ACTIVATION OF MOLECULAR HYDROGEN
BY
ELECTRON IMPACT

QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION
OF
NITROGEN DIOXIDE

MECHANISM OF THE PHOTOCHEMICAL DECOMPOSITION
OF
NITROGEN PENTOXIDE

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THE ACTIVATION OF MOLECULAR HYDROGEN BY ELECTRON IMPACT

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Introduction

In this research we have undertaken to study the activation of hydrogen molecules by electron impact under conditions in which we know the energies of the impinging electrons. The experiments of Cario and Franck[1] show that hydrogen molecules can be activated by excited mercury atoms by collisions of the second kind and that copper oxide and tungstic oxide can then be reduced. In their experiments the mercury atoms receive energy of 4.9 volts from the light source, which is sufficient to dissociate hydrogen molecules, the heat of dissociation of hydrogen being 3 to 4 volts. Furthermore, it has been known for some time that in a discharge tube hydrogen will disappear when a discharge is passed.[2] Hughes,[3] in particular, has investigated the electrical clean-up of hydrogen and nitrogen, and finds a definite decrease in the hydrogen pressure at 13.3 volts and higher. He adopts Langmuir's conclusion[4] that hydrogen is dissociated under these conditions, and that the decrease in pressure is due to the freezing out of atomic hydrogen on surfaces cooled by liquid air. His results will be referred to later in connection with our own experiments. In Hughes' investigations no copper oxide was present, and the minimum electron energy at which hydrogen disappears was not accurately determined. A number of experimenters[5] also have investigated the chemical reactivity of hydrogen activated by an electric discharge, but the energies of the impinging electrons were not known.

We shall discuss four possible mechanisms by which electrons may be expected to activate hydrogen molecules.

First, it might be that an electron having kinetic energy of 3 to 4 volts could transfer its energy to the hydrogen molecule and cause its dissociation into atoms. These in turn could then react with other substances. However, it is known that no kink occurs in current-potential curves of hydrogen near 4 volts, and it seems, therefore, that electrons having kinetic energy equal to the dissociation energy of hydrogen molecules

[1] Cario and Franck, Z. Physik, **11**, 161 (1922).

[2] An excellent discussion of these phenomena may be found in Dushman "High Vacuum," Gen. Electric Rev., **1922**.

[3] Hughes, Phil. Mag., **41**, 778 (1921).

[4] Langmuir, THIS JOURNAL, **34**, 1310 (1912); **37**, 417 (1915).

[5] Wendt and Landauer, ibid., **42**, 930 (1920); **44**, 510 (1922). Bonhoeffer, Z. physik. Chem., **113**, 199 (1924); and others.

cannot transfer their energy to these molecules. We then should expect to find no evidence of reaction when hydrogen is bombarded with 4-volt electrons, and our experiments actually do give no indication of reaction. This is in agreement with the commonly held idea that the dissociation of molecules does not occur as the direct result of electron impact.

Second, electrons may have to possess sufficient energy to resonate the molecule, which may then dissociate if its heat of dissociation is less than its resonance potential. The hydrogen molecule has, according to the latest results of spectroscopy,[6] a resonance potential at 11.6 volts. Electrons of this energy can raise hydrogen molecules into an upper quantum state. These activated molecules would ordinarily return to the normal state after a short time. However, they may either dissociate into atoms upon impact with other molecules and the atoms thus react, or the resonated molecules may act directly on any oxide or other substance on which they impinge.

A third mechanism of causing activation by electron impact might be that where the impinging electron transfers enough energy to the hydrogen molecule to cause its dissociation and resonance of one of the atoms. This process may be expected at 13 to 14 volts, which is the sum of the heat of dissociation and the resonance potential of the hydrogen atom. This is the mechanism postulated by Hughes.[3]

A fourth possibility may be considered. It may be necessary that an electron ionize a hydrogen molecule before the latter can be made to react. It was found by Anderson[7] and Storch and Olson[8] that nitrogen and hydrogen reacted to form ammonia when bombarded by 17-volt electrons. This voltage is near the ionization potentials of these molecules.

We may state at once the results of our experiments. *Electrons of 11.4 volts' energy can activate hydrogen molecules*, for we find that there is a definite pressure decrease when the accelerating voltage applied to our tube has this value. At the same voltage we also obtain a kink in the current-potential curves, using the Franck method.

Experimental Procedure

The experimental arrangement is shown in Fig. 1.

The filament F was made of platinum foil coated with calcium oxide. This was surrounded with a platinum can having in the end a circular grid G_1, 0.5 cm. in diameter made from platinum gauze of 52 mesh. The next electrode consisted of a copper cylinder B, 4.5 cm. in diameter with a platinum grid G_2, also of 52 mesh at the end. One millimeter behind this second grid was a platinum plate P. The distance between the

[6] Witmer, *Proc. Nat. Acad. Sci.*, **12**, 238 (1926).

[7] Anderson, *Z. Physik*, **10**, 54 (1922).

[8] Storch and Olson, This Journal, **45**, 1605 (1923).

filament and first grid was 1 mm., and between the two grids 4 cm. A copper cooling coil *C*, through which tap water could be circulated, was introduced into the tube by means of copper disk seals, and made good electrical and thermal contact with the copper cylinder. The copper cylinder and cooling coil were surface oxidized in a Bunsen flame before being placed in the tube, thus providing a large surface of copper oxide.

With the tube first used, which had no cooling coil, it was found that with the filament lighted, but with no accelerating field on, there was a noticeable rate of decrease of pressure. Since this effect may have been due to reduction by the hydrogen of the copper oxide heated by conduction from the hot filament, the cooling coil described above was introduced into the tube, with the result that there was no longer any decrease in pressure, but instead a smaller rate of pressure increase. This increasing pressure may possibly be due to slow evolution of gas from the heated filament or from the metal surfaces bombarded by electrons. It was too large to be accounted for by leaks, which were carefully tested for. These zero rates, however, caused no difficulty in determining the voltage at which reaction did begin.
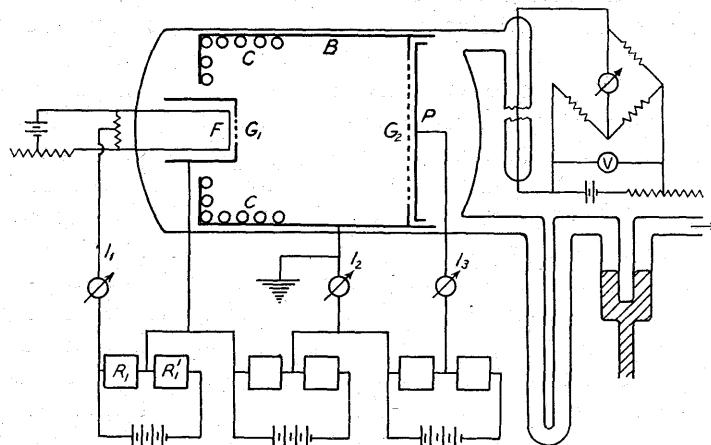

Fig. 1.—Experimental tube and wiring diagram.

The electrical connections are as shown. The total current, henceforth designated by I_1, and the current to the second can, I_2, were measured on the same galvanometer with a scale 1 meter long and 3 meters away. On the most sensitive shunt 8.16×10^{-9} amperes gave a deflection of 1 cm. Another galvanometer, giving a deflection of 1 cm. for 1.09×10^{-11} amperes on its most sensitive shunt, was used to measure the plate current I_3. The voltage applied between the filament and grid G_1 was calculated from the equation

$$E_1 = \frac{R_1}{R_1 + R_2} [E - I_1 R_2]$$

E is the voltage across the potentiometer, and R_1 and R_2 are the respective readings of the two resistance boxes (the sum of whose resistances was kept at 10,000 ohms). The term $I_1 R_2$ is introduced because of the electron current flowing from the filament to the other electrodes, hence through R_2 and back to the filament, and is relatively important at the emissions used (0.1 to 1 milliampere).

One side tube led to a liquid-air trap and mercury cut-off, thence to a palladium tube for admitting hydrogen, a McLeod gage, another mercury cut-off, and pumps. Another side tube led to a Pirani resistance gage which consisted of a thin tungsten wire

9 cm. long enclosed in a narrow glass tube. It was used according to the method described by Campbell,[9] and shown in the figure. By putting the gage in one arm of a Wheatstone bridge, the other three resistances of which were fixed and each one-third greater than the Pirani resistance at room temperature, any change in pressure could be followed by means of the voltage necessary to obtain a balance. The voltage was calibrated against the McLeod gage for a series of pressures of hydrogen up to 0.3 mm. of mercury. The Pirani gage was shielded from drafts, but no attempt was made to thermostat it. In order to follow small pressure changes, a more sensitive galvanometer was thrown across the bridge after a balance had been obtained, and readings were made with a telescope and scale 80 cm. away. With this set-up 1 cm. change in the scale reading corresponded to approximately 4×10^{-5} mm. in a total pressure of hydrogen of 0.2 mm. The volume of the tube up to the mercury cut-off was about 320 cc.

It will be seen that with this apparatus the following objectives can be attained. (a) Electrons emitted from the heated filament can be accelerated to a known velocity by the first grid and activate hydrogen molecules, which may then react with the copper oxide. (b) The water formed can be frozen out in the liquid-air trap with a resulting decrease in pressure. (c) The rate of decrease of pressure can be followed by means of the Pirani gage. (d) Mercury vapor is frozen out by the liquid air; thus, resonated mercury atoms cannot excite hydrogen molecules and cause reaction. (e) Current-potential curves can be taken by either the Franck or Lenard methods in the usual manner.[10]

The procedure adopted was as follows. After pumping out to 10^{-5} mm., hydrogen was admitted by heating the palladium tube in a gas flame, and readings were taken on the McLeod gage and on the voltmeter of the Pirani gage after liquid air had been placed about the liquid-air trap. The filament was then lighted and its temperature adjusted to give the emission desired at a definite accelerating voltage. After conditions had become steady, the mercury cut-off was closed and a series of readings with no accelerating field was taken on the rate of deflection of the sensitive galvanometer in the Pirani set-up. These readings constituted a set of "zero rates" for that particular run. Then the electrons were accelerated with a definite potential, and a similar set of rate measurements was taken. From time to time the mercury cut-off was opened and closed, allowing the hydrogen to come up to its original pressure. The voltage was increased in steps of 0.4–0.5 v. This process was repeated until rates had been obtained covering the voltage range desired. At the same time readings were taken of the total current I_1, and of I_2 and I_3. No field was applied between the two grids, but a retarding potential of 0.5 v. was maintained between the second grid and plate. In these runs either the total current I_1 or the sum of the currents $I_2 + I_3$ was kept constant by adjusting the filament temperature.

