THE DECOMPOSITION OF OZONE-NITROGEN PENTOXIDE MIXTURES

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TABLE OF CONTENTS

| | | Page |
|-----|--|------|
| 1. | Introduction | 1 |
| 2. | The Materials | 3 |
| 3. | Apparatus and Method of Procedure | 3 |
| 4. | Computation of the Partial Pressures | g |
| 5• | Experimental Results | 10 |
| | a. Ozone Blanks | 10 |
| | b. The Experiments at Atmospheric Pressure - | 11 |
| | c. The Experiments at Reduced Pressure | 27 |
| 6. | The Nitrogen Pentoxide Decomposition | 31 |
| 7. | The Ozone Decomposition | |
| | a. General Features of the Reaction | 35 |
| | b. The Method of Determining the Dependence of | |
| | the Rate of the Secondary Reaction on Ozone and Nitrogen Pentoxide | 37 |
| | c. The Order of the Secondary Reaction with | 7.0 |
| | Respect to Ozone | 38 |
| | d. The Order with Respect to Nitrogen Pentoxide | 42 |
| | e. The Effect of Oxygen | 7171 |
| g. | Discussion of the Results | 46 |
| 9. | Summary | 50 |
| 10. | References | 51 |

INTRODUCTION

When a mixture of ozone and nitrogen pentoxide is allowed to decompose, the reaction takes place in two stages. During the first stage, while ozone still remains, the ozone immediately oxidizes any nitrogen dioxide formed by the decomposition of nitrogen pentoxide; and the overall result is merely the decomposition of ozone in accordance with the reactions

$$0_3 = 3/2 \ 0_2 \ . \tag{1}$$

The second stage of the reaction, after the ozone is all used up, is then the well known first order decomposition of the nitrogen pentoxide according to the reaction

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2 \rightleftharpoons 2NO_2 + \frac{1}{2}O_2$$
. (2)

The start of this latter reaction is indicated by a break in the decomposition curve, the slope of the total pressure-time curve being greater at the beginning of the nitrogen pentoxide decomposition than at the end of the ozone decomposition; and also by the formation of brown NO_2 , which can be readily observed in case the initial pressure of the nitrogen pentoxide is high, 15 mm. or more. The purpose of this research was to study the ozone decomposition, especially the decomposition in the neighborhood of the point of inflection of the total reaction curve and possibly get a further insight into the mechanism of the N_2O_5 decomposition.

There is a disagreement among previous investigators concerning this decomposition. Daniels, Wulf, and Karrer² in connection with their research on a method of titrating nitrogen tetroxide with osone, recorded a lag in the time necessary for the appearance of nitrogen dioxide, which marks the start of the nitrogen pentoxide decomposition.

Hirst, 3 in an attempt to duplicate these results, found no similar effect. In two experiments carried out at 20°C and 47°C, he found that the rate of ozone decomposition depended only on the pressure of the nitrogen pentoxide present, as would be the case if the following mechanism were true,

$$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$$
 (slow reaction)
 $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ (fast reaction).

Hence the time necessary for the disappearance of the ozone as marked by the appearance of the brown nitrogen dioxide is given by

$$t = \frac{P_{03}}{K_1 P_{N_2 O_5}}, \qquad (4)$$

where K_1 is the specific reaction constant for nitrogen pentoxide, $p_{\rm N_2O_5}$ the partial pressure of the nitrogen pentoxide, and $p_{\rm O_3}$ the partial pressure of the ozone.

White and Tolman found, on the other hand, that the time of disappearance of the ozone was considerably less than that calculated by (4) above, quite contrary to the lag first recorded and to the results found by Hirst. They employed a colorimetric method for following the rate of decomposition of the nitrogen pentoxide, or rather the rate of formation of nitrogen dioxide. The initial pressure of the ozone was determined by trapping a sample of the oxygen-ozone mixture before it passed over the nitrogen pentoxide crystals, measuring its pressure, heating to 150° for 3 hours to decompose the ozone, and again measuring the pressure. Their method did not allow them to follow the actual rate of the ozone decomposition but only to observe the total time necessary for its decomposition. In the present research it was possible to follow the ozone decomposition as well as that of the nitrogen pentoxide.

THE MATERIALS

The nitrogen tetroxide was prepared by heating C.P. lead nitrate crystals. The water evolved was stopped in a small trap in the line, and the nitrogen tetroxide was then passed thru a phosphorus pentoxide drying tube and condensed in a tube immersed in an ice-salt mixture. This tube was then sealed off from the generating apparatus, and in the first 20 runs was then connected directly to the apparatus used in determining the rate of decomposition. In the later runs the nitrogen tetroxide was distilled under reduced pressure into a reservoir permanently sealed to the rate apparatus and containing phosphorus pentoxide. The ozone was prepared from Linde tank oxygen dried by passing over phosphorus pentoxide, using a Siemens ozonizer.

APPARATUS AND METHOD OF PROCEDURE

The preparation of the nitrogen pentoxide and the analysis of the oxygen-ozone mixture were made as described by White and Tolman. An oxygen-ozone mixture containing from 3% to 6% of ozone was passed thru jet D, at the rate of from 100 to 150 cc. a minute, where it was allowed to react with nitrogen tetroxide coming from the reservoir C. The flow of nitrogen tetroxide was regulated by means of heater G so that it was just decolorized on reaching trap B. After sweeping out the apparatus for several minutes an ice-salt freezing mixture was placed around trap B to condense the solid nitrogen pentoxide. When

from 1 to 2 cc. of nitrogen pentoxide had been collected in B, which took from 1/2 to 2 hours, the nitrogen tetroxide source was shut off by sealing at constriction H. The pentoxide crystals were further purified by a continued sweeping with the oxygen-ozone mixture for a time varying from 10 minutes to over an hour. The freezing mixture around B was then replaced by a water-bath at temperatures varying from 0° to 30°C, depending on the partial pressure of the nitrogen pentoxide desired in the reaction vessel.

The exit gases were run into a wash bottle containing turpentine to absorb the ozone and nitrogen pentoxide, and then thru a water
aspirator. In the later runs the turpentine was abandoned because of
its explosive nature, and a hot tube M was substituted. This tube was
made by winding about 20 feet of number 22 chromel wire around 20 inches
of asbestos-covered 1/4-inch pyrex glass tubing, and operated at 80 volts.
On passing thru this, the ozone and the nitrogen pentoxide were decomposed and the nitrogen tetroxide was in part dissolved in the water passing thru the aspirator.

When a considerable portion of the nitrogen pentoxide crystals had disappeared the flow of the gas mixture was stopped by shutting off the exygen supply at the tank. The reaction bulb A₁ was then sealed at the constrictions I. About 20 cm. of capillary tubing of 0.05 to 0.1 cm. bore between each of these constrictions and the reacting bulb prevented any considerably diffusion of the hot gases into the reaction vessel during the sealing off process. The pressure change was followed by means of an all-glass click gauge, F, as described by Smith and Taylor. 5

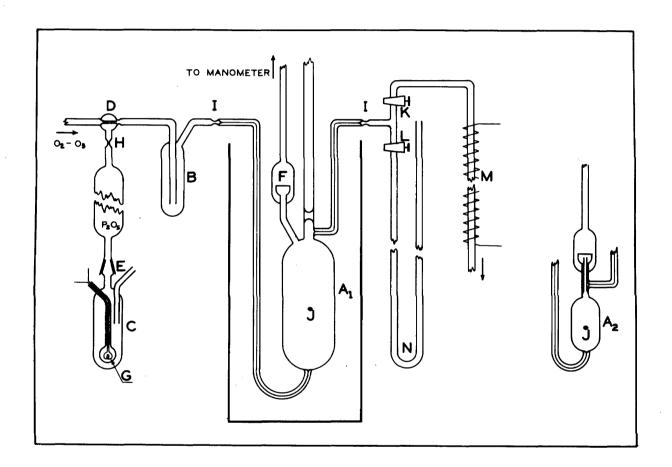


FIGURE 1

A thin bulb is blown in the end of a small pyrex tube, and is flattened in such a way that when the pressure difference between the inside and the outside of the bulb exceeds a critical value the flattened portion of the bulb buckles in, causing a click. This critical pressure for any given bulb was reproducible to 0.2 mm. or less. Three reaction vessels and click gauges were used in the course of the research. The first had a capacity of 320 cc. and a volume-to-surface ratio of about 1 cm. This was used in the first 14 experiments. At 35° the decomposition was so rapid that the time between the entrance of a sample of gas and its exit became a factor large in comparison to that of decomposition of the ozone; so in order to start with as high an initial ozone pressure as possible a bulb of 25 cc. capacity and a volume-to-surface ratio of 0.3 cm. was used. It was constructed as shown in the figure, 'A', in such a way that the gases had to traverse completely the space within the bulb and hence insure thorough sweeping out of the reaction vessel. This reaction vessel was used in experiments 15-24. The click diaphragm was broken in experiment 24; so a third bulb exactly like it was constructed and used in the rest of the experiments.

In order better to observe the appearance of the brown coloration at the start of the nitrogen pentoxide decomposition, the reaction bulb was silvered and then painted with optical black. Two small windows, J, 120° apart were then cut in this silver-paint layer. The contents of the bulb were illuminated by shining light from a 100-watt daylight bulb thru one of the openings, and a spot on the silvered wall

opposite the other opening was observed thru the latter. The brown color thus observed was much darker than that seem directly thru the bulb because of the multiple reflection which greatly lengthened the light path. It was found impossible to get a silvered surface that did not have a slight yellow coloration, due in part to the yellow cast of the glass itself; so the observation of the exact point at which the brown nitrogen dioxide started to form was not possible except in cases where the initial pressure of the nitrogen pentoxide was high.

The reaction vessel was immersed in a thermostat kept constant to within 0.01° and not more than 0.02° from the specified temperature as determined by a thermometer checked against a standard thermometer. The pressure readings were made at intervals of from 1/2 to 5 minutes until the nitrogen pentoxide decomposition was well under way. No stop-cocks were used in the gas train except in the exit tubes. However a ground glass joint (E) was used to connect the nitrogen tetroxide reservoir to the rest of the apparatus. DeKhotinsky cement, vaseline, and paraffin were used to seal this joint for the various experiments. The nitrogen dioxide reservoir was removed between experiments and sealed off. A glass plug was then used to close the apparatus.

In the first 24 experiments the oxygen flow was measured previous to ozonizing by means of a flowmeter using Nujol as the manometric liquid. In these same experiments a capillary sulfuric acid manometer was used in connection with the ozone analyzer. In the remaining runs a flowmeter with mercury as the manometric liquid was used and the ozone analyzer was eliminated.

