing with the wave length in the range studied. In view of this, and the fact that the greater part of the energy in the spectrum at room temperature lies at longer wave lengths, it was considered advisable to make rough measurements on the absorption coefficients farther in the infra red. The experiments are described and the results given later in this paper.

Daniels[10] also measured the decomposition rate of nitrogen pentoxide exposed to the radiation from a Nernst glower, and found no increase in rate other than that due to the rise in temperature of the gas. This would be expected on the modified form of the radiation hypothesis in which it is postulated that the energy of activation is acquired, not by the absorption of one high energy quantum by a molecule of average energy, but by the consecutive absorption of many quanta of low energy. At normal pressures, collisions of the second kind would distribute the energy of partially activated molecules between successive quantum absorptions according to the Maxwell distribution law, raising the temperature of the gas. The rate would then at all times be determined by the measured temperature of the mass of the gas. Experiments of this type are also open to the objection that the effective radiation may be wholly absorbed by a very thin layer of the gas at the high pressure employed and not reach the main body of the reacting material.

Professor G. N. Lewis suggested that it would be advisable, therefore, to study the influence of radiation on the rate of a unimolecular reaction in the absence of collisions, and at such low concentrations that the absorption would not materially affect the density of radiation of any fre-

---

[6] Hirst and Rideal, *Proc. Roy. Soc. (London)*, **109A**, 526 (1925).

[7] See, for example, Christiansen and Kramers, *Z. physik. Chem.*, **104**, 451 (1923).

[8] Lewis and Smith, THIS JOURNAL, **47**, 1508 (1925).

[9] Daniels, *ibid.*, **47**, 2856 (1925).

[10] Daniels, *ibid.*, **48**, 607 (1926).

quency throughout the reacting material. In order to do this a molecular stream was employed. Because of the necessity of maintaining the rectilinear nature of the stream it was considered inadvisable to employ nitrogen pentoxide or any molecule which breaks into two or more parts at the moment of reacting.

Pinene was therefore used, the racemization of which had been shown by Smith[11] to be one of the most satisfactory unimolecular reactions.

A similar experiment on the dissociation of iodine molecules in a molecular stream under the influence of radiation was performed by Kröger.[12] In this case, however, the order of the reaction at normal pressures has not been determined. Later work[13] on the heat of activation of the reaction from considerations of band spectra data makes possible recalculation of Kröger's data. This has been done and the results are recorded later in this paper.

The Total Absorption Coefficient of Nitrogen Pentoxide for Infra Red Radiation

Apparatus.—The study of absorption spectra at long wave lengths is made difficult by the fact that all materials which may be used as windows and prisms at shorter wave lengths absorb too highly for applicability in the extreme infra red. A very simple apparatus without windows was suggested by Professor Lewis with which determinations could be made of the coefficient of total absorption over all the black body spectrum at low temperatures. The source consisted of a black body kept at constant temperature, and the receiver was a sensitive thermopile.

Owing to the absence of windows a vacuum thermopile could not be used. The thermopile employed consisted of eight "Ideal" to "Manganin" junctions. The thermopile was some three inches long and could be slipped down the neck of an ordinary 500cc. flask as shown in Fig. 1; it was rigidly attached to a glass stopper, a glass tube carrying the leads out of the apparatus. The flask in which the thermopile was enclosed was blackened on the inside with lampblack and was placed in a metal container so that it could be completely surrounded with ice and water. A short neck through which the thermopile could be illuminated, projected from the side of the flask through the walls of the container. A sensitive galvanometer was connected to the thermopile, the deflection of which was read directly and used as a measure of the radiation intensity.

The absorption cell consisted of another 500cc. flask with two short necks sealed at opposite sides and projecting through the ends of a trough which surrounded the cell. The ends of the two necks, which were flush

---

[11] Smith, THIS JOURNAL, **49**, 43 (1927).

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

[13] Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).

with the ends of the trough, were closed by sliding shutters. The shutter at the end facing the thermopile could be filled with ice and water in order to maintain it at the same temperature as the rest of the wall surrounding the junctions.