[9] Campbell, *Proc. Phys. Soc. London,* **33,** 287 (1921).

[10] These methods are fully described in "Critical Potentials," Compton and Mohler, *Bull. Nat. Res. Council,* **1924,** and elsewhere.

Experimental Results

Reaction Measurements.—Careful investigation failed to give any evidence of reaction between 0 and 10 volts' accelerating potential. It was found, however, that reaction does begin around 11.4 volts. From 11.4 volts on, the rate of pressure decrease rises rapidly with the applied voltage until the ionization potential is just passed and the glow discharge sets in. Above ionization it was found in most of the runs that the rates increase only slowly with the voltage, but depend primarily on the number of electrons passing through the first grid.

Since electrons are not emitted from a heated platinum-calcium oxide surface until a certain accelerating voltage is applied, a corresponding correction must be applied to the voltage scale. This initial velocity correction was determined as follows. For a constant heating current, the accelerating voltage was increased in small steps from 0 to 5 v., and the total current I_1 read. The foot of the curve so obtained corresponds to the voltage at which the fastest electrons will just escape from the filament and gives the correction to be subtracted from the observed voltage at which reaction begins. Four determinations for different heating currents gave 1.12, 1.19, 1.20 and 1.21, average 1.2 v.

In Table I are given the voltages (from which the correction of 1.2 v. has been subtracted) at which reaction is found to begin. The average of these values is 11.4 v. The table contains all our experiments.

Table I

Voltage (Corrected) at Which Reaction Starts

Expt.	Pressure of H_2, mm. of Hg	Volts	Expt.	Pressure of H_2, mm. of Hg	Volts
1	0.262	11.8	7	0.203	10.9
2	.249	11.9	8	.244	11.2
3	.168	11.8	9	.175	12.0
4	.124	11.4	14	.162	10.9
5	.103	11.9	15	.193	10.4
6	.158	11.5	18	.185	11.5

Resonance Potential of Hydrogen.—In order to determine the significance of the value 11.4 v., Franck current-potential curves were taken in hydrogen and in hydrogen-helium[11] mixtures of the composition 0.1 mm. of hydrogen and 1.1 mm. of helium. In making these runs, I_1 was kept constant and readings taken of I_3. A retarding potential of 0.5 v. was applied between the plate and second grid, while the accelerating potential was increased in small steps. Prominent kinks occurred in the I_3 curves taken in pure hydrogen around 13.5 and 19 v. uncorrected. In the curves for the hydrogen-helium mixtures similar kinks were found,

[11] The helium used was that prepared previously. Glockler, *Phys. Rev.*, **27**, 423 (1926).

as also a new one at 22 volts, due to the first resonance potential of helium. By plotting the differences of successive I_3 readings the kinks were brought out very strongly. The voltages at which the kinks occurred were obtained from the maxima in these difference curves, which give the point at which the rate of change of slope is the greatest, thus corresponding to the middle of the electron velocity distribution. Two determinations by the Franck method gave the helium kink at 21.88 and 21.75 v., and a Lenard run, 21.90. From spectroscopy the value of the resonance potential of helium is 19.77 v., which has also been obtained by the method of electron impact. Therefore, by subtracting 19.77 from the above values the initial velocity correction can be obtained. This comes out 2.11, 1.98 and 2.13, average 2.08 v. Table II summarizes the values found for the first kink in hydrogen after the correction of —2.08 v. has been applied.

It is seen that the two methods used to determine the initial velocity correction give identical results for the voltage at which reaction starts and for the resonance potential of hydrogen.

TABLE II

RESONANCE POTENTIAL OF HYDROGEN

Expt. No.	10	11	12	13	14	15	16	17
H$_2$ pressure in mm.	0.128	0.28	0.16	0.162	0.162	0.175	0.1[a]	0.1[a]
Volts, corrected	11.28	10.93	11.27	12.09	11.58	11.73	10.83	11.33
Volts, averaged	11.38							

[a] Plus 1.1 mm. of He.

This experimental value of 11.4 v. agrees well with the value 11.6 derived by Witmer[6] from spectroscopic data for the first resonance potential of the hydrogen molecule. It is also seen to coincide with the voltage at which hydrogen begins to disappear and we may therefore conclude that the first step in the reaction at these voltages is the formation of resonated hydrogen molecules by collision with 11.4 electrons. The resonated hydrogen molecule may then react directly with the copper oxide or be dissociated by collision with other molecules and subsequently react. Of course, after the first resonance potential is passed, the process of activation may include higher energy levels, and when ionization is reached the mechanism of reaction may be considerably altered. Further work on these points is to be continued; we wish only to record here the fact that reaction does set in when the first resonance potential of the hydrogen molecule is reached.

In order to identify still further the beginning of reaction with the resonance potential, several runs were made in which both rates and Franck current-potential curves were taken. Fig. 2 illustrates two of these runs. *In each case, it was observed that the break in the Franck curve begins at the same point as that at which the hydrogen pressure starts to drop.*

Identification of the Reaction Product

In order to determine the nature of the final reaction product, one of the runs was continued until all of the hydrogen had reacted (pressure about 10^{-4} mm.). On removing the liquid air the pressure rapidly rose. After 30 minutes the liquid air was replaced. The pressure immediately fell to its original value. This is the opposite of the results of Hughes[3] (in the absence of copper oxide) for he found that on removing the liquid air

Expt. 18.—High emission   Expt. 14.—Low emission
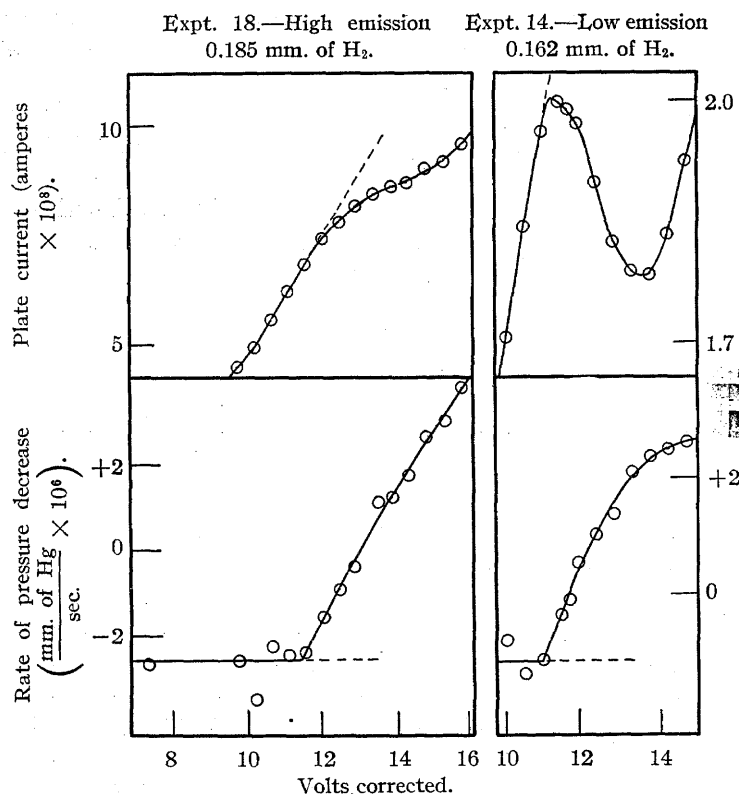0.185 mm. of H_2.   0.162 mm. of H_2.

Fig. 2.—Two runs illustrating the relation between the beginning of the break in the Franck current-potential curve and the voltage at which reaction starts.

and replacing it the pressure did not fall to its original value due to the presence of a non-recondensable gas. The non-recondensable gas he assumes, with Langmuir,[4] to be molecular hydrogen formed by the recombination of atomic hydrogen that had previously been frozen out on the walls at liquid-air temperature. To determine whether or not water was formed in our experiment the liquid air was again removed, the mercury cut-out opened, and the pressure read on the McLeod gage. The two

columns maintained a nearly constant difference of height except near the closed end of the capillary. After correcting for the small pressure of uncondensable gases, the difference of height was found to be 2.6 cm. The vapor pressure of water at the same temperature is 2.65 cm.

Summary

Hydrogen molecules have been activated by collisions with electrons of known energy and made to react with copper oxide. It is found that reaction begins at 11.4 volts. At the same time Franck current-potential curves show a resonance point at 11.4 volts. This agrees with the recent value of 11.6 volts for the first resonance potential of the hydrogen molecule as obtained from spectroscopy. It is concluded, therefore, that the first step in the activation process at low voltages is the formation of a resonated hydrogen molecule.

No evidence is found that 3- to 5-volt electrons dissociate hydrogen molecules.

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THE QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN DIOXIDE

By Roscoe G. Dickinson and Warren P. Baxter

Introduction

In a paper on "Photochemical Equilibrium in Nitrogen Peroxide,' Norrish[1] has described experiments in which a pressure increase was observed when NO_2 in a quartz vessel was illuminated by a quartz mercury vapor lamp. Under illumination the pressure increased rapidly at first, then more slowly, and reached a sensibly constant value after about fifteen minutes. When the illumination was cut off, the pressure dropped rapidly at first and then approached its original value comparatively slowly. The pressure increase could not be accounted for by heating alone. Norrish assumed that NO_2 was decomposed photochemically into NO and O_2; constancy of pressure was then attained when the rate of recombination of NO and O_2 became equal to the rate of photodecomposition of NO_2. This assumption received confirmation from the results of experiments carried out at various NO_2 pressures and with NO or O_2 initially present. Both of these gases cut down the pressure increase, and the NO did so more effectively than the O_2, as was expected from the fact that the rate[2] of recombination is proportional to $p_{NO}^2 p_{O_2}$.