COMPUTATION OF THE PARTIAL PRESSURES

Mall analyses were made from the pressure measurements. The manometer readings were corrected for the "click constant" and the pressures thus obtained were changes to millimeters of mercury at 0°. zero time was taken as that at which the nitrogen pentoxide decomposition started. To obtain this point the pressure was plotted against time using now the actual time and smooth curves were drawn thru the points. The point of intersection of the curve representing the ozone decomposition and that representing the nitrogen pentoxide decomposition determined the zero time as well as the pressure obtaining at that time. This gives a negative time scale for the ozone decomposition, which is used in all subsequent calculations. The ozone pressure at any time, t, is given by the expression, $P_{03} = 2(P_0 - P)$, where P is the pressure at time t and P_0 is that at time t = 0.

The shift in equilibrium between nitrogen tetroxide and nitrogen dioxide must be taken into consideration in evaluating the partial pressure of the nitrogen pentoxide in terms of changes in the total pressure. This was done by the graphical method of Daniels and Johnston, which consisted of making a plot on a large scale (1 cm. equivalent to 1 mm. change in pressure) of the change in the pressure of nitrogen pentoxide which corresponds to a change in the total pressure.

Calculations for constructing the plot were made in the following way. The total pressures at the time t=0, and t are given by the expressions

$$P_{o} = P_{o O_{2}} + P_{o N_{2}O_{5}}$$
 (5)

$$P = P_{O_2} + P_{N_2O_5} + P_{N_2O_4} + P_{NO_2}$$
 (6)

where P_{0} O_{2} and P_{0} $N_{2}O_{5}$ are the partial pressures of oxygen and nitrogen pentoxide at the time, t = 0, and $P_{O_{2}}$, $P_{N_{2}O_{5}}$, $P_{NO_{2}}$, and $P_{N_{2}O_{4}}$ are partial pressures at the time, t.

Combining (5) and (6) and letting Δ P equal the change in total pressure and Δ P_{N2O5} equal the change in partial pressure of nitrogen pentoxide, and considering the change in the oxygen pressure which results from the decomposition of nitrogen pentoxide, we obtain

$$\Delta P = P - P_0 = P_{N_2O_4} + P_{NO_2} - \frac{1}{2} \Delta P_{N_2O_5}$$
 (7)

Substituting

$$P_{N_2O_4} + P_{NO_2} = (1 + <) P_{N_2O_5}$$

in equation (7), where α is the degree of dissociation of nitrogen tetroxide, we obtain

$$P = (\frac{1}{2} + \alpha) P_{N_2 O_{55}}$$
 (8)

$$\frac{/-\alpha}{\alpha^2} = 8 \text{ K P}_{N_2 O_5},$$

using for K the value obtained from Schreber's equation?

$$\log K = \frac{2866}{T} - \log T - 9.132$$

and the plot described above, then construced in accordance with equation (8).

The partial pressure of the N2O5 at any given time is

$$P_{N_2O_5} = P_{O_1N_2O_5} - P_{N_2O_5}$$

The value of P_{0} $N_{2}O_{5}$ was determined by allowing the reaction to go to completion as shown by the constancy of the total pressure readings.

Osone Blanks: - Two runs, one at 25° and one at 35°, were made in which no nitrogen tetroxide was admitted. The ozone-oxygen mixture was passed thru the apparatus just as it was done in a regular experiment. A freezing bath was placed around the nitrogen pentoxide trap to freeze out any condensible impurities and this was replaced by a water bath at room temperature to drive these impurities over into the reaction vessel. In this way any catalyst, other than nitrogen pentoxide, that might effect the decomposition would be detected, since the thermal decomposition of ozone at these temperatures is negligible. In neither case was any appreciable pressure increase observed as shown by Table I.

TABLE I

| | $T = 25^{\circ} P_0$ | 03 = 35 mm. | | T = 35° | $P_{03} = 35 \text{ mm}.$ |
|--------------|----------------------|-------------|----------|---------|---------------------------|
| Time | Pressure | Time | Pressure | Time | Pressure |
| min | mm | m in | mm. | min | man |
| 0 | bulb sealed off | 40 | 742.9 | 0 | bulb sealed off |
| 1.7 | 742.8 | 55 | 742.9 | 1.3 | 738.8 |
| 2.4 | 742.9 | 80 | 742.9 | 2.8 | 738.1 |
| 3.1 | 742.9 | 120 | 742.9 | 4.7 | 738.1 |
| 3.1 7.5 | 743.0 | 290 | 742.9 | 10.0 | 737.65 |
| 19.3 | 742.9 | 400 | 742.9 | 16. | 737.7 |
| 19.3 25.6 | 742.9 | 26 hrs. | 742.9 | 25. | 737•7 |
| - | • | | | 50. | 737•7 |
| | | | | 5 day | |

An analysis of the ozone was made in each case. The high readings at the start of the 35° experiment may be due to a local heating of the gaseous mixture in the ends of the capillary in the sealing off process.

Catalysts might still be carried into the reaction vessel by the nitrogen tetroxide since this part of the apparatus was scaled off during these blank determinations. All substances used for scaling the ground glass joint were slowly acted upon by the nitrogen tetroxide; so that in the later experiments the nitrogen tetroxide container was finally scaled directly on to obviate any difficulty that might be arising from this point.* No effect on the experimental results was observed, nor was any effect observed as a result of using the different materials mentioned above for scaling the ground glass joint.

The Experiments at Atmospheric Pressure: - The experimental procedure adopted made it most convenient to carry out the experiments at a total pressure of one atmosphere. Of the 32 experiments performed, 26 were carried out in this way, 15 of which were at 25° and the rest at 35°. The 6 runs under reduced pressure will be taken up in a later section. The first 4 experiments were preliminary ones and their results are not included in the following. Experiments 14 and 15 were discarded because of leaks, due to imperfect sealing off of the reaction vessel, which were detected in trying to obtain the final pressures. The click gauge broke in the course of experiment 24. Four typical experiments are represented graphically in Figure 2, two at 25°, and two at 35° shown in figures 2a and 2b, respectively. It was not feasible to use the same scale in both cases; so the time scale used for the experiments at 35° is 5 times the other. In the original graphs a large scale was used for

^{*} All glass blowing then had to be done with the reservoir immersed in a freezing mixture. The glass blowing was always done thru a phosphorus pentoxide tube, taking care not to introduce more water vapor than necessary from the flame in making the various seals.

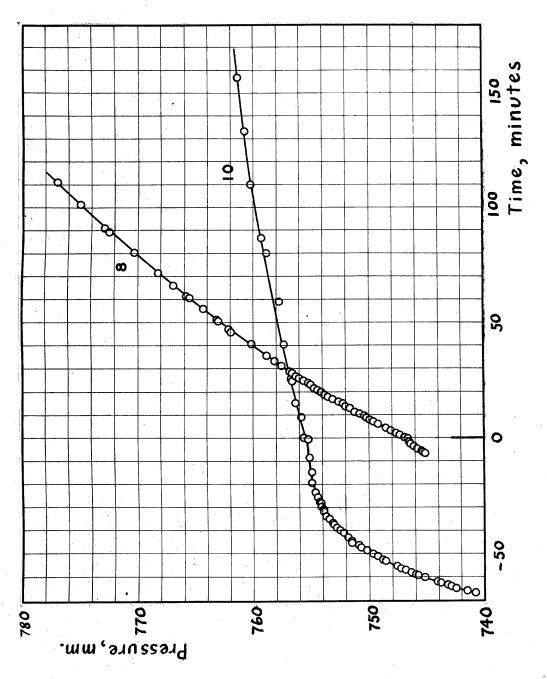
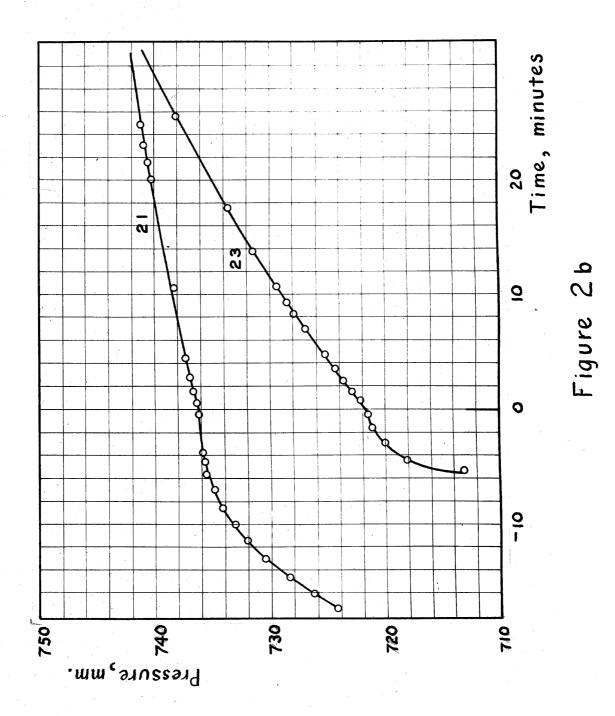


Figure 2a



the pressures, 1 cm. being equivalent to 1 mm. change in pressure, and in some cases a scale twice as large was used. It might be mentioned that the total pressures in experiment 21 have been lowered 25 mm. in making the plot. In experiments 8 and 23, the initial pressures of nitrogen pentoxide were comparatively high, 139 and 69 mm., respectively, and, accordingly, the ozone decomposition curve is short because at these high pressures the rate of ozone decomposition was so great that it was tery difficult to obtain the first pressure reading while an appreciable amount of ozone still remained. The initial pressures of nitrogen pentoxide were 17.8 and 19.8 mm., respectively, in experiments 10 and 21. At low initial pressures of nitrogen pentoxide the difficulty in finding the point that marked the end of the ozone decomposition was increased, partly because pressure changes were small, making the experimental error in their measurement large and partly because the brown color of nitrogen dioxide did not appear sharply as mentioned in a previous section.

Table 2 includes data for all the experiments except those discarded for the reasons mentioned above. Time is given in minutes, taking as zero time the time corresponding to the break in the decomposition curve. In the cases where the pressure of the nitrogen pentoxide is omitted calculations were not carried out for its decomposition. In experiment 28 the final pressure reading was not obtained; so the initial pressure of nitrogen pentoxide was calculated from the specific reaction rate and from the measured rate of decomposition of the pentoxide. The values obtained from the last 5 experimental points checked within

4 percent; and their average is certainly not more than 5 percent from the true value, judging from the precision with which similar calculations could be made in other experiments. In experiments 12 and 29 the points marking the start of the nitrogen pentoxide decomposition are very indefinite. Too small portions of the ozone decomposition curves were obtained in experiments 6, 7, 13, and 19 to be of value in any further calculations concerning the ozone decomposition.