The radiator was a glass flask, coated outside with lampblack, in which water or any other liquid could be boiled to maintain it at constant temperature.

Experiments.—By observing the galvanometer deflection at definite times after opening the shutter, the absorption coefficient was determined with pure dry air and with nitrogen pentoxide at known pressure in the absorption cell. After twenty seconds the galvanometer had practically come to equilibrium; the ratios of the two deflections, both at twenty seconds or both at thirty seconds, gave the same results within the limit of experimental error.

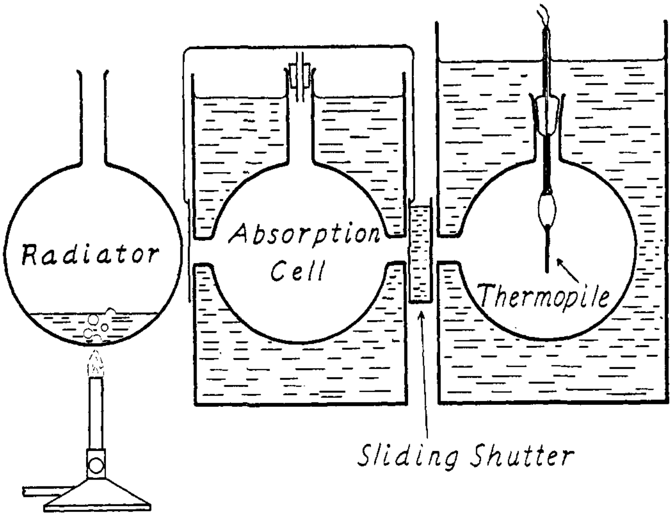

Fig. 1.

The partial pressure of nitrogen pentoxide was maintained by placing crystals of it with phosphorus pentoxide in the bottom of the cell, and in addition slowly introducing dry air which had been passed over crystals at the same temperature as the cell. The large volume of the cell compared with the small openings at the ends, some two square centimeters' cross section, together with the slow addition of gas, was considered sufficient to maintain a constant pressure over the short period of time the shutters were opened.

Boiling water and boiling acetophenone (202°) were used as temperature controls for the radiator.

Table I shows the recorded data for a typical experiment.

TABLE I

DATA OF A TYPICAL EXPERIMENT

	Galvanometer scale readings in tenths of mm. for time in sec. from opening of shutters						Galvanometer deflections from zero time in tenths of mm.		Average deflections and fraction transmission	
Time.	0	10	15	20	25	30	0–20	0–30		
Air	10	170	195	203	204	207	193	197		
	10	180	200	205	209	210	195	200	194.5	199.5
	10	175	200	206	210	211	196	201		
									0.746	0.757
N_2O_5	10	130	150	155	160	160	145	150	145	151
	10	140	152	155	160	162	145	152		
									0.756	0.757
Air	10	170	190	201	205	210	191	200	192	199.5
	12	168	189	203	209	211	193	199		
									0.735	0.742
N_2O_5	12	135	148	153	158	160	141	148		
	18	130	148	158	160	163	140	145		
	19	140	155	162	167	169	143	150	141	148
	19	130	151	160	165	168	141	149		
									0.735	0.733
Air	02	170	189	193	200	203	191	201		
	07	170	192	199	208	210	192	203	192	202
	10	178	196	205	209	212	195	202		
	12	178		203	208	214	191	202		

The absorption cell was 14.3 cm. long and the pressure of nitrogen pentoxide (26.8°) was 495 mm., the black body at 202°.

The ratios for the thirty-second and for the twenty-second deflections represent the fraction transmission of the gas. These agree with each other within the limits of experimental error, the values at thirty seconds being generally the more reliable. The average of these is taken as the result for this experiment.