In the present paper are described first some qualitative experiments which test further the correctness of Norrish's view that NO_2 is photochemically decomposed into NO and O_2, and then some measurements on the quantum yield of the reaction with monochromatic light. In contrast with the previous work, the present experiments were carried out under conditions where recombination should be negligible. Since the recombination is a third-order reaction, its rate becomes small at low pressures: for example, at $p_{O_2} = 0.04$ mm. and $p_{NO} = 0.08$ mm., the rate of decrease of p_{O_2} may be calculated from the measurements of Bodenstein and Lindner to be only 2.4×10^{-5} mm./hour at 22°. Hence, by keeping the pressures of the reaction products sufficiently small, it might be possible to treat the reaction simply as a photochemical decomposition rather than as a photochemical equilibrium. In order to measure the small amount of reaction product present in the larger amount of NO_2 used to secure sufficient light absorption, the NO_2 was frozen out with liquid air, and the residual gas measured with a quartz fiber gage,[3] the

[1] Norrish, J. Chem. Soc., 1927, 761.

[2] Bodenstein and Lindner, Z. physik. Chem., 100, 87 (1922).

[3] Haber and Kerschbaum, Z. Elektrochem., 20, 296 (1914); Coolidge, This Journal, 45, 1637 (1923).

use of this procedure under similar circumstances having already been found convenient.[4]   Measurements of a small amount of product also facilitate the use of relatively weak monochromatic light sources.

This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

The Apparatus

A diagram of the experimental arrangements is shown in Fig. 1.   The reaction chamber, A, was a Pyrex tube 20 cm. long and 3.2 cm. internal diameter with plane end windows fused on.   Always in communication
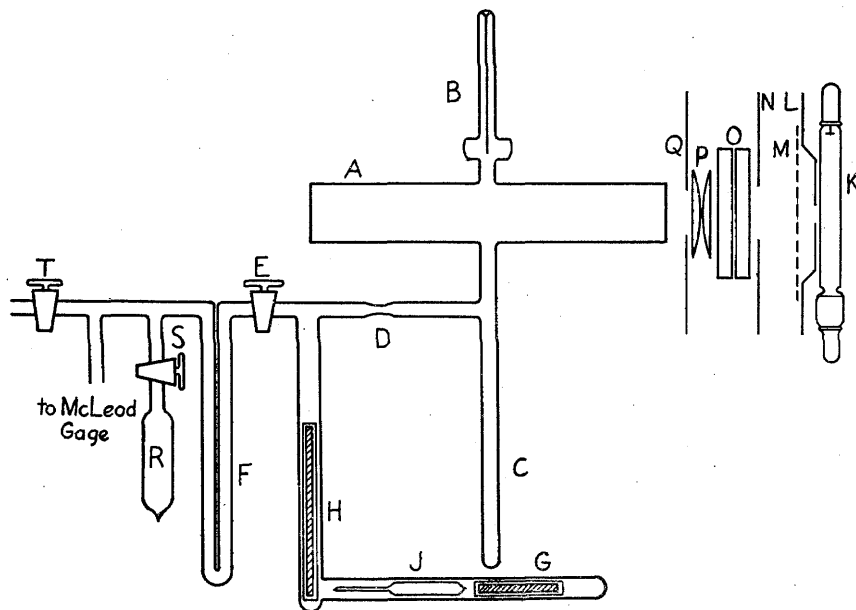
Fig. 1.

with this was the bifilar quartz fiber gage, B.   The side tube, C, could be immersed in liquid air.   This much of the apparatus up to the constriction, D, could be surrounded by a furnace for baking out during evacuation. The stopcock, E, led through the liquid air trap, F, to a McLeod gage, mercury vapor pump, etc.   The glass enclosed iron rods, G and H, were used respectively for magnetically moving the tube, J, and breaking off its capillary end.

Light from the mercury arc, K, operated from a storage battery, passed through a hole 1 cm. in diameter in the diaphragm, L.   When the shutter, M, was raised, the light passed through the diaphragm, N, the filters, O (described below), and was rendered slightly convergent by the glass

[4] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

lenses, P. The diaphragm, Q, defined the beam entering the reaction chamber; the beam was adjusted to travel the length of the chamber without striking the walls.

The calibration curve for the fiber gage was determined with the aid of the McLeod gage using air, oxygen and at the lower $p\sqrt{M}$ values hydrogen. One fiber gage which we attempted to use showed an unaccountably erratic behavior. Its readings could be markedly altered, for example, by leaning objects against certain parts of the glass apparatus; it seemed as if the vibration period of the gage were in resonance, or nearly so, with some period in the glassware. The gage with which the measurements reported were made was watched carefully and appeared to be free from these difficulties. It had a half-period of 271 seconds at 10^{-3} mm. of O_2, and 18.2 seconds at 4×10^{-2} mm.; nearly all of the measurements were made in this range.

The Materials

The nitrogen dioxide was prepared by heating c. p. lead nitrate in an all-glass apparatus, passing the gas evolved over P_2O_5 and condensing it in a trap cooled by an ice-salt mixture. After condensation of sufficient NO_2, the generating apparatus was sealed off. In preparation for use, the NO_2 was vaporized through a tube containing P_2O_5 and then through a series of small tubes with drawn-out capillary ends; when completely swept out by NO_2 at atmospheric pressure, these were quickly sealed off. The temperature and barometer reading at the time of sealing off were noted and the volumes of the tubes measured later.

The nitric oxide was prepared by the action of mercury on a solution of sodium nitrite in sulfuric acid.[5] The gas was passed over caustic soda, then over P_2O_5 and sealed up in small bulbs.

Tank oxygen was used without other purification than the use of liquid air to remove water vapor.

Tank hydrogen was stored in contact with metallic sodium.

Nitrogen was prepared by heating sodium trinitride.

Preliminary Experiments

The following experiments were made to determine whether a gas noncondensable by liquid air was produced by the illumination of NO_2, as expected, to determine its composition and to ascertain whether its quantity could be used as a measure of the extent of decomposition.

1. The reaction vessel was evacuated and baked out up to the point D. With liquid air applied at C and with the cock, E, closed, a tube, J, containing NO_2 was broken. The cock was opened, traces of uncondensed gas were pumped off and the apparatus was sealed off at D. Enough NO_2 was used to give about 7 mm. pressure at room temperature. The fiber

[5] Emich, *Monatsh.*, **13**, 73 (1892).

gage was read, the liquid air removed and the apparatus allowed to stand for fifteen minutes in the dark. The liquid air was then replaced and the gage again read. This was done to insure the absence of any unsuspected source of pressure development. The liquid air was again removed and the chamber illuminated for six minutes with the mercury arc without filters, lenses or diaphragms. On replacing the liquid air the pressure was found to be too high to measure and was probably at least 0.15 mm. This experiment showed that a non-condensable gas was indeed produced by illuminating NO_2.

2. Because of the high vapor pressure of liquid NO, gaseous NO alone would not be condensed out by liquid air at the pressures involved here; but in the presence of an excess of NO_2, it might condense out as N_2O_3 or otherwise. To determine whether this occurred, a tube, J, containing enough NO_2 to give a final pressure of 2.8 mm. was introduced and a smaller tube containing NO placed in a second side arm (not shown). The apparatus was prepared and the NO_2 admitted as above, but D was not sealed off. (Separate experiments showed that in these brief experiments the stopcock, E, did not give trouble with NO_2.) With the cock closed the fiber gage was read and the NO then admitted. The gage readings then gave 0.11 mm. of NO. The liquid air was next removed, the NO_2 allowed to vaporize in the dark and the liquid air immediately replaced. The gage showed then as good a vacuum as before the admission of the NO. From the results of such experiments it was concluded that the non-condensable gas produced by the illumination of NO_2 would not contain an appreciable amount of NO.

3. To show that the non-condensable gas was oxygen rather than nitrogen, a side bulb, R, was sealed on and sodium distilled into it *in vacuo* from a second bulb which was then sealed off. Blank experiments showed that oxygen quickly cleaned up when admitted to this bulb through S, whereas nitrogen cleaned up not more than 1%, if at all, in five minutes. The whole apparatus was evacuated and NO_2 transferred from J to C as usual. With stopcock E closed, the liquid air was removed from C and the chamber illuminated for two minutes without filters. The liquid air was replaced on C, and E was opened with S closed. The McLeod gage read 0.14 mm. (total volume of gas about 500 cc.). When the gas was admitted to the small sodium bulb by opening S, the pressure dropped to less than 10^{-4} mm. in three minutes. Experiments also were performed using only the radiation λ 3660 Å., with similar results.

4. These experiments are in agreement with and afford confirmation of Norrish's interpretation of the pressure rise on illumination of NO_2 as being due largely to decomposition of NO_2 into NO and O_2. In order to be able to use the residual oxygen pressure as a measure of the extent of decomposition, it was necessary to be sure that no important amount

of oxygen was removed by the solid N_2O_4 at liquid air temperature. The entire apparatus was evacuated; with liquid air at both F and C, and with E closed, about 0.1 mm. of oxygen was admitted to the McLeod gage system and T closed. Readings of the McLeod gage were made, E was opened and readings were again made. The experiment was then repeated, a considerable quantity of NO_2 having been first condensed in C in the usual manner. Then with E closed, the NO_2 was vaporized from and recondensed in C in the presence of the oxygen; E was opened and the McLeod gage read. The ratio of the initial to the final pressures (about 2.11) was the same to 2% in all cases. Therefore little if any oxygen was removed by the NO_2.

Measurement of Quantum Yield

Previous to each experiment on the quantum yield, the reaction chamber, fiber gage and tube C were evacuated and baked out for several hours without liquid air, and then for a further period with liquid air at F Then liquid air was applied at C, the stopcock, E, was closed, and a tube, J, containing NO_2 was opened; the NO_2 immediately froze out in C. The cock, E, was opened to pump off any residual gas and the apparatus was sealed off at D. The reaction chamber and accessories were then surrounded by a box which was light tight except for provision for admitting the desired radiation. When the NO_2 was subsequently allowed to vaporize for illumination, it came into contact with only glass and quartz. The temperature was not controlled but was always within a degree of 22°.

Three different filter combinations were used to monochromatize the light. Common to all of these was a 1-cm. layer of 6% cupric sulfate solution to remove infra-red.[6] To isolate the blue, λ 4350Å., 4 mm. of Corning glass G585 and 2 mm. of Noviol A were used; for the violet, λ 4050Å., 5 mm. of G586A and 1 cm. of a 4% solution of quinine hydrochloride; for the ultraviolet, λ 3660Å., 9 mm. of G586AW. Mercury arc spectra transmitted by these filters were photographed with various exposure times. The blue radiation contained only the blue Hg lines; the violet radiation contained far less than 1% of the groups at 3650 and 4350; the ultraviolet was free from the lines at 4050 but contained a few per cent. of the wave length 3350.