TABLE II
Temperature = 25°C

| Experim | ent | 5 | |
|---------|-----|------|-----|
| Po N205 | - | 23.7 | mm. |

| t | P | P03 | P _{N2} 05 | t | P | P ₀₃ | P _{N2} 05 |
|--------------------|----------------|---------------------|--------------------|----------------|-------|-----------------|--------------------|
| <u>min</u> 40.0 | 741.7 | <u>mm</u> . 11.6 | mn. | 102.5 | 753-4 | | 19.4 |
| 36.5 | 743.8 | 7.4 | • | 132.5 | 755.0 | | 18.1 |
| 32.5 | 744.9 | 5.2 | | 16 2. 5 | 756.1 | | 17.2 |
| 29.5 | 745.6 | 3.8 | | 182.5 | 756.9 | | 16.3 |
| 26.5 | 745.9 | 3.2 | | 212.5 | 757.8 | | 15.75 |
| 23.5 | 746.3 | 2.4 | | 432.5 | 763.9 | | 10.25 |
| 20.5 | 746.7 | 1.6 | | | | | • |
| 16.5 | 747.0 | 1.0 | | 00 | 774.2 | | 0. |
| 13.5 | 747.2 | •6 | | | | | |
| 10.5 | 747.3 | -4 | | • | | | |
| 7.5 | 747.3 | .4 | | | - | | |
| - 2.5 | 747.4 | .2 | 27.7 | | | | |
| 0. | 747.5 | 0. | 23.7 | | | | |
| + 2.5 | 747•9 748•1 | | 23.4 | | | | |
| 7•5 12•5 | 748.3 | | 23.3 23.1 | | | | |
| 18.5 | 748.9 | | 22.7 | | | | |
| 23.5 | 749.1 | | 22.55 | | | | |
| 27.5 | 749.5 | | 22.3 | | | | |
| 32.5 | 749.7 | | 22.15 | | • | | |
| 37.5 | 749.9 | | 22.0 | | | | |
| 43.5 | 750.0 | | 21.9 | | | | • |
| 54.5 | 750.7 | | 21.4 | | | | |
| 57.5 | 750.8 | | 21.35 | | | | |
| 63.5 | 751.2 | • | 21.05 | | | | |
| 72.5 | 751.4 | | 20.9 | | | | |

| Experiment 6 | | | Experiment 7 | | | | |
|---------------------------|------------------------|-----------------|----------------------|--------------|-----------------------------|-----------------|-------------------|
| $P_0 N_{205} = 110.1 mm.$ | | | | Po N205 | $P_{0 N_2 O_5} = 128.4 mm.$ | | |
| t , | P | P ₀₃ | P _{N2} 05 | t | P | P ₀₃ | P _{N205} |
| 6.8 4.7 | 744.0 744.5 | 2.4 1.4 | | 7.8 7.4 | 743•3 743•3 | 3.8 3.8 | • |
| 1.6 | 744.9 | .6 | | 7.0 | 743.2 | 3.8 | |
| 7 | 745.1 | .2 | | 6.3 | 743.3 | 3.8 | |
| 0.0 | 745-2 | 0.0 | 110,1 | 5•5 | 744.1 | 2,2 | |
| + .6 | 745.4 | * | 109.9 | 5.0 | 744.3 | 1.8 | |
| 2.6 | 746.0 | | 109.5 | ਸ਼ੇ• ਸ਼ੋ | 744.5 | 1.4 | |
| 5. 6. | 747.0 | | 108.5 | 3.8 | 744.6 | 1.2 | |
| 7.9 | 747.6 | | 108.4 | 3.4 | 744-7 | 1.0 | |
| 10.5 | 748.4 | | 107.8 | - 1.6 | 745.0 | .4 | 100 1 |
| 14.5 | 749.4 | | 107.1 | 0.0 + .6 | 745.2 | D. 0 | 128.4 128.2 |
| 16.6 | 749.9 | | 106.7 | + .6 2.4 | 745·5 746.1 | | 127.7 |
| 19.1 22.8 | 750.9 | | 105.9 | 3.5 | 746.4 | | 127.6 |
| | 751.6 | | 105.4 104.8 | 4.5 | 746.8 | | 127.2 |
| 25.4 28.8 | 752•3 753•3 | | 104.8 | 5.3 | 747.0 | | 127.1 |
| 31.5 | 754.1 | | 103.3 | 6.0 | 747.3 | | 126.9 |
| 36.0 | 755.1 | | 102.5 | 7-3 | 747.9 | | 126.5 |
| 40.6 | 756.2 | | 101.5 | 9.2 | 748.4 | | 126.1 |
| 46.3 | 757-3 | | 100.6 | 10.2 | 748.7 | | 125.9 |
| 51.7 | 758.5 | | 99.5 | 10.8 | 748.9 | | 125.7 |
| 61.9 | 760.9 | | 97.3 | 11.4 | 749.0 | | 125.7 |
| 73.0 | 763.1 | | 95.2 | 13.7 | 749.7 | | 125.2 |
| 77.9 | 764.0 | | 94.3 | 14.4 | 749.9 | | 125.0 |
| 79-3 | 764.4 | | 93 .9 | 17.8 | 751.2 | | 124.0 |
| 89.2 | 766.2 | | 92.1 | 18.5 | 751.4 | | 123.8 |
| 97.8 | 767.8 | | 90.5 | 22.2 | 752.6 | | 122.9 |
| 111.3 | 770.3 | | 88.0 | 23.1 | 752.8 | | 122.7 122.6 |
| 117.3 126.7 | 770. 8 772.6 | | 87.5 | 23.7 28.1 | 753.0 754.2 | | 121.6 |
| 128.5 | 772.9 | | 85.6 85. 3 | 28.9 | 754.4 | | 121.4 |
| 166.5 | 778.7 | | 79.0 | 32.8 | 755-2 | | 120.7 |
| 167.8 | 779.0 | * | 78.7 | 33.5 | 755.4 | | 120.5 |
| 191.7 | 782.3 | | 74.9 | 42.5 | 758.1 | | 118.1 |
| 196.7 | 782.9 | | 74.2 | 43.1 | 758.3 | | 118.0 |
| 246.5 | 789.2 | | 67.0 | 59.3 | 762.3 | | 114.3 |
| 250.2 | 789.5 | | 66.7 | 60.1 | 762.4 | | 114.2 |
| | | * | • | 76.0 | 766.1 | | 110.5 |
| ∞ | 841.4 | | 0.0 | 124.5 | 776.2 | • | 100.1 |
| | | | | 126.2 | 776.4 | | 99.9 |
| | | • | | 197.5 | 788.0 | | 86.7 |
| | | | , | 202.5 | 788.0 | | 85. 8 |
| | | | | 350.5 | 807.0 | | 63.7 |
| | | | | ∞ | 854.6 | | 0.0 |

| Experim Po N ₂ O ₅ | | Experiment 8 (cont.) Po N205 = 138.8 | | | | | | |
|--|---|--------------------------------------|---|--|--|-----------------|---|--|
| · t | P | P ₀₃ | P _{N205} | t | P | P ₀₃ | P _{N2} 05 | |
| 6.6.54.3.2.1.0.1.2.3.4.6.7.8.9.9.8.5.2.9.3.0.1.2.0.1.1.9.3.2.1.1.5.1.5.6.9.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1 | 745.1.4.56.6.9.36.1.526.92.4.8.26.0.26.1.58.1.4.7.0.26.0.36.8.4.1.8.1.9.1.34.8.1.4.56.6.9.36.1.526.92.4.8.26.0.26.1.58.1.4.7.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.26.0.26.0.36.8.4.1.8.1.9.1.26.0.26.0.26.0.26.0.26.0.26.0.26.0.26 | 3.6 2.4 1.6 1.90 0.0 | 138.6 138.6 138.6 138.7 137.6 136.5 137.6 137.6 137.6 137.7 137.6 137.7 | 50.9 51.6 56.4 61.1 61.9 66.5 72.0 80.9 89.9 91.7 101.9 111.7 200.4 201.4 365 562 1460 2730 | 763.0 763.1 764.3 765.5 766.9 766.9 772.9 772.9 775.0 793.1 814.3 858.4 862.7 863.3 | | 125.5 125.4 124.3 123.1 122.8 121.6 120.8 116.2 115.8 113.6 111.3 92.9 92.7 66.6 39.8 7.1 1.1 | |

Temperature 25°C

| Experiment 9 | | | Experiment 10* | | | | |
|--------------|----------------|-----------------|-------------------------------|-------------------------------|----------------|-----------------|-------------------|
| Po N205 | = 46.0 mm | 1. | $P_{0 N_{2}O_{5}} = 17.8 mm.$ | | | | |
| t | P | P ₀₃ | P _{N205} | t | P | P ₀₃ | P _{N205} |
| 29.6 | 741 | 21.2 | | 66.7 | 740.8 | 29.0 | |
| 28.2 | 742.2 | 19.4 | | 6 5. 8 | 741.5 | 27.6 | |
| 27.0 | 743.1 | 17.6 | | 64.7 | 742.5 | 25.6 | |
| 25.3 | 744.6 | 14.6 | • | 63.2 | 743.2 | 24.2 | |
| 23.7 | 746.0 | 11.8 | | 61. g | 744.1 | 22.4 | |
| 22.0 | 747.0 | 9.8 | | 5 8.9 | 745.8 | 19.0 | |
| 19.9 | 748.2 | 7.4 | | 57•5 | 746.4 | 17.8 | |
| 18.5 | 748.9 | 6.0 | | 55•7 | 747•3 | 16.0 | |
| 15.1 | 749-9 | 4.0 | | 53.9 | 748.0 | 14.6 | |
| 14.0 | 750.2 | 3.4 | | 52.0 | 748.8 | 13.0 | |
| 12.2 | 750.8 | 2.2 | | 49.7 | 749.7 | 11.2 | |
| 10.7 | 751.0 | 1.8 | | 46.8 | 750.7 | 9.2 | |
| 9.8 | 751.1 | 1.6 | | 114.8 | 751.5 | 7.6 | |
| 8.7 | 751.2 | 1.4 | | 43.3 | 751.6 | 7.3 | |
| 7.6 | 751.4 | 1.0 | | 41.5 | 752.0 | 6.6 | |
| 6.7 | 751.5 | . క | | 39.4 | 752.5 | 5.6 | |
| 5.8 | 751.5 | . g | | 38.2 | 752.8 | 5.0 | |
| 4.8 | 751.7 | .4 .2 | | 37.4 | 752.9 | 4.7 | |
| .4 1 | 751.8 | 0.0 | | 36.2 | 753 .1 | 4.4 4.0 | |
| 0.0 | 751.9 751.9 | 0.0 | 46.0 | 35• <i>3</i> 34 . 6 | 753•3 753•4 | 3.8 | |
| + .3 | 752.0 | 0.0 | 45.9 | 33.4 | 753.6 | 3 .3 | |
| 3.4 | 752.9 | | 45.3 | 31.9 | 753.8 | 3.0 | |
| 5.Ц | 752.9 | | 45.3 | 31.3 | 753.9 | 2.8 | |
| 5.4 6.3 | 753.0 | | 45.2 | 30.3 | 753.9 | 2.8 | |
| 7.7 | 753-2 | | 45.1 | 29.3 | 754.0 | 2.5 | |
| 10.7 | 753.4 | | 44.9 | 27.7 | 754.1 | 2.4 | |
| 14.9 | 753.9 | | 44.6 | 27.1 | 754.2 | 2.2 | |
| 20.4 | 754.4 | | 44.2 | 25.2 | 754.4 | 1.8 | |
| 26.1 | 755.1 | | 43.7 | 23.0 | 754.6 | 1.4 | |
| 27.2 | 755.2 | | 43.6 | 1ģ. g | 754.9 | . 8 | |
| 3 7-5 | 756.4 | | 42.8 | 14.4 | 754.9 | .8 | |
| 48.2 | 757.4 | | 42.0 | - 8.0 | 755.0 | • 5 | |
| 59•3 | 758-5 | | 41.1 | 0.0 | 755 -3 | .2 | |
| 68.1 | 759-3 | | 40.5 | 0.0 | 75 5•3 | 0.0 | 17.8 |
| 70.2 | 759-5 | | 40.3 | + .7 | 755.6 | | 17.6 |
| 89.4 | 761.3 | | 38 . 8 | 9.4 | 755 . 8 | | -17-5 |
| 115.1 | 763.3 | | 37.1 | 16.4 | 756.3 | | 17.1 |
| 116.6 | 763.5 | | 36.9 | 25.0 | 756.6 | | 16.9 |
| 160;1 | 766.8 | | 32.9 | 25.9 | 756.7 | | 16.8 |
| 290 | 774.6 | | 26.3 | 40.7 | 757+3 | | 16.3 |
| 428 | 780.6 | | 20.2 | 59.2 | 757 • 7 | | 16.0 |
| 1083 | 793-5 | | 5.7 | 80.3 | 758.8 | | 15.1 |
| ∞ . | 798.5 | | 0.0 | 87.0 | 759.2 | | 14.8 |