TABLE II

SUMMARY OF EXPERIMENTAL RESULTS

Exp. no.	Temp. of cell °C.	Press. of N_2O_5	Trans-mission, F	Temp. of radiator, °C.	Coeff. of abs. $\alpha = \frac{\log 1/F}{c \times l}$ cm.^{2} molecules^{-1}
1	24.6	410	0.769	100	1.25×10^{-21}
2	0.0	51	.825	100	7.32
3	26.8	495	.747	100	1.16
4	0.0	51	.808	100	8.27
5	.0	51	.849	100	6.36
6	.0	51	.872	202	5.37
7	20.0	275	.689	202	2.65
8	27.0	500	.713	202	1.32
9	27.0	500	.743	202	1.18
10	0.0	51	.805	202	8.26
11	.0	51	.818	202	7.64
12	.0	51	.716	202	12.61
13	.0	51	.786	202	9.20

Owing to the fact that the transmission was measured directly, the absorption, which is the logarithm of the reciprocal of the transmission, could not be obtained with any accuracy at low pressures. Even at 0°, at which temperature the pressure is 51 mm. and the absorption about 9.2%, the results were extremely erratic. Table II shows a summary of the experimental results.

In Table II, Col. 1 is the number of the experiment, Col. 2 the temperature of the absorption cell, which temperature controls the pressure of nitrogen pentoxide given in Col. 3. Col. 4 is the transmission, or fraction of the total energy incident on the thermopile after passing through the cell containing nitrogen pentoxide. Col. 5 is the temperature of the black body radiator. The value of the absorption coefficient (log $1/F)/c \times l$, in which c is the concentration in molecules per cc. and l is the length of the cell (14.3) in cm., is given in Col. 6.

Results.—The value of α obtained in Table II is found to be the same within the experimental error for the black body radiator at 100 and 202°. It is also found to be of the same order of magnitude as the absorption observed by Daniels[9] for wave lengths shorter than 7μ.

The coefficient of absorption is the α of the equation

$$\frac{E_1}{E_2} = e^{\alpha \times l \times c} \tag{1}$$

in which E_1 is the energy incident upon, and E_2 the energy transmitted by, a cell of length l containing gas at a concentration c. This equation is strictly true only for energy of single frequencies. The α of Table II is the average of the α's for all frequencies obtained, not by integrating the differential equation

$$\frac{\partial E_\nu}{E_\nu} = \alpha_\nu \times c \times \mathrm{d}l \tag{2}$$

for all frequencies, but by determining the average α found in the integrated form. The α_0 or average of the α_ν in the differentiated form, which would experimentally be the α at zero values of concentration times length of cell, would be expected to be larger than the values found at high pressures. To estimate the value of α_0, the logarithm of α has been plotted against the pressure in Fig. 2 and the curve obtained has been extrapolated to the axis of zero pressure. The antilogarithm of the intersection has been taken as the most probable value of $\alpha_0 = 3 \times 10^{-20}$.

Although the value of α_0 so obtained may be in error ten-fold, the observations are sufficiently accurate for the purpose of the experiment. In the units in which α_0 is expressed it represents the fraction of a beam of black body radiation one square centimeter in cross section which would be extinguished by a single molecule of nitrogen pentoxide. The maximum value of α_0 calculated by Lewis and Smith[8] is the cross section of the quantum as derived from their equation

$$\alpha_0 = \sigma = \frac{\lambda^2}{8\pi} = \frac{c^2}{8\pi\,\nu^2} \qquad (3)$$

Taking the wave length $\lambda = 9\mu$ as that corresponding to the greatest energy in the black body spectrum at 300°K., we find that by equation (3) the cross section $\sigma = 3.2 \times 10^{-8}$ cm.^{2} is found to be 10^{12} times the value of α_0 found in this experiment.

Using the maximum value of the absorption coefficient from their equation, Lewis and Smith[8] calculated the reaction rate constant of nitrogen pentoxide to be 3×10^2 sec.$^{-1}$ at 300°K., which is 10^7-fold greater than the experimental value of 4×10^{-5} sec.$^{-1}$. The absorption coefficient determined experimentally should then be expected to give a rate of about 10^5-fold too little. Calculations have been made, assuming nitrogen pentoxide to be a molecule of 14 degrees of freedom, as do Lewis and Smith, integrating the number of molecules absorbing quanta of sufficient energy to activate them over the total number of molecules, and using the same absorption coefficient for all molecules and all wave lengths. The value of the rate constant $K = 1 \times 10^{-10}$ sec.$^{-1}$ so obtained is smaller than the experimental by a factor of 2.5×10^{-6}.