The intensity of the light entering the reaction chamber was measured in the following manner. At the beginning and end of each illumination the reaction chamber was moved aside and a Moll thermopile with an aperture 6 mm. in diameter was placed in its stead at the center of the diaphragm, Q; the thermopile was connected with a sensitive, low resistance, reflecting galvanometer and a series of measurements of the change

[6] Coblentz, *Bur. Stand. Bull.*, 9, 110 (1913).

in deflection when the shutter M was opened and closed (by remote control) was made.   In these measurements, but not in the calibration, the aperture of the thermopile was covered with a slip of the same glass used for the reaction-chamber window; this automatically corrected for reflection loss.   The slight non-linearity of the galvanometer scale was calibrated by measuring the deflections corresponding to small potentials imposed on the galvanometer by a suitable high resistance potentiometer arrangement.   The corrected galvanometer deflection produced when the thermopile was placed in a beam of given intensity was determined with the aid of a carbon filament lamp calibrated by the Bureau of Standards; the detailed directions given for the use of this lamp as a radiation standard were followed.   The beam entering the reaction chamber was not entirely uniform in intensity over the diaphragm; by taking, in a separate experiment, readings with the thermopile in front of various parts of the diaphragm, a factor was determined to reduce the intensity at the center of the diaphragm to the average intensity over the diaphragm.

Several successive illuminations with corresponding measurements of light intensity and oxygen pressure were made on each sample of NO_2. As the half period of a fiber gage is more sensitive to pressure changes the lower the pressure, the first illuminations on a given sample were always briefer than the subsequent ones.

The fraction of the light transmitted by the NO_2 was measured at the end of the experiment by placing the thermopile in a fixed position at the rear of the reaction chamber and observing the change in galvanometer deflection when the shutter was operated both with and without liquid air applied at C.   One minus the ratio of these deflections gave the fraction of light absorbed.

At the end of some of these runs (including No. 12, which had the highest final pressure), the apparatus was allowed to stand in the dark for about fifteen hours without liquid air; after replacing the liquid air at the end of this interval, no detectable change in the pressure of the non-condensable gas was observed.

The Experimental Results

In the accompanying table are given the results of all our quantum yield determinations except some with blue light which were found to be unreliable because of stray light and an erratic fiber gage. · The partial pressures of NO_2 and N_2O_4 present at the time of illumination were calculated from the volume and temperature of the reaction vessel, the volume of the bulb, J, together with the temperature and barometer reading at the time of sealing it off, and the constant[7] for the equilibrium between NO_2 and N_2O_4.   The yield tabulated in the last column is the number

[7] Schreber, Z. physik. Chem., 24, 651 (1897).

TABLE I

QUANTUM YIELD DETERMINATIONS

No.	Wave length, Å.	p_{NO_2}, mm.	$p_{N_2O_4}$, mm.	Fraction of light absorbed	p_{O_2}, initial, mm.	p_{O_2}, final, mm.	Δp_{O_2}, mm.	Exposure time, min.	Galv. deflect., cm.	Yield
5	4350	5.8	0.40	0.902	0.00303	0.00697	0.00394	87.0	8.22	0.0045
					.00697	.01246	.00549	129.0	7.50	.0047
					.01312	.02369	.01057	178.0	8.24	.0059
									Mean	.0050
6	4350	14.2	2.4	.986	.00008	.00691	.00683	147.0	8.90	.0039
					.00691	.01691	.01000	227.0	8.34	.0040
									Mean	.0040
12	4050	3.5	0.15	.753	.00024	.00472	.00448	10.00	3.07	.359
					.00472	.01073	.00601	15.00	2.84	.348
					.01073	.02417	.01344	35.00	2.73	.346
					.02417	.04342	.01925	55.00	2.56	.337
									Mean	.348
11	4050	11.1	1.5	.994	.00055	.00791	.00736	5.00	3.12	.376
					.00791	.01332	.00541	4.00	2.93	.369
					.01332	.02643	.01311	10.00	2.80	.374
									Mean	.373
8	3660	3.5	0.15	.748	.00064	.00558	.00494	5.00	3.42	.792
					.00558	.01112	.00554	6.51	3.08	.757
					.01112	.02393	.01281	15.00	2.91	.804
									Mean	.784
7	3660	9.3	1.0	.982	.00000	.00729	.00729	2.01	4.41	.739
					.00729	.01442	.00713	2.00	4.17	.767
					.01442	.03177	.01735	5.00	3.85	.808
									Mean	.771
10	3660	10.9	1.4	.988	.00093	.00600	.00507	5.00	2.68	.784
					.00600	.01446	.00846	9.00	2.42	.805
					.01446	.02961	.01515	18.00	2.21	.790
									Mean	.793
9	3660	39.7	18.7	.993	.00219	.00711	.00492	5.00	2.78	.729
					.00711	.01343	.00632	7.00	2.61	.714
					.01343	.02504	.01161	13.00	2.48	.742
									Mean	.728

of molecules of oxygen produced per quantum absorbed and was obtained from the following formula,

$$\text{Yield} = \frac{N \cdot r \cdot \Delta p \cdot v}{RT} \left(\frac{d \cdot 10^7 b \cdot A \cdot i \cdot a \cdot 60t \cdot 10^{-8} \lambda}{hc} \right)^{-1}$$

The factor outside the parentheses is the number of molecules of oxygen produced; the factor within is the corresponding number of quanta absorbed. The symbols have the following significance

N = the Avogadro number, 6.062×10^{23}
Δp = increase in oxygen pressure, mm. of Hg
v = volume of reaction system, 193 cc.
T = absolute temperature, between 294 and 296° in different experiments
R = gas constant, 82.07×760 mm.-cc./degree
r = a correction factor, 1.06, to correct for the fact that 4.5 cc. of the gas was at liquid air temperature

d = mean corrected galvanometer deflection, cm. of scale
b = light intensity to give one centimeter of corrected scale deflection, 11.54 $\times$ 10^{-8} watts/sq. mm.
A = area of diaphragm in square millimeters; 707 in Expts. 5, 6, 7, 11; 280.5 in Expts. 8, 9, 10, 12
i = factor to reduce intensity at center of diaphragm to average intensity over diaphragm; 0.84 in Expts. 5, 6, 7, 11; 0.91 in Expts. 8, 9, 10, 12
a = fraction of radiation absorbed
t = time of illumination, minutes
λ = wave length of radiation, Å.
h = Planck's constant, 6.554 $\times$ 10^{-27} erg-secs.
c = velocity of light, 3.00 $\times$ 10^{10} cm./sec.

Discussion of Results

Successive illuminations of a single sample do not show definitely an increase or decrease of yield. This fact affords an additional presumption that the measurements are not seriously in error from such causes as thermal dissociation, recombination or adsorption of oxygen.

In the range of pressures studied, the yields are not markedly dependent on the pressures of NO_2 and N_2O_4. In the determinations with λ 3660Å. the NO_2 pressure was varied 11-fold; the corresponding variation in the N_2O_4 pressure was 125-fold.

The yield is, however, greatly dependent on the wave length of the radiation. The radiation λ 4350Å. is comparatively ineffective, while the radiation λ 3660Å. gives a yield only 23% less than that to which Norrish's mechanism would lead if all the radiation of this wave length produced reaction. The first step in this mechanism is assumed to be the production of a nitrogen dioxide molecule[8] in a higher quantum state, NO_2', by the absorption of a quantum by NO_2. The second step is assumed to be $NO_2' + NO_2 = 2NO + O_2$. In the absence of degradation to heat, or of other loss of the excitation energy, this would lead to the production of one molecule of oxygen per quantum absorbed or a yield of unity.

Two possible explanations suggest themselves for the rapid increase in yield in the neighborhood of λ 4100Å.: (1) Reaction between an excited NO_2 and a normal molecule can take place only when the excitation exceeds a critical energy value, ϵ_0. When the quantum supplied has less energy than ϵ_0, the deficit must be made up from thermal energy; as the deficit will be larger at longer wave lengths, in fewer cases will the thermal energy be sufficient to make it up. However, it is doubtful whether the observed increase in yield with frequency is sufficiently sharp to be accounted for in this manner. (2) The probability that an excited

[8] Norrish has pointed out that dissociation of NO_2 as a primary process would require the production of an atom of either oxygen or nitrogen; in view of the high energy content of either of these atomic forms, there is not sufficient energy available to permit a dissociation process. That a quantized state is the first result of absorption follows also from the well-known fact that the absorption spectrum is discontinuous. Absorption spectra which we have photographed show this to be true not only in the visible but also in the neighborhood of λ 3660Å.

NO_2 will on collision undergo reaction rather than thermal degradation increases rapidly as its excitation increases in the neighborhood of 70,000 calories per mole (corresponding to violet light).

Summary

Experiments are described which are in confirmation of Norrish's view that gaseous NO_2 is decomposed by light into NO and O_2. By employing a technique permitting experimentation at sufficiently low partial pressures of NO and O_2, recombination of these gases could be made slow enough to neglect. This permitted quantum yield determinations to be made treating the reaction simply as a decomposition rather than as a photochemical equilibrium. For the quantum yields, expressed as molecules of oxygen produced per quantum absorbed, the following mean values were obtained: λ 4350Å., 0.0046; λ 4050Å., 0.36; λ 3660Å., 0.77. These yields were found to be not markedly dependent on the pressure in the range studied.