TABLE II (cont.)

| Experime | ent 10* (c | ont.) | | Experim | ent 11 (co | nt.) | |
|----------------------------------|----------------|-----------------|-------------------|----------------|----------------|--------------|--------------|
| Po N205 | = 17.8 mm | i. | | Po N2Os | = 35.2 m | ١. | |
| t | P | 10 | 70 | | | | |
| U | r | P ₀₃ | P _{N205} | t | P | P03 | $P_{N_2O_5}$ |
| 110.4 | 760.2 | | 14.0 | 32.4 | 760.35 | | 32.8 |
| 128.7 | 760:7 | | 13.7 | 42.1 | 761.0 | | 32.3 |
| 146.9 | 761.3 | | 13.2 | 52.3 | 761.75 | | 31.9 |
| 190 | 762.7 | | 12.1 | 66.4 | 762.7 | | 31.0 |
| 224 | 763.7 | | 11.3 | 80. 8 | 763.85 | | 30.2 |
| 917 | 773.6 | | 2.6 | 92.3 | 764.7 | | 29.4 |
| ~ | | | | 96.2 | 765.1 | | 29.1 |
| ~ | 776.3 | | 0.0 | 117.1 | 766.3 | | 28.1 |
| | | | | 148.5 | 768.4 | | 26.3 |
| | | | | 195.1 | 770.9 | | 24.1 |
| Warm a statement | -m.4. 3.3 | | | 275.5 | 774-7 | | 20.5 |
| Experime | | _ | | 301 | 775-7 | | 19.5 |
| Po N ₂ O ₅ | = 35.2 mm | 1. | | 432 | 780.2 | | 15.0 |
| 35.0 | 745.5 | 23.0 | | ∞ | 794.2 | | 0.0 |
| 34.1 | 746.2 | 21.6 | | | 13.02 | | ••• |
| 33-3 | 746.8 | 20.4 | | | | | |
| 31.7 | 748.2 | 17.6 | | | | | |
| 31.0 | 748.6 | 16.7 | | Experim | ent 12 | | |
| 29.2 | 749.6 | 14.8 | | Po NaOs | = 9.5 mm. | | |
| 27.9 | 750.7 | 12.6 10.8 | | , | | | |
| 26.3 24.7 | 751.6 752.5 | 9.0 | | 105.9 | 742.7 | 28.4 | |
| 21.3 | 753.9 | 6.2 | | 105.4 | 742.9 | 28.0 | |
| 19.7 | 754.4 | 5.2 | | 104.6 | 743.1 | 27.6 | |
| 18.8 | 754.7 | 4.5 | | 103.6 | 743.6 | 26. 6 | |
| 15.7 | 755-5 | 3.0 | | 102.8 101.9 | 743.8 744.1 | 26.2 | |
| 12.6 | 756.0 | 2.0 | | 100.8 | 744.6 | 25.6 24.6 | |
| 10.7 | 756.3 | 1.4 | | 98.9 | 745.2 | 23.2 | |
| 9.7 | 756.45 | 1.1 | | 98.4 | 745.6 | 22.6 | |
| 8.8 | 756.55 | .9 | | 96.3 | 746.1 | 21.6 | |
| 6.6 | 756.75 | •5 | | 93.2 | 747.3 | 19.2 | |
| 3.9 | 756.85 | •3 | | 90.9 | 748.0 | 17.8 | |
| - 3.1 | 756.85 | •3 | | 88.4 | 748.8 | 16.2 | |
| 0.0 | 757.0 | 0.0 | 35.2 | 85.4 | 749 • 7 | 14.4 | |
| + 3.0 | 757-35 | | 35.0 | 81.2 | 750.6 | 12.6 | |
| 4.4 | 757 • 55 | | 34. g | 78 .8 | 751.2 | 11.4 | |
| 5.0 | 757.65 | | 34.8 | 75.3 | 751.9 | 10.0 | * |
| 6.7 | 757.85 | | 34.65 | 71.7 | 752.7 | 8.4 | |
| 8.8 | 758.05 | | 34.5 | 66.5 | 753•7 | 6.4 | |
| 11.9 | 758.25 | | 34.3 | 61.7 | 754.2 | 5.4 | |
| 24.7 | 759-55 | | 3 3.4 | 59.9 | 754.6 | 4.6 | |

| | ent 12 (con = 9.5 mm. | t.) | | Experime | ent 28 (co | nt.) | |
|--|--|---|-------------------|---|---|-----------------|--|
| ·t | P | P ₀₃ | P _{N205} | t | P | P ₀₃ | P _{N205} |
| 55.7 51.8 46.9 38.8 30.8 27.5 18.8 - 4.7 0.0 +11.7 26.7 42.0 101 164 385 | 754.9 755.2 756.0 756.1 756.2 756.3 756.7 756.9 757.2 757.9 759.8 763.9 | 4.0 3.4 2.6 1.8 1.6 1.4 1.1 | 9•5 | + .4 1.7 2.6 3.3 4.5 6.0 7.1 8.5 11.4 12.8 15.7 17.1 21.3 22.8 | 759.85 760.25 760.6 760.8 761.0 761.6 762.1 762.7 763.1 763.1 765.1 765.3 765.5 | | 89.3 89.0 88.6 88.5 88.7 87.7 87.3 86.5 86.5 86.5 |
| ∞ | 769.0 | | | 30.9 31.9 42.7 | 766.5 766.8 76 8.8 5 | | 84.4 84.1 8 5. 5 |
| Experim | ent 28 | | | 44.3 59.5 | 769.2 771.8 | | 82.2 79.9 |
| | = 89.4 mm. | (calc.) | | 60.4 | 762.0 | | 79•7 |
| 0 N ₂ U ₅ | | (, | | 90.0 | 777.05 | | 75.1 |
| 16.7 | 750.45 | 18.6 | | 91.5 | 777.25 | | 74.9 |
| 15.6 | 751.65 | 16.2 | | 104.3 | 779-15 | | 73.0 |
| 14.7 | 752.75 | 14.0 | | 106.1 | 779-4 | | 72.8 |
| 14.1 | 753-55 | 12.4 | | 169 | 787.85 | | 64.2 |
| 13.2 | 754-45 | 10.6 | | 170 | 787.95 | | 64.1 |
| 12.5 | 755-2 | 9.1 | | 202 | 792.6 | | 59.1 |
| 11.7 | 755.95 | 7.6 | | 204 | 792.8 | | 58.8 |
| 10.9 | 756.4 | 6.7 | | 252 | 797.6 | | 53.4 |
| 10.2 | 756.9 | 5.7 | ٠ | 254 | 797.6 | | 53.4 |
| 9.0 | 757-45 | 4.6 | | | | | |
| 8.1 | 757.9 | 3.7 | | | | | |
| 6.5 | 758.6 | 2.3 | | | | | |
| 5.7 | 758 . 9 | 1.7 | | | | | |
| 5.1 | 759.1 | 1.3 | | | | | |
| 4.0 3.1 | 759-2 | 1.1 | | | | • . | |
| 2.1 | 759.4 | • 7 | | | | | |
| | 759-5 | • 🤊 | | | | | |
| 1.3 | 759.6 | ·5 ·3 ·1 | | | | | |
| 6 | 759 - 7 | | do h | | | | |
| 0.0 | 759•75 | 0.0 | 89.4 | | | | |