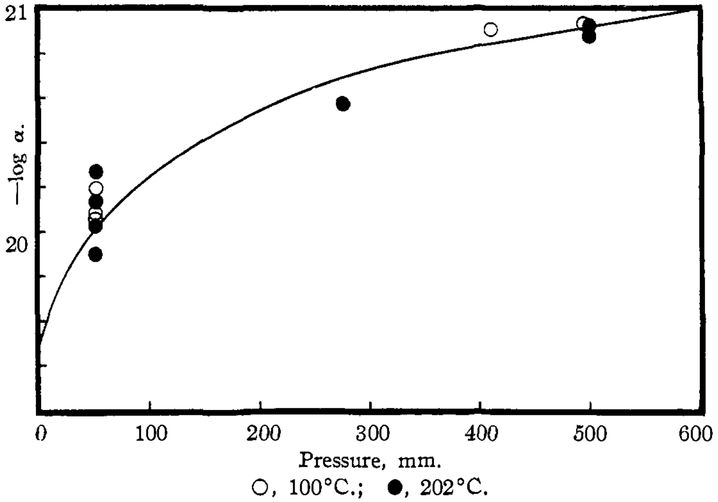

Fig. 2.

The Racemization of Pinene under the Influence of Radiation

Apparatus.—For the determination of the racemization of pinene under the influence of radiation in a molecular stream, a micro-polarimeter tube, the capacity of which was only one-tenth of a cubic centimeter, was used in the measurement of the optical rotation. It was necessary to collect about three-tenths of a cubic centimeter on the receiving surface to allow for the loss in transferring the liquid and in filling the tube.

Stern[14] showed that in a molecular stream determined by two slit orifices the

---

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

maximum concentration in the stream was independent of the width of the first orifice, hereafter called the nozzle to avoid confusion with the second, or defining, orifice. This is necessitated by the fact that the maximum pressure which may be permitted in the gas behind the nozzle is such that the mean free path of the molecules is of the order of magnitude of the width of the slit, in order to avoid collisions after emission into the first chamber. In the case of a nozzle of circular cross section, however, the maximum obtainable concentration in the stream will increase with the diameter of the nozzle, since the quantity of gas flowing through at any given pressure increases with the cross-sectional area, or square of the diameter of the nozzle; whereas the maximum permissible pressure decreases with the first power of the diameter. The stream will then be expected to remain perfectly defined by the geometrical design of the apparatus, and the quantity of material incident on the receiving plate will increase directly with the pressure up to this threshold value. Above this pressure the stream loses its perfect definition and becomes fuzzy at the edges. It was found experimentally, however, that the amount of material collected on the receiver increased directly with the pressure far above this maximum pressure. At these higher pressures the radius from the nozzle, beyond which the concentration of the gas is so low that no collisions between molecules take place, can be calculated, and this radius, rather than the diameter of the nozzle, is the significant factor in determining the dimensions of the stream. Since perfect definition of the stream was not required in this experiment, but merely the inclusion of all but a small fraction of the pinene within certain limits, to avoid contact with the furnace, the experiments were performed with a greater pressure behind the nozzle than would be permissible for most molecular stream work.

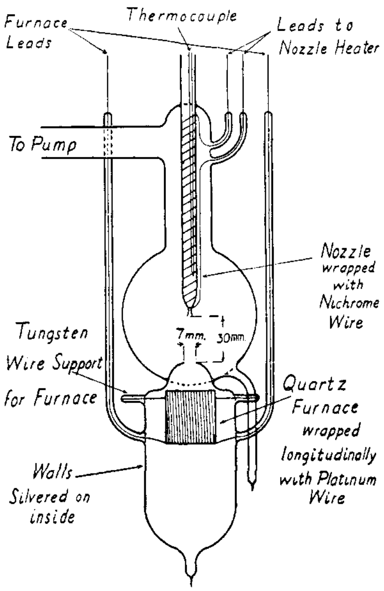

Fig. 3.