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MECHANISM OF THE PHOTOCHEMICAL DECOMPOSITION
OF
NITROGEN PENTOXIDE

It is well known from the work of Daniels and Johnston,[1] White and Tolman,[2] and others,[3] that the thermal decomposition of nitrogen pentoxide into nitrogen dioxide and oxygen, according to the reaction

$$N_2O_5 \longrightarrow 2NO_2 + \tfrac{1}{2}O_2 \; ; \quad 2NO_2 \leftrightharpoons N_2O_4 \tag{1}$$
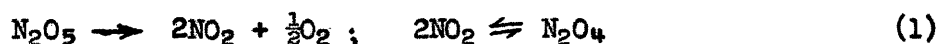
is a truly homogeneous, first-order, gaseous reaction. Daniels and Johnston[4] also studied the effect of visible light on this reaction. The method of experimentation they adopted was to illuminate, with sunlight or light from a tungsten lamp, a glass bulb containing nitrogen pentoxide crystals immersed in water at $0°C$, and measure the pressure increase on illumination. By the use of light filters, these authors were able to demonstrate that light above λ 4600 Å is ineffective in decomposing nitrogen pentoxide, but that illumination with shorter wave-lengths leads to decomposition of this gas. By a series of experiments in which the nitrogen dioxide content in their reaction vessel was varied from 0 to 30 mm. and also by the use of screens of gaseous nitrogen dioxide, Daniels and Johnston were able to establish the important result that the presence of nitrogen dioxide is necessary for the photochemical decomposition of the pentoxide with blue and near ultraviolet light. Thus the decomposition of nitrogen pentoxide is photosensitized by the dioxide. This result is in agreement with the fact that the pentoxide is colorless and should not absorb in the blue, while the dioxide is strongly yellow colored and has high absorption in the blue region of the spectrum.

Two important suggestions have been made as to the mechanism of this sensitized photochemical reaction. Fazel and Karrer[5] advance the hypothesis that a light quantum is absorbed by a nitrogen dioxide molecule, which is thus raised to a higher quantum state, and that this excited molecule, NO_2', then makes a collision of the second kind with a pentoxide molecule, transferring the energy of activation to the pentoxide molecule. The activated nitrogen pentoxide molecules then decompose in the same manner as in the thermal decomposition. This mechanism may be pictured thusly,

$$NO_2 + h\nu \longrightarrow NO_2'$$

$$NO_2' + N_2O_5 \longrightarrow N_2O_5' + NO_2$$

$$N_2O_5' \longrightarrow 2NO_2 + \tfrac{1}{2}O_2$$
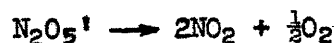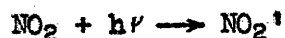
Norrish,[6] on the other hand, has shown that nitrogen dioxide is decomposed by light from a quartz mercury arc into nitric oxide and oxygen. His mechanism is, first, the production of an excited nitrogen dioxide molecule, which then collides with another dioxide molecule and yields two molecules of nitric oxide and one of oxygen. The nitric oxide thus formed is supposed to react then with the nitrogen pentoxide to give nitrogen dioxide.

$$NO_2 + h\nu \longrightarrow NO_2'$$

$$NO_2' + NO_2 \longrightarrow 2NO + O_2$$

$$NO + N_2O_5 \longrightarrow 3NO_2$$
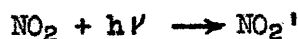
The overall reaction is

$$2NO_2 + h\nu + 2N_2O_5 \longrightarrow 6NO_2 + O_2 \ .$$

For the Norrish mechanism to play an important part in the
photochemical decomposition of nitrogen dioxide, it is necessary for
the thermal reaction between nitric oxide and nitrogen pentoxide to
be rapid, since the recombination of nitric oxide and oxygen is known
from Bodenstein's[7] results to be fast, and there will be competition
between the oxygen and nitrogen pentoxide for the nitric oxide.
Busse and Daniels[8] have shown, by mixing nitric oxide and nitrogen
pentoxide and observing the immediate appearance of the brown dioxide,
that indeed this reaction is very rapid. Norrish's mechanism is thus
quite possible, and it might be expected that the relative importance
of these two methods for the photodecomposition of nitrogen pentoxide
depend on the relative proportions of pentoxide and dioxide present,
and on the relative efficiencies of the processes occurring when the
excited nitrogen dioxide collides with a nitrogen pentoxide or nitro-
gen dioxide molecule.

In order to distinguish between these competing mechanisms,
Professor R.G. Dickinson and the author have studied the photochemical
decomposition of nitrogen pentoxide using the same light source and
filter combinations that were used previously in the determination
of the quantum yield in the photochemical decomposition of nitrogen
dioxide. In that work, it was shown that the yields expressed in
molecules of oxygen produced per quantum absorbed were 0.0046, 0.36,
and 0.77 for the wave-lengths λ 4350, 4050, and 3660 Å respectively.
It is to be noticed that, if the light absorbed is one hundred percent
effecient, both the mechanisms described above would lead to two mole-

cules of nitrogen pentoxide decomposed per quantum absorbed, but,
since the production of nitric oxide depends so markedly on the wave-
length of the impinging light, even qualitative measurements with
monochromatic light might distinguish between these two mechanisms.
It will be seen from the experiments described below that the extent
of the photochemical decomposition of nitrogen pentoxide may be
quantitatively predicted from the photochemical decomposition of
nitrogen dioxide into nitric oxide and oxygen.

Experimental Arrangement: - The present work on the photo-
chemical decomposition of nitrogen pentoxide was carried out at 0°C
with nitrogen pentoxide and nitrogen dioxide present only in the
gaseous phase. At this temperature the vapor pressure of nitrogen
pentoxide is 51 mm. and the thermal rate of decomposition is negligible.
The experimental setup is shown in Figure 1. The reaction vessel, A,
made of Pyrex glass, was oblong shaped with flat sides 2.2 cm. wide and
6.5 cm. in height. Three of these sides were silvered to conserve
light, while the front surface was unsilvered and served as a window
for the entrance of the light. The clicker-type glass-diaphragm
gauge, B, described by Smith and Taylor,[9] was used to measure the
pressure after the apparatus was sealed off at C and C'. Pressure
readings were reproducible to 0.1 mm. The constriction C was drawn
down fine enough so that on heating it quickly collapsed, causing
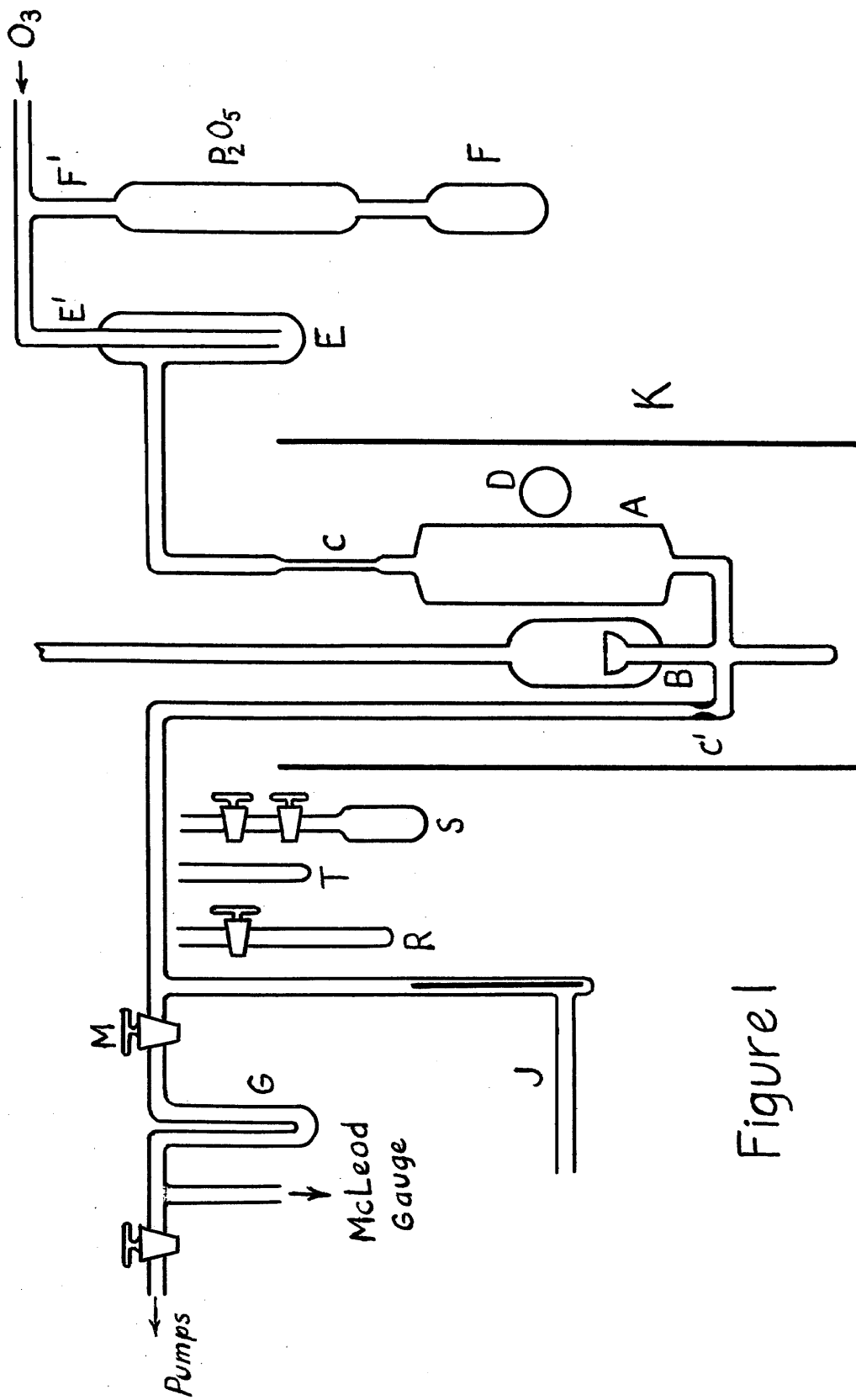little decomposition of the nitrogen pentoxide on sealing off.

Figure 1

A thermostat, K, consisting of a flat-sided glass jar, occupied the position indicated in Figure 1. On the front surface of the surface thermostat was cemented a sopper-sulfate cell 1.2 cm. in thickness in such a way as to leave a space of 2.2 cm. between the cell and the front of the thermostat. This space was filled with water to avoid difficulties due to condensation of water vapor on the surface of the thermostat and also to minimize loss of light by reflection from the several surfaces through which the light had to pass. In this space could be placed, in turn, the three filter combinations, described in the work on the photodecomposition of nitrogen dioxide, for isolating the groups of lines from the mercury arc at λ 4350, 4050, and 3660 Å. These filters were mounted on brass sheets with openings 4.5 cm. square in each of them. A mercury arc lamp was placed immediately in front of the copper-sulfate cell in line with the reaction vessel. A tin reflector was placed around the back and sides of the lamp to conserve light and to protect the observer. A shutter between the mercury arc and the copper sulfate cell allowed illuminations to be carried on at will. A Moll thermopile, mounted in a water-tight brass container and fitted with a shutter, was rigidly placed immediately beside the reaction vessel, as indicated at D, Figure 1, thus enabling intensity measurements to be made during the illumination. Care was taken to keep the thermostat, the filters, the mercury arc lamp and reflector in as nearly identical positions as possible in each of the runs.