Temperature = 25°C

Experiment 29*

| Po N205 | = 18.0 m | n. | |
|---|---|--|-------------------|
| t | P | P ₀₃ | P _{N205} |
| 78.62 77.75.7 76.64.50 70.7 77.7 77.7 77.7 77.7 70.7 70.7 7 | 749.0 750.3 752.1 753.9 756.4 757.5 760.6 762.9 763.5 767.5 767.9 768.4 769.2 769.3 769.3 770.1 770.4 770.4 772.6 | 40.6 34.8 30.8 25.6 21.2 15.4 10.9 6.5 5.6 6.1 6.1 6.1 6.1 6.1 6.1 6.1 6 | 18.0 |
| 00 | 790.3 | | |

| Experiment 13 Po N205 = 88.8 mm. | | | m Experime Po N ₂ O ₅ | ent 16 = 25.3 mm | • | |
|---|----------------------------------|---|---|--|---|---|
| t P | P ₀₃ | P _{N205} | t | P | POB | $P_{N_2O_5}$ |
| t P 2.2 740.3 1.5 740.9 -1.2 740.9 0.0 740.9 1.1 742.0 2.0 748.8 2.9 743.9 2.0 744.9 4.5 745.5 5.1 745.9 5.6 746.4 6.1 746.8 7.8 748.0 8.4 748.8 10.1 750.1 11.0 750.9 16.2 755.1 20.8 758.3 29.3 764.9 106.0 797.3 143.3 806.3 203.5 823.8 370.8 827.8 420.8 832.1 ≈ 832.1 | P ₀ 3 1.2 0.0 0.0 0.0 | P _{N2} 0 ₅ 88.88.1 87.72.6 88.89.7 86.26 87.77 70.1 88.89.2 88.3 89.2 89.3 89.3 89.3 89.3 89.3 89.3 89.3 89.3 | 143.2.2.5353358914702406 21995297413046195165664 143.2.53535358914702406 21995297413046195165664 | 748.56.38.32.16.91.356.77777777777777777777777777777777777 | Pos 20.2 17.2 15.0 11.6 7.8 4.0 3.4 2.0 1.2 1.0 0.0 | 25.2 8 7 5 3 2 2 4.7 5 3 2 2 2 3 .1 0 2 2 2 2 3 .1 0 2 2 2 2 1 .3 0 0 0 18.6 16.6 12.5 10.0 |
| · | | | 155.4 • | 780.0 78 8. 4 | | 7·5 0.0 |

| Experim Po N205 | ent 17 = 4.4 mm. | Experiment 17 (cont.) | | | | | | |
|--|---|--|--------------|--|---|-----------------|-------------------|--|
| t | P | P03 | $P_{N_2O_5}$ | t | P | P ₀₃ | P _{N205} | |
| 46.6 5 7 9 7 8 9 8 8 8 1 4 6 6 5 7 6 5 4 0 8 1 5 9 8 7 7 5 7 2 7 8 0 0 2 4 3 4 2 3 5 6 6 5 7 6 5 4 0 8 1 5 9 8 7 7 5 7 2 7 8 0 0 2 4 3 4 2 3 5 6 6 5 7 6 5 4 0 8 1 5 9 8 7 7 5 7 2 7 8 0 0 2 4 3 4 2 3 5 6 6 6 5 7 6 5 4 0 8 1 5 9 8 7 7 5 7 2 7 8 0 0 2 4 3 4 2 3 5 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 | 745.10 31 72 96 1 377 777 755.10 31 72 96 1 377 777 777 777 777 777 777 777 777 7 | 27.1 26.1 25.1 25.1 27.1 27.1 27.1 27.1 27.1 27.1 27.1 27 | | - 2.9 - 0.0 + 1.0 5.1 10.1 12.1 12.1 12.1 12.1 12.1 146.3 146 | 758.05 758.05 758.2 758.2 758.25 758.5 758.85 758.85 759.7 758.85 759.7 760.15 760.15 764.1 764.1 | 0.0 | 4.4 | |
| 12.2 11.4 10.3 9.4 8.2 | 757•7 757•75 757•9 757•95 758•0 | • 7 • 6 | | | | | | |

| $\begin{array}{c ccccccccccccccccccccccccccccccccccc$ | Experiment 18 | | | | Experiment 18 (cont.) | | | | |
|---|---------------|--------|-----------------|--------------|-----------------------|---------|-----------------|--------------|--|
| 25.3 747.2 23.7 52.3 766.3 23.6 749.3 19.5 62.9 767.2 22.2 751.0 16.1 92.9 769.2 20.3 752.7 12.7 107.6 770.3 18.8 754.1 9.9 132 771.6 17.5 755.0 8.1 134 771.7 15.8 756.0 6.1 13.4 756.75 4.6 777.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 Po N ₂ O ₅ = 77.5 mm. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | Po N205 | = 13.7 | m. | | | • | | | |
| 23.6 749.3 19.5 62.9 767.2 22.2 751.0 16.1 92.9 769.2 20.3 752.7 12.7 107.6 770.3 18.8 759.1 9.9 132 771.6 17.5 755.0 8.1 134 771.7 15.8 756.0 6.1 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 $P_0 N_2O_5 = 77.5 mm$. 8.2 758.3 1.5 4.6 747.6 | t | P | P ₀₃ | $P_{N_2O_5}$ | t | P | P ₀₃ | $P_{N_2O_5}$ | |
| 23.6 749.3 19.5 62.9 767.2 22.2 751.0 16.1 92.9 769.2 20.3 752.7 12.7 107.6 770.3 18.8 759.1 9.9 132 771.6 17.5 755.0 8.1 134 771.7 15.8 756.0 6.1 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 $P_0 N_2O_5 = 77.5 mm$. 8.2 758.3 1.5 4.6 747.6 | 25.3 | 747.2 | 23.7 | | 52.3 | 766.3 | | | |
| 22.2 751.0 16.1 92.9 769.2 20.3 752.7 12.7 107.6 770.3 18.8 754.1 9.9 132 771.6 17.5 755.0 8.1 134 771.7 15.8 756.0 6.1 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 Po N ₂ O ₅ = 77.5 mm. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | | | | 767.2 | | | |
| 20.3 752.7 12.7 107.6 770.3 18.8 754.1 9.9 132 771.6 17.5 755.0 8.1 134 771.7 15.8 756.0 6.1 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 Po N ₂ O ₅ = 77.5 mm. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | | | | 769.2 | | | |
| 18.8 754.1 9.9 132 771.6 17.5 755.0 8.1 134 771.7 15.8 756.0 6.1 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 Po N ₂ O ₅ = 77.5 mm. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | | | | | | | |
| 17.5 755.0 8.1 134 771.7 15.8 756.0 6.1 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 $P_0 N_2O_5 = 77.5 mm$. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | 10.5 | | | | | 771.6 | | | |
| 15.8 756.0 6.1 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 $P_0 N_2O_5 = 77.5 mm$. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | | | | 771.7 | | | |
| 13.4 756.75 4.6 777.1 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 $P_0 N_2O_5 = 77.5 mm$ 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | 756.0 | 6.1 | | - 54 | 111 | | | |
| 13.5 757.0 4.1 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 Po N ₂ O ₅ = 77.5 mm. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | h 6 | | 00 | 777.1 | | | |
| 12.0 757.6 2.9 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 Po N205 = 77.5 mm. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | | | | 111 | | | |
| 10.8 757.9 2.3 Experiment 19 9.6 758.05 2.0 $P_{0 N_{2}O_{5}} = 77.5 \text{ mm}$ 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | | | | | | | |
| 9.6 758.05 2.0 $P_{0 N_{2}O_{5}} = 77.5 \text{ mm}$. 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | | | | | Ernari | ment 19 | | | |
| 8.2 758.3 1.5 7.1 758.45 1.2 4.6 747.6 | 10.8 | | | | | | m. | | |
| 7.1 758.45 1.2 4.6 747.6 | | | | | -0 N ⁵ O | 5 | | | |
| | | | 1.9 | | 4.6 | 747-6 | | | |
| 5.2 (50.0 ·y | | | 1.2 | | | | | | |
| 1 m 1 n n n n n n n n n n n n n n n n n | | | • 5 | | - 1.7 | 747.6+ | | | |
| 3.8 758.75 .6 - 1.7 747.5° 2.9 758.85 .4 0.0 747.4 0.0 77.5 | | | •0 | | , | 7)17)1 | 0.0 | 77 E | |
| | | | •4 | | | | 0.0 | | |
| | | | | | | | | 75.6 | |
| | | | | | 2.0 | | | 7)1 6 | |
| | | | 0.0 | 13.7 | 9.0 | | | | |
| + 1.3 759.2 8.3 753.85 72.9 | | | • | | 8.5 | | • | | |
| 2.0 759.5 10.6 755.4 71.8 | | | | | | | | | |
| 3.2 759.75 13.0 757.2 70.5 | | | | | | | | (0.5 | |
| 4.1 759.85 16.3 759.6 68.6 | | | | | | | • | | |
| 4.9 759.95 17.8 760.6 67.8 | | | | | | | | 6/.8 | |
| 5.5 759.95 19.6 761.9 66.7 6.4 760.15 29.7 767.95 61.7 | 5-5 | 759•95 | | | | | | 66.7 | |
| | | | | | | | | 61.7 | |
| 7.8 760.75 31.2 768.5 61.3 | 7.8 | 760.75 | | | | | | | |
| 9.2 760.9 44.0 775.4 55.2 | 9.2 | 760.9 | | | | 775.4 | | 55.2 | |
| 11.0 761.05 45.7 776.4 54.3 | 11.0 | | | | | | | 54.3 | |
| 12.0 761.15 71.8 787.1 44.3 | 12.0 | 761.15 | | • | | | | | |
| 12.6 761.25 80.8 790.3 41.1 | 12.6 | 761.25 | | | | | | | |
| 14.4 761.45 82.3 790.8 40.6 | 14.4 | 761.45 | | | | | | | |
| 15.5 761.65 93.0 794.1 37.3 | | | | | | | | | |
| 16.1 761.7 94.5 794.55 36.8 | | | | | 94.5 | | | | |
| 17.1 761.85 107 799.1 32.2 | | | | | | | | | |
| 19.4 762.25 161 809.4 21.5 | | 762.25 | | | | | | | |
| 20.5 762.25 164 809.6 21.3 | - | | | | 164 | | | | |
| 23.0 762.8 172 811.0 19.8 | | 762.8 | | | 172 | 811.0 | | 19.8 | |
| 30.3 763.75 175 811.6 19.1 | | | | | | 811.6 | | 19.1 | |
| 36.8 764.45 | | 764.4F | | | | • | | - | |
| 41.5 765.15 ∞ 829.7 0.0 | | | | | ~ | 829.7 | | 0.0 | |
| 44.2 765.5 | | | | | | - • | | | |

TABLE II (cont.)