The molecular stream apparatus was constructed of Pyrex glass, as shown in Fig. 3. A tube wrapped with nichrome wire and having a thermocouple inside of it projected downward into a chamber; the end of the tube, drawn to a nozzle, was 3 cm. above the center of a circular orifice 7 mm. in diameter which defined the stream. Below this orifice the stream passed into a glass tube about 6 cm. in diameter which carried the furnace and on the bottom of which the pinene impinged. The bottom of this tube was drawn to a fine teat for convenience in draining. The complete apparatus was immersed in liquid air during the experiments. The nozzle had a smallest diameter of one millimeter and flared outward slightly after the design of steam turbine nozzles. The first chamber was connected by means of short glass tubing over 2 cm. in diameter through a liquid-air trap to a mercury-vapor vacuum pump which pumped directly into a high vacuum line evacuated by a second such pump. A McLeod gage measured the pressure in this secondary vacuum line, the construction of the lines being such that the pressure in the apparatus was less than one quarter that measured in the gage.

To produce the radiation field a cylindrical quartz tube 33 mm. in diameter and 35 mm. high was nicked at the ends with a saw and wound longitudinally inside and out with platinum wire. About 390 cm. of wire 0.508 mm. in diameter, making 55 complete turns, was used. The furnace was supported in the chamber by its heavy copper leads and by five tungsten wires, projecting radially inwards from short side tubes in the wall of the chamber. The inner walls of the chamber were silvered to reduce loss of radiation to the liquid air. A voltmeter connected to the leads into the furnace, together with an ammeter in series with the circuit, permitted measurements of the energy input.

Experiments.—The pinene used was distilled several times into liquid air under a high vacuum to remove residual gases. Immediately before the experiment sufficient material for the run was redistilled into a container connected to the nozzle. The apparatus was well baked out, surrounded with liquid air and the nozzle and furnace heated to the desired temperature. The pinene was then allowed to pass through the nozzle at 4mm. pressure by lowering a mercury trap.

During the course of the experiment frequent observations were made of the temperature of the nozzle, which was maintained within 3 of 93°, and of the amperes flowing through the furnace and the voltage at the leads. In the last experiment made at the highest temperature the ammeter reading was 6.1 amperes with a maximum variation of 0.1 ampere, and the voltmeter read 53.2 volts with a variation of 1 volt. The pressure was measured, by means of the McLeod gage, frequently during the experiment and was always observed to be less than 10^{-4} mm. after the experiment had been going on for a few minutes. As before mentioned, the pressure in the apparatus was probably less than one quarter of this value.

When all the pinene had passed into the apparatus the furnace current was stopped and air permitted to enter the chambers. The liquid air was removed and the pinene drawn out of the bottom of the furnace chamber by breaking the teat.

During all distillations of pinene, mercury from the traps collected on the liquid-air cooled surface with the pinene and formed a black, colloidal solution. After standing for an hour, the mercury settled to the bottom, leaving clear pinene. The liquid collected in the apparatus was similarly black at first but after standing became as clear as the original sample.

If pinene were allowed to strike the furnace at the temperature of the experiment sufficient decomposition resulted to create a marked increase in pressure. The fact that the pressure remained low during the course of the experiments was considered sufficient proof that no appreciable quantity of pinene touched the furnace. There was always observed a slight increase in pressure at the beginning of the experiment, probably due to traces of residual gases in the liquid.

About 4 cc. of pinene passed through the nozzle per hour, three hours being necessary to collect sufficient material at the receiving surface to insure ease of analysis.

After the experiments were completed a black thermocouple was sealed into the bottom of the furnace chamber. The temperature observed in the center of the furnace under conditions duplicating an experiment recorded the density of radiation through which the stream passed. During the course of the experiments, due largely to the distillation of platinum from the furnace and to several minor accidents of operation, the silvered walls of the furnace chamber had become blackened. Calculations at that time showed them to be less than 50% reflecting. Undoubtedly during the experiments, especially the earlier ones performed when the mirrored walls were in good condition, the density of radiation was much higher than that about to be calculated, making the results even more conclusively unfavorable to the radiation hypothesis than the succeeding calculations would indicate. The resistance of a piece of the same platinum wire that was used in the furnace was determined at 0°, at 100°, and at 444.6°. This calibration and the measured resistances of the furnace at 0° and during the experiments made possible fairly accurate estimates of the average temperature of the platinum wire when the furnace was in operation.