Temperature control was maintained by keeping the thermostat well packed with ice. A fine jet of air in a glass tube 1 cm. in diameter pumped water in a steady stream from the bottom of the thermostat to near the tip. A thermojunction, near the bottom of the reaction vessel, with the other junction in a Dewar tube filled with ice and water, showed that the temperature was maintained constant to 0.1 degree or better. The front surface of the reaction vessel and the thermopile were placed as close as possible to the front of the thermostat and care taken to keep ice from between this space.

Preparation of Materials: - Nitrogen dioxide was prepared as described previously by the decomposition of lead nitrate. The liquid nitrogen tetroxide was kept in the reservoir, F, Figure 1. A set of small bulbs of gaseous nitrogen dioxide was prepared and these were used as the source of nitrogen dioxide present at the beginning of a run.

Nitrogen pentoxide was prepared by a commonly used method of oxidizing nitrogen dioxide in a stream of ozone and collecting the nitrogen pentoxide in the trap, E, surrounded by a freezing bath of ice and concentrated hydrochloric acid.

Tank oxygen was dried over phosphorus pentoxide and then passed through the Siemens ozonizer.

Experimental Procedure: - The procedure adopted in filling the apparatus was to first collect nitrogen pentoxide in the trap, E, the stopcock, M, being closed and the excess gases passing out through the tube, J. When sufficient nitrogen pentoxide crystals had been collected in E, the supply of nitrogen dioxide was sealed off at F', the stream of ozone being continued for a short time. The ozonizer was now turned off and, after sweeping out the excess ozone, the apparatus was sealed at E'_2. A bulb of nitrogen dioxide was now placed in the tube, J, which was then sealed off. Liquid air was applied to the trap, E and G, the stopcock, M, opened, and the whole system evacuated. The click gauge was protected from breakage by evacuating both sides simultaneously. When the system was well evacuated, the bulb of nitrogen dioxide was opened in the manner described previously, the nitrogen dioxide immediately freezing out in the trap, E. After a final evacuation, the apparatus was sealed off at C', then ice baths were placed around the reaction vessel and the supply of nitrogen dioxide and pentoxide in E. When the pressure no longer continued to rise, the tube, C, was sealed off. In order to determine the original pressure of oxygen or other noncondensible gas, liquid air was applied to the trap, H, and the pressure read. In no case was this pressure as large as 0.5 mm. The liquid air was now removed, the thermostat put in place, packed with ice, and the initial pressure read.

A preliminary run with this arrangement showed that measurable pressure increases took place when illuminations of moderate duration with λ 3660 and 4050 were made. Accordingly, the following procedure was adopted. The mercury arc was started and run for a time to become steady, pressure readings being taken at intervals. The

shutter was now opened with pressure readings still being made during illumination. During this time, measurements were made on the light intensity by reading the galvanometer connected with the thermopile when the shutter on the thermopile was opened and closed at intervals of one minute. The illumination was now discontinued but pressure readings were still made. The time of opening and closing the shutter was accurately noted. Another illumination was now carried out with a different filter interposed. In this way, several illuminations could be made during a run with each of the wave-lengths used before the supply of nitrogen pentoxide was exhausted. It was found that the apparatus could be left over night, if well packed in ice, without appreciable decomposition of nitrogen pentoxide.

The exhaustion of the nitrogen pentoxide was made evident when, during an illumination, the pressure would rise normally at first, but soon, the rate of pressure increase falling off, reach a nearly constant value and begin decreasing when the shutter was closed. This effect is typical of the results obtained by Norrish with pure nitrogen dioxide and tetroxide and explained by him as due to the decomposition of nitrogen dioxide into nitric oxide and oxygen on illumination, a maximum pressure being reached when the rate of formation of nitric oxide and oxygen became equal to the thermal rate of recombination of these gases to form the dioxide again. In our experiments the above effect becomes possible when the nitrogen pentoxide has been decomposed completely and thus can no longer react with any nitric oxide formed. Curves showing this Norrish effect are illustrated in Figure 3.

The final total pressure was obtained from readings made several hours after the last illumination, which gave sufficient time for recombination of nitric oxide and oxygen to be essentially complete. The final pressure of oxygen was obtained by freezing out the nitrogen dioxide in the tube, H, with liquid air, measuring the pressure of un-condensed oxygen at room temperature, increasing this pressure by two percent because of the fact that a definite volume of oxygen was at liquid air temperature, and finally reducing the value of the oxygen pressure to 0°C. Because of the slow diffusion in the presence of oxygen, it was found necessary to wait for several hours before the nitrogen dioxide was completely frozen out.

Experimental Results with Nitrogen Pentoxide: - Figure 2 shows a series of illuminations made in sequence with light of wave-lengths λ 3660, 4350, and 4050, respectively. These curves are typi-cal of experiments made in the presence of nitrogen pentoxide. The light intensities corresponding to the curves shown were 4.16 for λ 3660, 15.9 for λ 4350, and 4.65 for λ 4050 in centimeters of scale deflection. These curves indicate confirmation of Norrish's mechanism, namely, the first step apparently is the photochemical de-composition of nitrogen dioxide into nitric oxide and oxygen, which is then followed by a dark reaction between nitric oxide and nitrogen pentoxide. Thus, λ 4350 was, within small experimental error, without effect on the decomposition of nitrogen pentoxide, while the violet, λ 4050, produced approximately half as much decomposition as did λ 3660 in the same length of exposure, agreeing well with the previous-

Figure 2
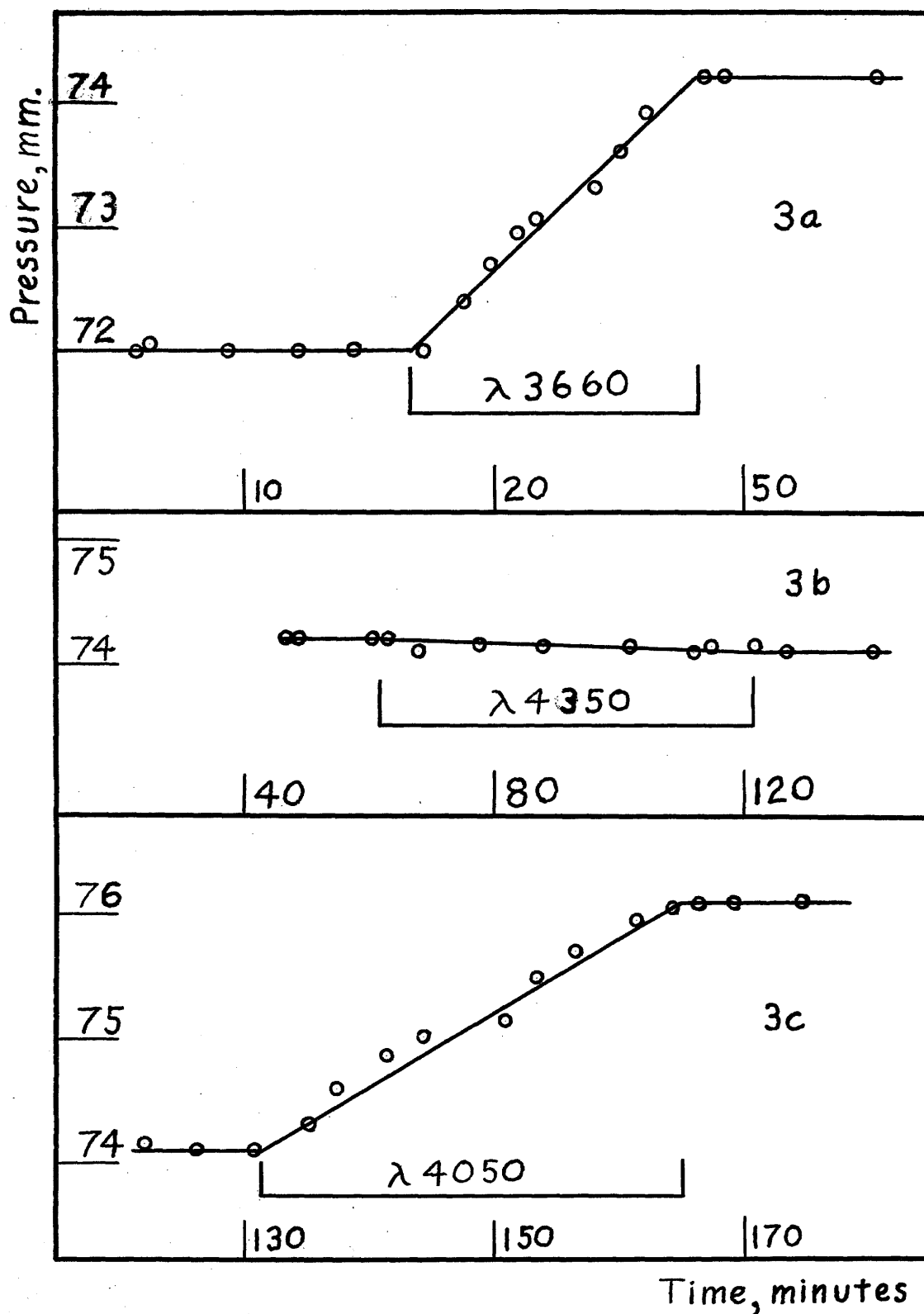
ly determined yields of 0.0046, 0.36, and 0.77 with these same wavelengths in the case of the decomposition of nitrogen dioxide. As shown later, absorption of light was fairly complete at the pressures of nitrogen dioxide in these cases.