| Experim Po N ₂ O ₅ | | | | Experiment 21 $P_0 N_2 O_5 = 19.8 mm$. | | | | |
|---|--|-----|--|--|---|---|--|--|
| t | P | P03 | P _{N2} 05 | t | P | P ₀₃ | P _{N2} 05 | |
| 2422014555617203373246753051337 - + 1234568172033732467530513537 | 749.6 751.9 751.9 752.3 7552.4 7555.1 7556.1 7556.1 757.5 757.5 760.5 764.7 766.7 766.7 777.8 777.8 777.8 777.8 778.7 786.7 | 5.4 | 43.9 42.9 41.0 | 17.9 15.9 19.5 19.5 19.5 19.5 19.5 19.5 19 | 749.3 751.3 753.4 755.5 757.05 758.1 759.9 760.7 760.9 761.2 761.3 762.4 763.3 765.9 765.9 766.1 769.5 774.2 786.4 786.4 | 23.8 19.8 15.6 11.4 8.3 6.2 4.0 2.6 1.2 1.0 0.0 | 19.8 19.7 19.5 19.3 19.1 19.0 18.4 17.7 16.8 16.5 16.4 14.1 | |
| • | 802.4 | | 0.0 | | | | | |

| Experiment 22. | | | Experime | | | | |
|--|---|--|-------------------|---|--|--|--|
| Po N2O5 | = 15.7 mm | • | | Po N ₂ O ₅ | = 68.5 mm | • | |
| t | P | P ₀₃ | P _{N205} | t | P | P ₀₃ | P _{N205} |
| 22.0.73.62.2.0.8.6.7.1.4.7.8.0.2.2.6.0.5.4.2.2.4.4.2.1.0.0.9.8.9.7.1.3.9.0.1.2.3.4.5.6.7.8.9.9.3.1.3.9.0.1.2.3.4.5.6.7.8.9.9.3.1.3.9.0.1.2.3.4.5.6.7.8.9.9.3.1.3.9.0.1.3.9.0.1.2.3.4.5.6.7.8.9.9.3.1.3.9.0.0.1.3.9.0.0.1.3.9.0.0.1.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0.0 | 736.6.6.7777777777777777777777777777777 | 30.2 24.4 21.0 17.8 14.8 5.2 1.4 1.8 1.4 1.8 1.4 1.8 1.4 1.0 0.0 | 15.7 | 5.4.9 - 6.0 - 6.0 - 6.0 - 7.5 - | 713.1 718.1 720.0 721.1 721.6 721.6 722.1 723.6 724.3 725.2 726.9 728.45 733.55 738.05 738.05 757.9 758.35 768.35 768.65 | 17.0 7.0 3.2 1.0 .2 0.0 | 68.1 66.1 66.0 66.0 66.0 66.0 66.0 66.0 66 |

The Runs at Reduced Pressure: - The thermal decomposition of ozone is not only second order with respect to the ozone concentration but its rate is also proportional to the reciprocal of the first power of oxygen pressure. To see whether oxygen had this inhibiting effect on the catalyzed decomposition some experiments were carried out at reduced pressure. Three experiments were made at a total pressure of 1/2 atmosphere and three at 1/4 atmosphere, two of which had too low initial nitrogen pentoxide pressures to enable the changes in pressure to be measured with any reasonable degree of accuracy, and hence to allow the determination of the point of inflection on the curves. experiments were all made at 25°. The experimental procedure had to be modified somewhat in making these runs. A mercury manometer, N, Fig. 1, was connected to the tube leading from the reaction bulb. After stopping the flow of the gas mixture the constriction in the inlet tube was sealed off. The stopcock, L, shutting the manometer off from the rest of the system was opened and the reaction vessel was partially evacuated thru stopcock, K. When the total pressure was reduced to 1/2 or 1/4 atmosphere stopcocks K and L were closed and the reaction bulb quickly sealed off at the constriction in the exit tube. The pressure was then followed exactly as before.

It was found that the click gauges would stand an atmosphere excess pressure on the inside of the bulb but rarely over 1/3 atmosphere excess on the outside. Hence the system outside the click gauge was always partially evacuated first. The results of the four experiments are given in Table III.

TABLE III

| Experime | _ | | • • | Experim | ent 25 (co | nt. | |
|--------------|--------------------|------|--------------------------------|--------------------|----------------|-----------------|-------------------|
| Po N205 | = 6.05 mm | • | | | | | |
| t min | P mm. | PO3 | P _{N2} O ₅ | t | P | P ₀₃ | P _{N205} |
| 129.0 | 407.2 | 18.8 | | 61.0 | 415.75 | 1.7 | |
| 127.4 | 407.5 | 18.2 | | 59.6 | 415.9 | 1.4 | |
| 126.0 | 407.8 | 17.6 | | 58.6 | 415.9 | 1.4 | |
| 124.7 | 408.1 | 17.0 | | 57.9 | 415.95 | 1.3 | |
| 123.8 | 408.3 | 16.6 | | 57.0 | 416.0 | 1.2 | |
| 122.7 | 408.3 | 16.6 | | 56.1 | 416.0 | 1.2 | |
| 121.3 | 408.6 | 16.0 | 5 | 53.8 | 416.0 | 1.2 | |
| 119.8 | 409.1 | 15.0 | | 52.1 | 416.1 | 1.0 | |
| 118.6 | 409.35 | 14.5 | | 50.9 | 416.1 | 1.0 | |
| 117.4 | 409.55 | 14.1 | | 50.1 | 416.15 | . 9 | |
| 116.4 | 409.7 | 13.8 | | 49.1 | 416.15 | .9 | |
| 114.9 | 409.9 | 13.4 | | 48.3 | 416.2 | .8 | |
| 112.0 | 410.6 | 12.0 | | 45.0 | 416.2 | .g | |
| 110.0 | 410.9 | 11.4 | | 42.3 | 416.25 | •7 | |
| 107.8 | 411.05 | 11.1 | | 38 . 9 | 416.25 | •7 | |
| 106.4 | 511.5 | 10.2 | | 32.8 | 416.35 | •5 | |
| 104.6 | 411.7 | 9.8 | | 31.7 | 416.35 | •5 | |
| 103.0 | 411.95 | 9.3 | | 21.8 | 416.45 | •3 | |
| 101.8 | 412.2 | 8.8 | | 20.5 | 416.4 | • 4 | |
| 97.1 | 412.6 | g.0 | | 10.0 | 416.5 | .2 | |
| 95.2 | 413.0 | 7.2 | | - 9.2 | ¥16.5 | .2 | |
| 93.8 | 413.15 | 6.9 | | 0.0 | 416.6 | 0.0 | 6.05 |
| 92.7 | 413.35 | 6.5 | | + 8.5 | 416.7 | | |
| 91.3 | 413.55 | 6.1 | | 9.5 | 416.75 | | |
| 88.6 | 413.65 | 5.9 | | 26.0 | 417.4 | | |
| 86.5 | 413.8 | 5.6 | | 27.0 | 417.4 | | |
| 85.3 | 413.9 | 5.4 | | 32.0 | 417.65 | | |
| 82.8 | 414.3 | 4.6 | | 36.0 | 417.7 | | |
| 81.0 | 414.6 | 4.0 | | 37.7 | 417.6 | | |
| 79.8 | 414.6 | 4.0 | | 39.5 | 417.6 | | |
| 78.8 | 414.7 | 3.8 | | 與.5 | 418.1 | | |
| 77.9 | 414.75 | 3.7 | | 42.5 | 418.1 | | |
| 76.6 | 414.8 | 3.6 | | 43.4 | 418.0 | | |
| 75.7 | 414.9 | 3-4 | | 111 . 7 | 418.0 | | |
| 74.8 | 414.9 | 3.4 | | 54.5 | 418.35 | | |
| 73.7 | 414.95 | 3.3 | | 57 | 488.35 | | |
| 72.3 | 415.0 | 3.2 | | 83 | 418.35 | | |
| 71.0 | 415.1 | 3.0 | | 100 | 418.65 | | |
| 67.1 66.3 | 415.6 | 2.0 | | 101 | 418.6 | | |
| | 415.6 | 2.0 | | 116 | 418.85 | | |
| 65.4 | 415.6 | 2.0 | | 117 | 418.9 | | |
| 64.3 | 415.7 | 1.8 | | 180 | 419.1 420.4 | | |
| 63.5 | 415.7 | 1.8 | | 235 240 | 420.4 | | |
| 62.7 61.8 | 415.75 | 1.7 | | | 416.6 | | |
| 01.0 | 5 15.75 | 1.7 | * | € | 7±0•0 | | |

| Experime | nt 26 * | | | | ent 27 * | | • |
|---|---|--|------------------------------------|--|--|-----------------|--------------------------------|
| Po N205 | = 6.4 mm. | | | Po N205 | = 14.4 mm | • | |
| t | P | P ₀₃ | $^{\mathrm{P}}\mathrm{N_{2}O_{5}}$ | t | P | P ₀₃ | P _{N205} |
| \$ 9423731285 1317.4.2.3731285 105.1.05.1.8.3426250.3607391.7 123538350 1350 150 | P 511757657683990.01222.013344044444444444444444444444444444444 | Pos 21.00 16.2 8 9 5 8 0 5 6 9 4 6 3 2 9 6 4 3 0 8 7 6 4 2 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | P _{N2} O ₅ | t 2546008 552831164328780800087725555305 2546008 41361.8.7.5.6.4 3287808000877255555305 | P .1555555555555555555555555555555555555 | | P _{N2} O ₅ |
| | 406.6 407.1 409.8 412.65 | | | 38.5 45.0 52.3 58.0 63.8 76.0 | 410.3 410.5 410.7 411.0 411.2 411.55 411.6 | | |

Temperature = 25°C

Experiment 27* (cont.)