About six experiments in all were completed, the radiation density in the furnace chamber corresponding to temperatures of from 830°K. to 1053°K. In none of the experiments was there a detectable racemization. The optical rotation could be measured in the micro-polarimeter tube which was used to an accuracy of about 3%.

Conclusions

The geometrical dimensions of the furnace were such that it subtended the 0.726 part of the complete solid angle about a point in the center. The platinum wire covered 0.270 of the total area of the inside surface of the quartz. From this, and from an equation given by Geiss[15] for the emissivity of platinum at the temperature T,

$$E = \gamma T^{\phi} \sigma T^4 \tag{4}$$

in which $\gamma = 6.22 \times 10^{-4}$, $\phi = 0.767$, and σ is the Stefan Boltzman radiation constant, it was calculated that the energy density of radiation emitted from the platinum wire should be, at a point in the center of the furnace,

$$U_{Pt} = 0.726 \times 0.270 \times \gamma \times T^{\phi}_{Pt} \times C \times T^4_{Pt} \tag{5}$$

in which CT^4 is the density of radiation in a hohlraum completely surrounded by walls at the temperature T.

Assuming quartz to be 90% a black body, since the temperature was such that most of the emitted radiation was of longer wave length than the limit of transparency, the contribution of the quartz to the radiant energy at a point in the center was calculated to be

$$U_Q = 0.726 \times 0.730 \times 0.900 \times C \times T^4_Q \tag{6}$$

The actual density of energy was known to be

$$U_T = C \times T^4_{th} \tag{7}$$

from the measured temperature T_{th} of the thermocouple. Using the average temperature of the platinum wire determined from the resistance data for T_{Pt}, and equating the sum of equations (5) and (6) to equation (7), the temperature of the quartz, T_Q, was evaluated.

The density of energy of various frequencies in a hohlraum at the temperatures T_{Pt} and T_Q was calculated from the Planck equation, the densities for T_{Pt} were multiplied by the factor $(0.726 \times 0.270 \times \gamma \times T^{\phi}_{Pt})$, and those for T_Q by $(0.726 \times 0.730 \times 0.900)$; the two were then added. The results for the different experiments were represented by curves of densities plotted against frequencies.

To determine the lowest temperature at which pinene should show noticeable racemization in the time of the experiment, use was made of the experimental equation relating the specific reaction rate constant K to the absolute temperature T.

$$K = ke^{-h\nu/KT} \tag{8}$$

in which $\nu = 4.60 \times 10^{14}$ sec.$^{-1}$, the frequency corresponding to the energy of activation, 43,710 calories, found by Smith,[8] and k is a constant having the value 2.6×10^{14} sec.$^{-1}$.

---

[15] Geiss, *Physica*, **5**, 203 (1925).

From the velocity of the molecules leaving the nozzle and the length of the radiation field, the time during which the molecules were exposed to the radiant energy was calculated to be 1.2×10^{-4} sec. Using this time and assuming that the reaction could be detected if it progressed 6% (about twice the experimental error in reading the polariscope), the value which the reaction rate constant K would have in order that the pinene should be racemized was calculated to be 431 sec.^{-1}. This value was used in equation (8) and T_m, the minimum temperature at which pinene should show appreciable (6%) racemization in the time for which it was exposed to the radiation of the furnace, was determined to be 800°K.