In Table I are collected the experimental data obtained from runs made in the presence of nitrogen pentoxide. Data of Run 1 are omitted since this was a preliminary experiment carried out before arrangements were made for the measurement of light intensity. Qualitatively, the run agrees with those following and leads to the same qualitative conclusions. The headings of Table 1 are self-explanatory. The third and fourth columns give the pressures before and after each experiment. These values were obtained from the series of pressure readings made before and after each illumination when the temperature control was best. The last column gives the pressure increase for a ten-minute exposure and for unit scale deflection, calculated from the data of the proceeding columns. The rates given for experiments 2 h, 3 k, and 4 g, were obtained from the slopes of curves similar to those in Figure 2, but in which illumination was continued until the nitrogen pentoxide was completely decomposed. Calculation showed, however, that over the portions of the curves that these rates were taken from, nitrogen pentoxide was still present in appreciable quantities.

TABLE I

No	λ Å	Pressure initial mm	final mm	Δp mm	Exposure time min	Intensity cm	Δp/10min./1cm.
2a	4350	62.0	62.2	0.2	10.0	13.5	0.01
b	3660	62.2	64.3	2.1	20.0	3.39	.31
c	4050	64.3	65.95	1.65	21.8	3.95	.19
d	3660	66.05	68.8	2.75	34.0	2.70	.30
e	4050	68.8	71.5	2.7	30.0	6.43	.14
f	4350	71.7	71.7	0.0	30.2	18.4	.00
g	3660	71.7	75.1	3.4	30.2	4.88	.23
h	3660					4.06	.29
3a	3660	72.0	74.2	2.2	22.8	4.16	.23
b	4350	74.2	74.1	-0.1	60.0	15.9	-.00
c	4050	74.1	76.1	2.0	33.7	4.65	.13
d	3660	76.55	79.7	3.15	33.2	3.60	.26
e	4050	79.7	81.9	2.2	44.7	4.04	.12
f	4350	81.9	81.8	-0.1	60.1	13.8	-.00
g	3660	81.8	86.5	4.7	31.5	6.07	.24
h	3660	86.5	91.8	5.3	39.4	6.00	.22
i	4050	91.8	96.25	4.45	57.7	6.00	.13
j	3660	96.25	101.5	5.25	39.4	5.95	.22
k	3660					5.80	.25
4a	3660	47.2	50.0	2.8	20.8	6.44	.22
b	4050	50.0	52.2	2.2	35.7	5.70	.11
c	3660	52.2	55.8	3.6	26.8	4.50	.30
d	3660	55.8	61.25	5.45	43.7	4.54	.27
e	4050	61.25	65.25	4.0	40.6	7.28	.14
f	3660	65.6	71.4	5.8	21.5	10.29	.26
g	3660					8.84	.27

Calibration with Nitrogen Dioxide: - In an endeavor to obtain information as to the absolute efficiencies of the photochemical decomposition of nitrogen pentoxide, several illuminations were made with λ 3660 after the nitrogen pentoxide was completely decomposed. From the initial slopes of these nitrogen dioxide decompositions was calculated the rate of formation of nitric oxide per unit light intensity, which was then compared with the rate of decomposition of nitrogen pentoxide determined from experiments made at approximately the same pressure of nitrogen dioxide. Two of these experiments are shown in Figure 3. It is obvious that the initial slope could not be accurately obtained because of the small pressure rise before equilibrium is reached, but these experiments were sufficient to demonstrate agreement as to order of magnitude between the rates of photochemical decomposition of nitrogen dioxide and nitrogen pentoxide with λ 3660.

To obtain data which would, besides correcting for incomplete absorption of λ 4050 and 3660, afford a quantitative comparison between the rate of photochemical formation of nitric oxide and decomposition of nitrogen pentoxide, a series of experiments was made in which nitrogen dioxide was introduced into the reaction vessel, illuminated for only a short time, frozen out with liquid air, and the pressure of oxygen formed measured on a McLeod gauge. In these short experiments recombination of nitric oxide and oxygen could be neglected. For the purpose outlined above, a reservoir, S, containing nitrogen dioxide, was sealed to the apparatus at the point indicated in Figure 1, as was also a trap, T, and R, which served as a receptacle for nitrogen

Figure 3
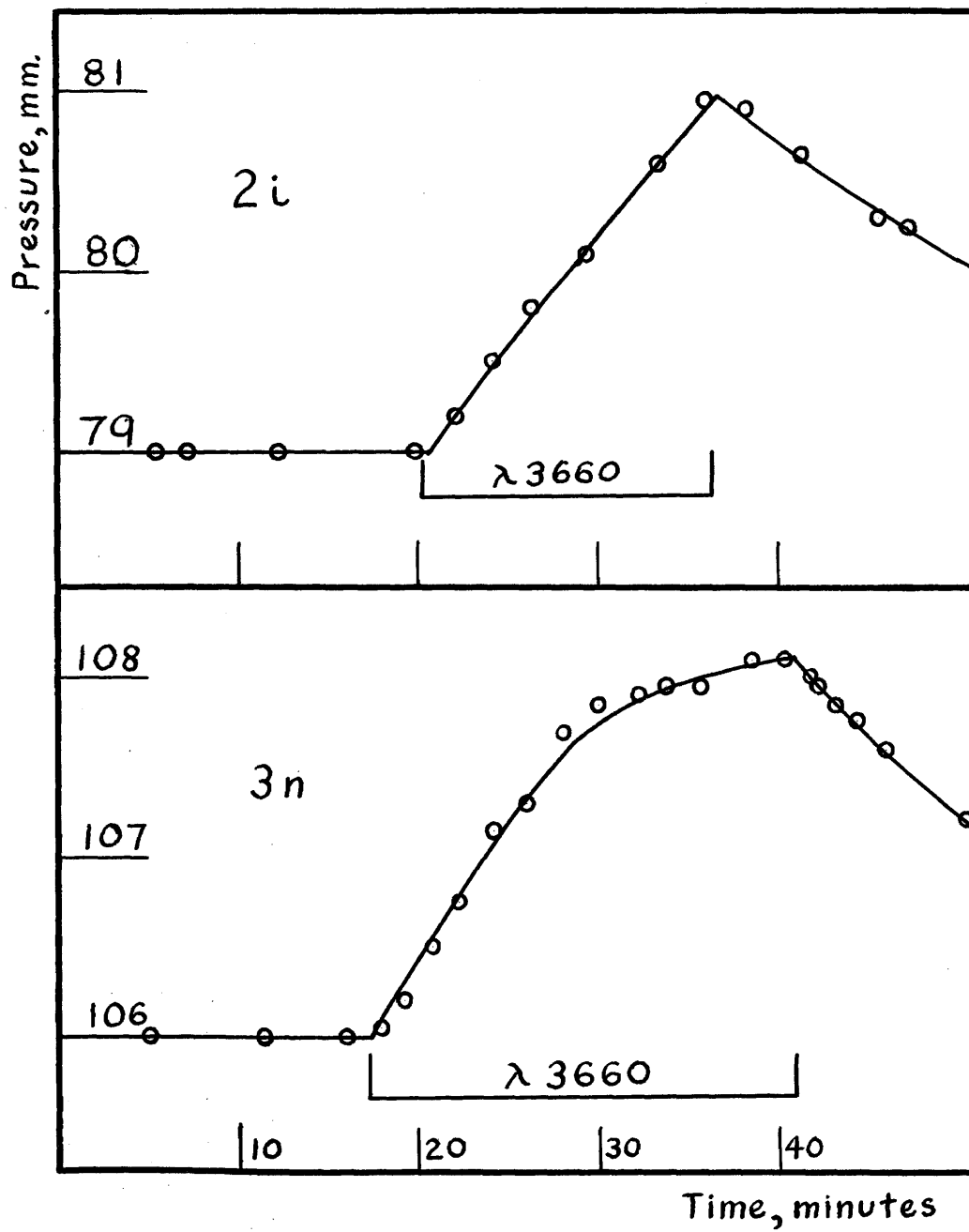
dioxide after it had been illuminated once. In these experiments the apparatus was sealed off at C. Liquid air was maintained at a constant level around the trap, G, and the thermostat kept packed with ice. The nitrogen dioxide in S was kept frozen out with liquid air, out of contact with stopcock grease, until introduced into the reaction vessel.

The method followed was to evacuate the whole system, close stopcock M, remove the liquid air from the reservoir, S, thus introducing some nitrogen dioxide into the apparatus, freeze this out in T, evacuate well, then remove the liquid air from around T with the stopcock closed. The pressure of nitrogen dioxide and tetroxide was now measured, and a short illumination made with λ 4050 or 3660. Immediately after illumination, liquid air was applied at T, the stopcock opened, and the pressure of oxygen read on the McLeod gauge. In this way, a series of determinations could be quickly made. It has been shown in the previous research that nitric oxide is frozen out along with nitrogen dioxide.

The volume of the apparatus between the points C and C' was found by filling with water, emptying and weighing to be 37.8 cc. By trapping air in the McLeod gauge, reading its pressure, then allowing this air to expand into the rest of the apparatus, which had in the meantime been well evacuated, and measuring the pressure again, sufficient data were obtained to calculate the pressure the oxygen formed would exert if it were all in a volume of 37.8 cc. at 0°C.

The results of these experiments are given in Table 2. Two runs are omitted because of obvious errors. In the last column of the

table is given the corresponding decrease of pressure of nitrogen

pentoxide for a ten-minute illumination at unit intensity, calculated

from the data of the preceding columns, assuming two molecules of

nitrogen~pentoxide~decomposed to one of oxygen formed, as demanded by Norrish's

mechanism. The calculated rates plotted against the pressure of nitro-

gen dioxide are shown in Figure 4. The determinations with λ 3660

are quite scattered but the smooth curve as drawn may be considered to

be not greatly in error.