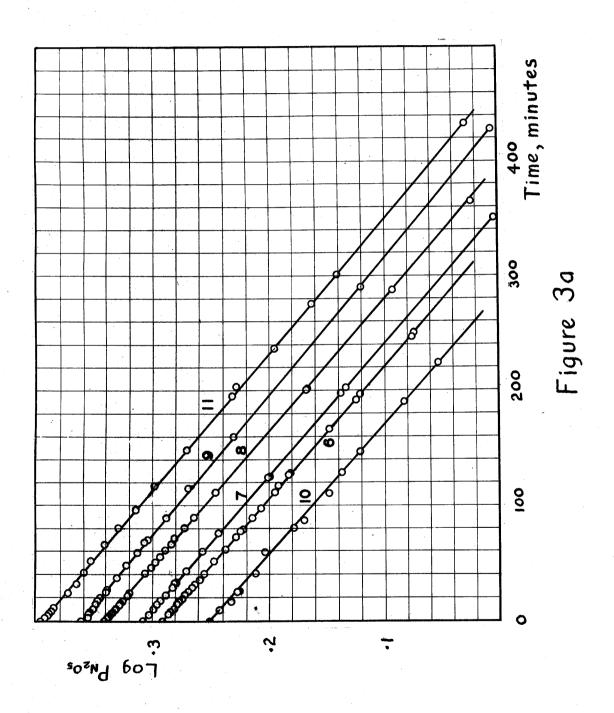
| 88.0 412.05 89.5 412.15 102.0 412.4 1103 412.45 116 412.85 118 412.95 118 412.95 119 413.35 1205.35 120 416.4 165 414.35 166 418.15 167 416.4 168 418.15 169 418.15 160 160.5 160 160 160.5 160 160 160 160 160 160 160 160 160 160 | t | P | P03 | PN205 | t | P | P ₀₃ | P _{N205} |
|--|----------|------------|------------|-------|-------------|-----------------------|-----------------|-------------------|
| 89.5 | 88.0 | 412.05 | | | 31.0 | 205.05 | | |
| 102.0 412.4 22.45 18.3 205.15 .4 113 412.45 18.3 205.25 .2 118 412.95 10.3 205.25 .2 113 413.35 7.5 205.3 .1 129 413.35 | | | | | | | | |
| 116 | | | | | 24.7 | 205.15 | . 4 | |
| 118 | | 412.45 | | | | | | |
| 133 | | | | | | | | |
| 139 | | | | | | | | |
| 162 | | | | | | | | |
| 165 | 139 | 413.3 | | | | 205.3 | | |
| 270 | 162 | 414.25 | | | _ | 205.4 | | |
| 368 418.15 205.45 8.6 205.5 11.0 205.55 14.25 205.6 14.25 205.6 16.5 205.65 19.9 205.8 Experiment 32 Po N ₂ O ₅ = 5.75 mm. 25.0 205.9 28.7 205.9 28.7 205.95 28.7 205.95 28.7 206.0 85.6 201.6 7.5 35.3 206.0 85.6 201.6 7.4 46.2 206.2 83.4 201.65 7.4 46.2 206.2 81.9 201.7 7.3 63.0 206.4 81.9 201.7 7.3 63.0 206.4 78.6 201.9 6.9 70.7 206.5 78.6 201.9 6.9 87.5 206.75 71.8 202.25 6.2 90.2 206.85 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 67.5 203.35 4.0 123 207.25 59.0 203.8 3.1 126 207.25 59.0 203.8 3.1 137 207.25 59.0 203.8 3.1 127 59.0 203.8 3.1 127 59.0 203.8 3.1 127 59.0 203.8 3.1 127 59.0 203.8 3.1 127 59.0 203.8 3.1 127 59.0 203.8 3.1 127 59.0 203.8 3.1 126 207.25 59.1 204.3 2.1 164 207.5 48.7 204.45 1.8 214 208.25 48.7 204.45 1.8 214 208.25 48.7 204.45 1.8 214 208.25 48.7 204.7 1.3 366 209.35 39.5 204.75 1.2 | 165 | 414.35 | | | | 205.35 | 0.0 | 5.75 |
| ## ## ## ## ## ## ## ## ## ## ## ## ## | 2/0 | | | | | 205.45 | | |
| ### ### ### ### #### #### #### #### #### | 300 | 410.19 | | | | 205.45 | | |
| 14.25 | ~ | 1126 2 | | | | | | |
| 16.5 205.65 19.9 205.8 22.7 205.8 22.7 205.8 22.7 205.8 22.7 205.8 22.7 205.9 28.7 205.95 28.7 205.95 28.7 205.95 28.7 205.95 28.7 205.95 28.7 205.95 28.7 205.95 206.0 285.6 201.6 7.5 43.7 206.2 206.2 206.2 206.3 201.6 7.4 46.2 206.2 206.3 201.7 7.3 52.9 206.3 201.8 7.1 63.0 206.4 70.7 206.5 203.3 201.8 7.1 70.7 206.5 206.75 206.85 202.25 5.2 206.9 206.85 207.2 206.85 207.2 206.9 207.2 206.9 207.2 | | 750+6 | | | | | | |
| Experiment 32 Po N ₂ O ₅ = 5.75 mm. 25.0 205.9 86.4 202.0 8.3 30.7 206.0 85.6 201.6 7.5 43.7 206.2 83.4 201.65 7.4 46.2 206.2 83.4 201.65 7.4 46.2 206.2 81.9 201.7 7.3 52.9 206.3 80.3 201.8 7.1 63.0 206.4 78.6 201.9 6.9 70.7 206.5 73.9 202.25 5.2 90.2 206.85 73.9 202.25 5.7 92 206.9 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 65.5 203.35 4.0 123 207.25 59.0 203.8 3.1 137 207.25 59.0 203.8 3.1 137 207.35 59.9 203.95 2.8 141 207.35 59.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 49.7 204.7 1.3 366 209.35 39.5 204.75 1.2 35.8 204.85 1.0 | | • | | | | | | |
| Experiment 32 Po N ₂ O ₅ = 5.75 mm. 86.4 202.0 8.3 30.7 206.0 85.6 201.6 7.5 35.3 206.05 84.6 201.65 7.4 46.2 206.2 81.9 201.7 7.3 63.0 206.4 78.6 201.9 6.9 87.5 206.75 73.9 202.5 5.7 92 206.85 73.9 202.5 5.7 92 206.85 73.9 202.5 5.7 92 206.9 71.8 202.7 5.3 110 207.2 67.5 203.1 4.5 113 207.2 67.5 203.1 4.5 113 207.2 67.5 203.3 5 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 54.8 204.15 2.2 141 207.35 54.8 204.15 2.2 160 207.6 129 207.6 1204.3 2.1 164 207.6 1214 208.25 125 209.35 126 207.55 127 208.65 128 207.65 129 208.65 1204.6 1.5 214 208.25 129 208.65 129 208.65 129 208.65 1204.6 1.5 279 208.65 129 208.65 129 208.65 1204.7 1.3 366 209.35 | | | | | | 205.8 | | |
| Po N ₂ O ₅ = 5.75 mm. 25.0 205.9 28.7 205.95 86.4 202.0 8.3 30.7 206.0 85.6 201.6 7.5 35.3 206.05 84.6 201.65 7.4 46.2 206.2 83.4 201.65 7.4 46.2 206.2 81.9 201.7 7.3 63.0 206.4 78.6 201.9 6.9 70.7 206.5 78.6 201.9 6.9 87.5 206.75 73.9 202.5 5.7 92 206.85 73.9 202.5 5.7 92 206.9 71.8 202.7 5.3 110 207.2 67.5 203.1 4.5 113 207.2 67.5 203.1 4.5 113 207.2 67.5 203.3 5 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 54.8 204.15 2.2 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 48.1 204.6 1.5 279 208.65 39.5 204.75 1.2 366 209.35 39.5 204.75 1.2 366 209.35 | Experim | ent 32 | | | | 205.8 | | |
| 86.4 202.0 8.3 30.7 206.0 85.6 201.6 7.5 35.3 206.05 84.6 201.65 7.4 43.7 206.2 83.4 201.65 7.4 46.2 206.2 81.9 201.7 7.3 63.0 206.4 78.6 201.8 7.1 70.7 206.5 76.3 202.25 6.2 87.5 206.75 73.9 202.5 5.7 92 206.9 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 42.1 204.7 1.3 366 209.35 | _ | • | | | | | | |
| 86.4 202.0 8.3 30.7 206.0 85.6 201.6 7.5 35.3 206.05 84.6 201.65 7.4 43.7 206.2 83.4 201.65 7.4 46.2 206.2 81.9 201.7 7.3 63.0 206.4 78.6 201.8 7.1 70.7 206.5 76.3 202.25 6.2 87.5 206.75 73.9 202.5 5.7 92 206.9 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 61.9 203.35 3.7 126 207.25 59.0 203.8 3.1 137 207.25 59.0 203.8 3.1 137 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 | 0 NSO2 | - 5. 15 mm | le . | | | | | |
| 85.6 201.6 7.5 35.3 206.05 84.6 201.65 7.4 43.7 206.2 83.4 201.65 7.4 46.2 206.2 81.9 201.7 7.3 63.0 206.4 78.6 201.9 6.9 70.7 206.5 73.9 202.25 6.2 90.2 206.85 73.9 202.5 5.7 92 206.9 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 65.5 203.35 3.7 126 207.25 59.0 203.8 3.1 137 207.35 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 46.1 204.6 1.5 279 208.65 42.1 204.75 1.2 35.8 | 86. L | 202.0 | 8.3 | | | 2 06 .0 | | |
| 84.6 201.65 7.4 43.7 206.2 83.4 201.65 7.4 46.2 206.2 81.9 201.7 7.3 52.9 206.3 80.3 201.8 7.1 70.7 206.5 78.6 201.9 6.9 87.5 206.75 73.9 202.25 6.2 90.2 206.85 73.9 202.5 5.7 90.2 206.85 71.8 202.7 5.3 110 207.2 67.5 203.1 4.5 113 207.2 67.5 203.1 4.5 113 207.2 65.5 203.35 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 59.0 203.8 3.1 137 207.35 59.8 204.15 2.2 160 207.55 54.8 204.15 2.2 160 207.55 54.8 204.15 1.8 214 208.25 51.1 204.3 2.1 164 207.6 46.1 204.6 1.5 279 208.65 39.5 204.75 1.2 366 209.35 39.5 204.75 1.2 366 209.35 | | | | | 35.3 | | | |
| 83.4 201.65 7.4 52.9 206.2 81.9 201.7 7.3 63.0 206.4 78.6 201.9 6.9 87.5 206.75 76.3 202.25 6.2 90.2 206.85 71.8 202.7 5.3 110 207.2 67.5 203.1 4.5 113 207.2 65.5 203.35 4.0 123 207.255 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 59.0 203.8 3.1 137 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 366 209.35 | | | 7.4 | | | | | |
| 81.9 201.7 7.3 63.0 206.4 78.6 201.9 6.9 87.5 206.75 206.75 90.2 206.85 73.9 202.5 5.7 92 206.9 110 207.2 111 207.2 165.5 203.35 4.0 123 207.25 161.9 203.5 3.7 126 207.25 159.0 203.8 3.1 137 207.35 156.9 203.95 2.8 141 207.35 154.8 204.15 2.2 160 207.55 151.1 204.3 2.1 160 207.55 151.1 204.3 2.1 164 207.6 164 207.6 164 207.6 165.1 204.6 1.5 214 208.25 166 209.35 35.8 204.75 1.2 366 209.35 35.8 204.85 1.0 | | | | | | | | |
| 80.3 201.8 7.1 70.7 206.4 78.6 201.9 6.9 87.5 206.75 76.3 202.25 6.2 90.2 206.85 73.9 202.5 5.7 92 206.9 110 207.2 169.7 202.9 4.9 111 207.2 167.5 203.1 4.5 113 207.2 165.5 203.35 4.0 123 207.25 123 207.25 126 203.95 3.7 126 207.25 137 207.35 14.1 207.35 14.1 207.35 14.1 207.35 14.1 207.5 14.1 207.5 14.1 207.6 14.1 204.3 2.1 164 207.6 164 207.6 165.1 204.6 1.5 214 208.25 160 207.55 16.1 204.6 1.5 214 208.25 160 209.35 39.5 204.75 1.2 366 39.35 304.85 1.0 | | 201.7 | | | | | | |
| 76.3 202.25 5.2 90.2 206.85 73.9 202.5 5.7 92 206.9 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 65.5 203.35 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 48.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 35.8 204.85 1.0 | | 201.8 | | | | 206.4 | | |
| 73.9 202.5 5.7 92 206.85 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 65.5 203.35 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 366 209.35 | 78.6 | 201.9 | 6.9 | | | 206.5 | | |
| 71.8 202.7 5.3 110 207.2 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 65.5 203.35 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 35.8 204.85 1.0 | | 202.25 | 5.2 | | | | | |
| 69.7 202.9 4.9 111 207.2 67.5 203.1 4.5 113 207.2 65.5 203.35 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 366 | | | | | | | | |
| 67.5 203.1 4.5 111 207.2 165.5 203.35 4.0 123 207.25 126 207.25 126 207.25 126 207.25 126 207.25 126 207.25 126 207.25 126 207.25 126 207.25 127 207.35 128 204.15 2.2 160 207.55 11 204.3 2.1 164 207.6 164 207.6 164 207.6 165 214 208.25 160 207.55 124.1 204.6 1.5 164 207.6 165 214 208.25 160 207.55 126 204.7 1.3 366 209.35 155.8 204.75 1.2 204.75 1.2 204.85 1.0 | | | | | | | | |
| 65.5 203.35 4.0 123 207.25 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 137 207.35 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 35.8 204.85 1.0 | 69.7 | | | | | | | |
| 61.9 203.5 3.7 126 207.25 59.0 203.8 3.1 126 207.25 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 214 208.25 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 35.8 204.85 1.0 | | | | | | | | |
| 59.0 203.8 3.1 137 207.25 56.9 203.95 2.8 141 207.35 54.8 204.15 2.2 160 207.55 51.1 204.3 2.1 164 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 204.85 1.0 | 65.5 | | | | | | | |
| 56.9 203.95 2.8 54.8 204.15 2.2 51.1 204.3 2.1 48.7 204.45 1.8 46.1 204.6 1.5 42.1 204.7 1.3 39.5 204.75 1.2 35.8 204.85 1.0 | • | | | | 126 | | | |
| 54.8 204.15 2.2 51.1 204.3 2.1 48.7 204.45 1.8 46.1 204.6 1.5 42.1 204.7 1.3 39.5 204.75 1.2 35.8 204.85 1.0 | | | | | | | | |
| 51.1 204.3 2.1 160 207.6 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 35.8 204.85 1.0 | | | | | | | | |
| 48.7 204.45 1.8 214 208.25 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 366 209.35 35.8 204.85 1.0 213.05 | - | | | | | 207.55 | | |
| 46.1 204.6 1.5 279 208.65 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 366 209.35 35.8 204.85 1.0 213.05 | | | | | | | | |
| 42.1 204.7 1.3 366 209.35 39.5 204.75 1.2 35.8 204.85 1.0 | | | | | | | | |
| 39.5 204.75 1.2 35.8 204.85 1.0 90 213.05 | | | | | | | | |
| 35.8 204.85 1.0 | | | | | 3 66 | 209.35 | | |
| | | | | | | | | |
| | 33.5 | 204.95 | | | .00 | 213.05 | | |