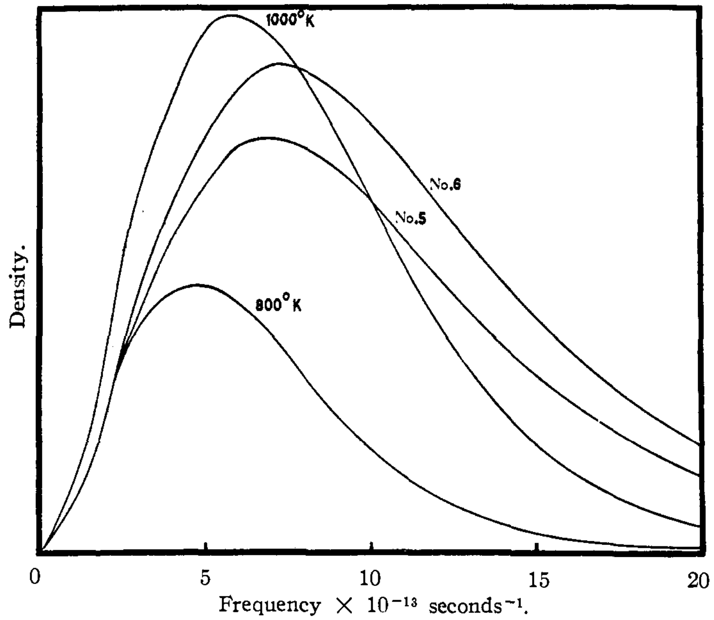

Fig. 4.

In Fig. 4 the curve for the energy density of radiation plotted against the frequency as calculated from the Planck equation is given for $T = 800°$. Curves 5 and 6 in the same figure are the curves for the distribution of radiation in the furnace chamber under the conditions of Experiments 5 and 6, the highest temperatures at which observations were made. In these experiments the average temperatures of the platinum wire were 1700°K. and 1790°K., respectively, the temperature of a black body in equilibrium with the radiation in the center of the chamber 1004°K. and 1053°K., and the calculated temperature of the quartz 1065°K. and 1123°K., respectively.

The curves show that for Experiment 5 above frequencies of 3×10^{13} [$\lambda = 10\mu$] and for Experiment 6 above frequencies of 2×10^{13} [$\lambda = 13\mu$]

the radiation in the furnace chamber is of greater density than in a hohlraum at 800°K. The curve for radiation in a hohlraum at 1000°K. is also shown in the figure. At this temperature only the 10^{-6} part of the pinene should have remained unracemized. The greater part of the curves of both experiments lies above the curve for 1000°K.

Kröger[12] has attempted to measure the dissociation of iodine in an apparatus similar to the one employed in this research, using a cylindrical platinum furnace. Calculations were made on the basis of these data, using a theoretical heat of activation not available to Kröger at the time of publication. Franck[13] has shown that the energy to which an iodine molecule must be raised by the absorption of radiation in order to dissociate is greater than the heat of dissociation by 22,000 cal. Using the heat of activation thus calculated, 57,000 cal., we may estimate the rate of dissociation of iodine at any temperature by the use of the equation first proposed by Dushman[16]

$$K = \nu e^{-h\nu/KT} \tag{9}$$

which differs from Equation (8) only in the substitution of ν for the experimentally determined k. This equation has been found to agree closely with the experimental rate constants of all the unimolecular reactions so far investigated, and although all theoretical derivations so far advanced may be objectionable it appears to be empirically applicable to unimolecular rate constants.

Kröger states that in his experiments no dissociation was observed and that the accuracy of his measurements was of the order of 1%. Following the method employed with pinene and assuming the length of his radiation field to be 6 cm., and the velocity of the molecules to correspond to 29.3°, we find the T_m in this case to be 934°K. Kröger estimates the temperature of his furnace in the experiment at the highest temperature to be 1300°K. At this temperature the density of radiation of frequency 6×10^{14}, chosen as a convenient reference since it is the frequency corresponding to the heat of activation, is about 10^4-fold the density of the same frequency at 934°K. The density in the furnace chamber of all frequencies must be smaller than that calculated for 1300°K. by some factor dependent on the shape of the furnace employed, and for sufficiently low frequencies this factor would decrease the density to a lower value than that corresponding to a hohlraum at 934°K. It, nevertheless, appears evident that the rate of dissociation of iodine by radiation alone is much slower than that calculated by Equation (9).