TABLE 2

No	p_{O_2} observed mm	time min	λ 3660 intensity cm	p_{NO_2} mm	$p_{N_2O_4}$ mm	$\Delta p_{N_2O_5}/10min./1cm$
5	0.0269	2.17	7.36	4.9	1.9	0.262
6	.0404	2.03	6.66	11.1	10.4	.464
7	.0224	2.00	5.80	3.9	1.3	.299
8	.0412	1.99	5.59	20.3	35.4	.575
9	.0407	2.00	4.82	26.7	61.0	.658
10	.0323	1.50	8.13	17.8	26.9	.413
12	.0285	1.51	7.81	27.7	65.7	.376
			λ 4050			
13	.0325	3.01	6.52	27.2	63.2	.257
14	.0255	2.97	6.57	10.3	8.9	.203
15	.0162	3.01	6.24	4.3	1.5	.134

Figure 4
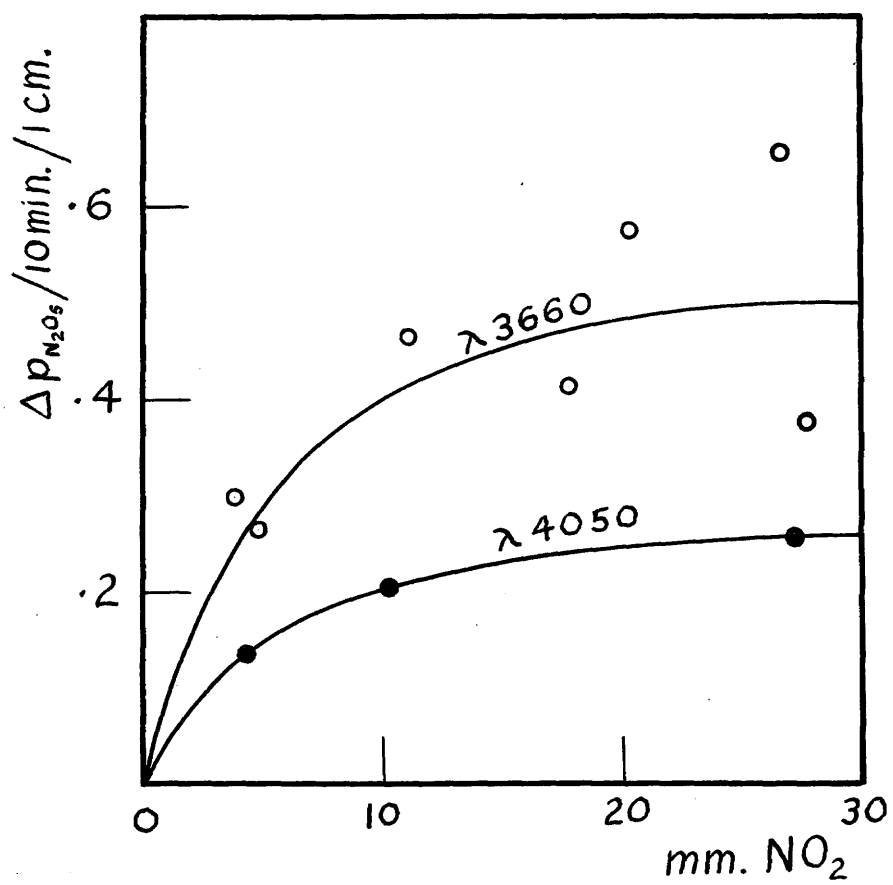
Comparison of the Rates of Photochemical Decomposition of
Nitrogen Dioxide and Pentoxide: - In Table 3 are collected the data on
the photochemical decomposition of nitrogen pentoxide with light of
wave-lengths 3660 and 4050 Å, respectively, and compared with the data
of Table 2. Because of the shift of the relative partial pressures of
nitrogen dioxide and tetroxide with the sum of the pressures of these
two gases, the amount of nitrogen pentoxide decomposed is not propor-
tional to the observed pressure increase in different parts of a run.
Instead, it may be easily shown that

$$- \frac{d\,p}{d\,p_{N_2O_5}} = 1.5 - \frac{4\,p_{NO_2}}{4\,p_{NO_2} + K} \,,$$

where p is the total pressure and K is equal to $p^2{}_{NO_2}/p_{N_2O_4}$, which has
the value 11.7 at 0°C, when pressures are expressed in millimeters of
mercury.[10] A curve of $- d\,p/d\,p_{N_2O_5}$, plotted against the pressure of
nitrogen dioxide enables one easily to convert observed pressure in-
creases to millimeters of nitrogen pentoxide decomposed, using the mean
value of the pressure of nitrogen dioxide during an illumination. This
method of computation is justified, since the pressures increases are
small, and also since $d\,p/d\,p_{N_2O_5}$ does not change rapidly in the range
of nitrogen dioxide pressures usually prevailing in these experiments.
The mean partial pressures of nitrogen pentoxide, nitrogen dioxide and
tetroxide, and oxygen during any experiment were determined with the
aid of graphical methods from the initial and final total pressures
and the final pressure of oxygen.

TABLE 3

Wave-length, 3660 Å

No	P_{NO_2}	$P_{N_2O_4}$	$P_{N_2O_5}$	P_{O_2}	$P_{N_2O_5}/10$ min/1 cm.	
					Obs.	Calc.
4 a	4.1	1.5	42.0	0.7	0.24	0.26
4 c	8.2	5.7	25.8	3.9	.39	.37
4 d	11.2	10.7	29.4	7.2	.39	.42
3 a	11.6	11.5	48.6	1.1	.33	.42
3 d	14.4	17.7	41.0	5.0	.39	.45
2 b	16.3	22.7	23.4	0.8	.48	.46
4 f	16.4	23.0	14.6	14.5	.40	.46
3 g	17.2	25.2	32.2	9.4	.38	.47
2 d	18.2	28.3	16.7	4.3	.47	.47
4 g	18.7	29.9	6.0	19.0	.42	.48
3 h	19.4	32.1	24.2	13.3	.36	.48
2 g	20.7	36.6	7.3	8.8	.37	.48
2 h	21.7	40.2	3.0	12.2	.46	.49
3 j	23.2	45.9	8.4	21.2	.37	.49
3 k	24.2	50.4	3.5	23.7	.41	.50

Wave-length, 4050 Å

No	P_{NO_2}	$P_{N_2O_4}$	$P_{N_2O_5}$	P_{O_2}	Obs.	Calc.
4 b	6.1	3.2	39.2	2.2	0.13	0.16
3 c	12.7	13.8	45.9	2.6	.19	.22
4 e	13.9	16.5	22.5	10.5	.20	.22
3 e	15.6	20.8	37.2	6.9	.19	.23
2 c	17.2	25.2	20.2	2.4	.30	.23
2 e	19.4	32.1	12.6	6.3	.22	.24
3 i	21.3	38.8	16.5	17.3	.21	.24

These final results are tabulated in order of increasing
nitrogen dioxide pressures. The sixth column of Table 3 gives the
observed pressure decrease of nitrogen pentoxide for a ten minute il-
lumination at unit light intensity; the last column is the correspond-
ing rate calculated from the expected production of nitric oxide given
by the smoothed curves of Figure 4.

Discussion of Results and Conclusions: - From the agreement

between the data of the last two columns of Table 3 and from the inef-

fectiveness of λ 4350, it may be concluded that the photochemical decom-

position of nitrogen pentoxide is conditioned largely by the photochem-

ical formation of nitric oxide from nitrogen dioxide, as first suggested

by Norrish.[6] It is highly improbable that such agreement between the

rates of these two decompositions would result if the mechanism of this

photosensitized reaction involved collisions of the second kind between

excited nitrogen dioxide molecules and nitrogen pentoxide, in view of

such widely differing efficiencies with λ 4350, 4050 and 3660. Experi-

ments 4 a and 4 b are quite significant in this respect, since, in these

cases, the ratio of nitrogen pentoxide to nitrogen dioxide was about

nine to one. Although the nitrogen dioxide pressure in these two experi-

ments was so low that light absorption was appreciably incomplete, re-

sulting in slower rates of decomposition than usual, the actual rates

observed agree, within experimental error, with the rates expected from

the experiments made with nitrogen dioxide alone.

It is to be noticed that oxygen has but slight, if any, in-

hibiting effect on the photodecomposition of nitrogen pentoxide. Such

an inhibiting effect should be expected if oxygen were to oxidize the

nitric oxide before reaction with nitrogen pentoxide had taken place.

Busse and Daniels[8] have observed previously that addition of air has

no marked effect on the rate of this photodecomposition, in agreement

with the results obtained here. These authors point out that, since

the rate of reaction of nitric oxide with nitrogen pentoxide is very

rapid and presumably first order with respect to nitric oxide, while

the reaction of this gas with oxygen is proportional to the square of
the pressure of nitric oxide,[7] the latter reaction should be negligible
even though the concentration of oxygen be considerably greater than
that of nitrogen pentoxide.

The agreement between the last two columns of Table 3 makes
it possible to obtain the absolute efficiencies of light of wave-lengths
3660 and 4050 Å in the decomposition of nitrogen pentoxide, since the
efficiencies of these two wave-lengths in the decomposition of nitrogen
dioxide have been previously determined and reported in a preceding por-
tion of this thesis. In that work, it was shown that 0.77 molecules of
oxygen were produced for each quantum of λ 3660 absorbed, with a corres-
ponding figure of 0.36 for λ 4050. It follows that approximately
1.54 molecules of nitrogen pentoxide are decomposed for one quantum of
λ 3660 absorbed, and 0.72 per quantum of λ 4050.

The absorption of blue light, λ 4350, was not determined in
these experiemnts, but a conservative estimate, based on absorption
measurements made in the previous research on nitrogen dioxide, showed
that absorption should be at least as great as fifty percent. Assuming
then, fifty percent absorption, and allowing a pressure increase of
0.2 mm., which might have escaped detection, experiments 2 a, 2 f, 3 b,
and 3 f lead to the result that λ 4350 is not more than 10, 2.4, 1.3,
and 1.6%, respectively, as efficient as λ 3660. This result is con-
sistent with the efficiencies, 0.0046 and 0.77, of these two wave-lengths
in the decomposition of nitrogen dioxide.

I wish to express here my gratitude to Professor Roscoe G.
Dickinson, who suggested this problem, for his advice and active cooper-
ation in the prosecution of this research.

SUMMARY

The photochemical decomposition of gaseous nitrogen pent-
oxide in the presence of nitrogen dioxide has been investigated with
light of three wave-lengths, λ 4350, 4050, and 3660 Å. By a compari-
son of the rates of photochemical decomposition of nitrogen pentoxide
and nitrogen dioxide, it is concluded that the mechanism of this sen-
sitized photochemical decomposition is essentially that suggested by
Norrish, namely, first the formation of nitric oxide and oxygen from
the photodecomposition of nitrogen dioxide, followed by thermal reac-
tion between nitric oxide and nitrogen pentoxide.

Oxygen has no marked inhibiting effect on this reaction.

The quantum yield, expressed in molecules of nitrogen
pentoxide decomposed per quantum absorbed, is, approximately, 1.54
and 0.72 for light of wave-lengths 3660 and 4050 Å, and less than
0.03 for λ 4350.