In the case of iodine the rate of dissociation, by radiation, using the calculated heat of activation, is lower than the rate of reaction normally found in thermal reactions of the same energy of activation, whereas the

[16] Dushman, This Journal, **43**, 397 (1921).

experiment with pinene shows that using the known (extrapolated) rate, radiation alone does not cause reaction.

Theoretical Discussion

The results of these experiments appear definitely to show that in neither of the two reactions considered, the decomposition of nitrogen pentoxide or the racemization of pinene, can the activation by the absorption of radiant energy alone be of sufficient rapidity to play an important role in the reaction.

It should be pointed out, however, that in the calculations of the probable rate of activation by collisions as made by Rice and Ramsperger[17] the chance that one molecule of energy ϵ will acquire an additional energy $\Delta\epsilon$ in one collision drops rapidly as the value of ϵ, the energy which the molecule already possesses, is increased. The chance that a molecule of energy ϵ will acquire the additional energy $\Delta\epsilon$ in a fixed period of time by the absorption of radiant energy depends only on the density of radiation of frequency $\nu = \Delta\epsilon/h$, and on the absorption coefficient of the molecule for radiation of this frequency. The smaller energy difference between quantum states at high energies and the greater *a priori* probability of the higher states indicate that the absorption coefficient for low-frequency radiation may increase rapidly with the energy ϵ of the molecule. This is in accord with the experimentally observed increase in the infra red absorption coefficients of many gases with rise in temperature.

It is probably true, therefore, that as we consider higher and higher steps of energy acquisition the relative importance of the absorption of radiation increases in comparison to the transfer of energy by collisions. However, calculations already made of the rate of activation by radiation, using the absorption coefficient of nitrogen pentoxide, expressly included the possibility of activation by the absorption of low energy radiation by molecules of high energy existing in equilibrium numbers. It would, therefore, be necessary, if this process is to play an important part in the normal mechanism of activation, that these molecules of abnormal energy (but unactivated) possess an enormously higher absorption coefficient than the normal molecule.

In this case the absorption of energy by collisions would be the mechanism of greatest rapidity up to a certain energy above which the activation due to radiation would become the predominant factor in the mechanism of producing activated molecules for the reaction. If such a mechanism were the true one the rate of the reaction could not be even approximately maintained in the absence either of collisions or of radiation. This possibility is in no way inconsistent with experimental facts presented here or elsewhere and should not be neglected in considerations

---

[17] Rice and Ramsperger, This Journal, **49,** 1617 (1927).

of the possible mechanisms of chemical reaction. Such a mechanism would also show a lowering of the specific reaction rate at low pressures found for some typical unimolecular reactions by Hinshelwood and Thompson,[18] Hinshelwood[19] and Ramsperger,[20] and discussed by Rice and Ramsperger[17] in connection with the mechanism of activation.

Acknowledgment should be made to Professor G. N. Lewis at whose suggestion this work was started and whose constant advice and aid made the research possible.

Summary

The absorption coefficient for black body radiation of low temperatures has been measured for nitrogen pentoxide. The values obtained were of sufficient accuracy to determine that the rate of activation of nitrogen pentoxide by radiation alone is of insufficient rapidity to account for the observed decomposition rate.

The racemization of pinene under the influence of radiation in a molecular stream was also studied. Under the conditions of the experiment there were no collisions and the concentration of gas was sufficiently low to avoid decreasing the radiation density by absorption in the outer layer. The concentration of radiation over the greater part of the frequency range was far above that in a hohlraum at a temperature sufficiently high to produce racemization in the time of exposure used in the experiment. No racemization was observed.

Attention was called to the fact that a theory involving both collisions and radiation as necessary for observed rates of activation was conceivable and not incompatible with experimental phenomena, although radiation *alone* could not be important in either of the two reactions studied.

BERKELEY, CALIFORNIA

---

[18] Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*, **113A**, 221 (1926).

[19] Hinshelwood, *ibid.*, **114A**, 84 (1927).

[20] Ramsperger, THIS JOURNAL, **49**, 912 (1927).