^{*} Every second or third reading over a portion of a.run recorded.

In experiments 25 and 27 the final pressure readings were made after heating the reaction vessel to 60° for a period of $1\frac{1}{2}$ hours and then thermostating again at 25°, allowing ample time for equilibrium conditions to be reached as shown by the constancy of the pressure readings. In experiment 26 the reaction was allowed to proceed for 40 hours. The reaction vessel was then heated as before, thermostated, and the pressure again measured. The pressure readings obtained before and after this treatment agreed to within 0.1 mm. In experiment 32 the reaction was allowed to go to completion at 25°.

THE NITROGEN PENTOXIDE DECOMPOSITION

Since the pressure readings were made at irregular time intervals and at very short intervals at the start of the nitrogen pentoxide decomposition a graphical method rather than the usual interval method was considered the best way to average the data, in obtaining the specific first order reaction constant, k_1 , for the decomposition of ndtrogen pentoxide. Log $P_{N_2O_5}$ was plotted against the time in minutes, and k_1 determined from the slope of the straight line that best fits the points thus obtained. These calculations were carried out only for the twelve best experiments, six at 25° and six at 35°, namely those for which the initial point of the nitrogen pentoxide decompositionwas most definitely marked. This, in general, was the case when the initial concentration of the pentoxide was high. These results at 25° and at 35° are represented in Figures 3 a and 3 b, respectively.



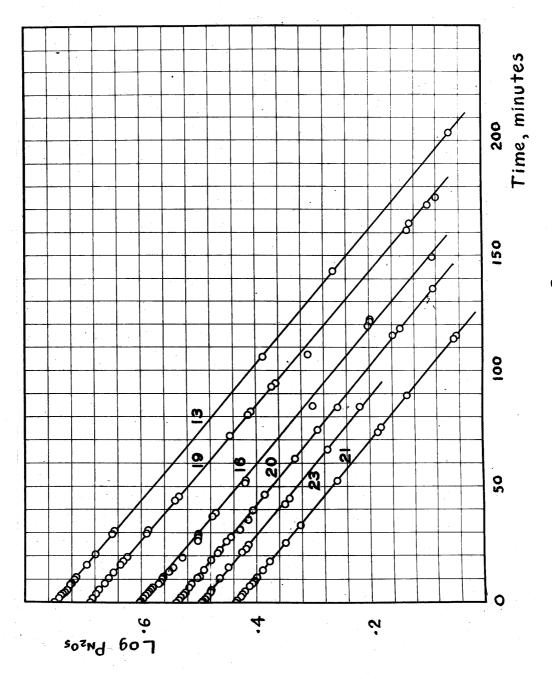


Figure 3b

In making the plots arbitrary log scales were used, the one at 35° being one-half that at 25°. On the other hand, the time scale for the curves at 35° is twice the other. The straight lines fit the data well within the experimental error, and good agreement between the various runs is obtained as shown by Table 4.

TABLE IV

| | T = 25 | 5 ° | | T = 35° | • |
|-------------|---------|---------------------------|------|----------------------------------|---|
| Exp. | Po N2O5 | $k_{1, \text{min}}^{103}$ | Exp. | Po_N ₂ O ₅ | k, x 10 ³ min. ⁻² |
| 6 | 110.1 | 2.00 | 13 | 89,4 | 7.82 |
| | 128.4 | 2.00 | 16 | 25.3 | 7.84 |
| ġ | 139 | 2.00 | 19 | 77.5 | 7.91 |
| 7 8 9 | 46 | 1.92 | 20 | 43.7 | 7.81 |
| 10 | 17.8 | 2.03 | 21 | 19.8 | 7.70 |
| 11 | 35.2 | 1.97 | 23 | 69 | 7.81 |
| | Average | 1.99 | | Average | 7.81 |

These results are also in agreement with the values .00203 and .00805 found by Daniels and Johnston. They lead to the value, 24,970 cal/mol, for the energy of activation as compared to the average value, 25,100 cal/mol, given by the above investigators for this temperature interval.

THE OZONE DECOMPOSITION

General Features of the Reaction: - Attention was next turned to the first stage of the decomposition of the gaseous mixtures, namely, the decomposition of the ozone. From the simple mechanism

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2 \stackrel{\checkmark}{=} 2NO_2 + \frac{1}{2}O_2 \text{ (slow)}$$
 (3)
 $2NO_2 + O_3 \rightarrow N_2O_5 + O_2 \text{ (fast)}$

one obtains for the rate of ozone decomposition the expression

$$-d P_{03}/d t = k_1 P_{N_2 O_5}, (9)$$

where k is again the specific reaction constant for nitrogen pentoxide. From these considerations one would expect that for any given run the rate would be constant, since the pressure of nitrogen pentoxide is constant as long as ozone remains. In two qualitative determinations Hirst found the time necessary for the disappearance of the ozone to be in agreement with that calculated from the integrated form of (9)

$$t = P_{03} / k_1 P_{N_2 O_5}. \tag{4}$$

In these experiments the initial pressure of ozone was, however, only 2.7 mm., and at low pressures the measured rate would not be expected to differ much from the calculated rate as will be shown later.

This investigator also reported some qualitative experiments in which the initial pressures of the ozone were approximately known.

Assuming 3 percent by volume (the lower limit given) ozone in the ozone-oxygen mixture, rough calculations have been made from equation (4) for the time necessary for the appearance of the brown coloration of nitrogen dioxide. And as shown in Table V, the actual time for the appearance of the brown color in Hirst's experiments was in general considerably shorter than that calculated from his equation.

TABLE V

| T | P _{N2} 05 | PO3 | k x 10 ³ min | t observed | t calculated |
|-----|--------------------|-----|-------------------------|---------------|-----------------|
| 47° | 64 | 14 | 37 | 3 | 7 |
| 60° | 47•5 | 9 | 170 | 0 | 1.1 |
| 20° | 47 | 9 | 1.2 | 160-170 | 160 |
| 33° | 52 | 12 | 6 | 9 | 3 6 |
| 35° | 23•5 | 6.4 | 7.8 | 7 | 35 |

The exception at 20° may be due to the fact that at this temperature the rate of formation of nitrogen dioxide is so small that several minutes would be required for the formation of a detectable amount of it. However, nothing is known concerning the amount of ozone used up immediately in oxidizing any tetroxide present at the start.

In the colorimetric determination of the decomposition of nitrogen pentoxide carried out by White and Tolman the time necessary for the appearance of brown nitrogen dioxide was several times shorter than the value calculated as above. Their experimental arrangement made it possible to detect very small concentrations of nitrogen dioxide, and hence observe quite accurately the time at which the ozone had just disappeared. The ozone analysis was made preliminary to mixing with nitrogen pentoxide; so allowance was made for the time necessary for the gas mixture to traverse the tube preliminary to sealing off. This was, however, almost negligible at the temperature, 20°C, which was used in most of the experiments. In their experiments the initial pressure of ozone varied from 9.6 to 36.6 mm. and that of the nitrogen pentoxide from 1.04 to 21 mm.

The results of the present researchare quite in accordance with those of White and Tolman. Our method had the advantage that it enabled us to follow the ozone decomposition throughout its course. It was found that, although the rate of decomposition was much higher than that accounted for by (3), it always approached the rate predicted by this mechanism as the pressure of the ozone approached zero, and increased rapidly as the pressure of the ozone increased, hence any expression for the rate of decomposition must reduce to (9) for zero ozone pressure. One possibility is that the decomposition consists of two simultaneous reactions, the primary reaction, given by (3), and some secondary catalytic reaction depending on the pressure of ozone as well as on that of the pentoxide. Mathematically this is given by

$$-dP_{03}/dt = k_1P_{N_2O_5} + F(P_{N_2O_5}, P_{03}), \qquad (10)$$
 where F is a function of the pressures of both the ozone and pentoxide.

The Method of Determining the Dependence of the Rate of the Secondary Reaction on Ozone and Nitrogen Pentoxide: - As stated above $F(P_{N_2O_5}, P_{O_3})$ is in general a function of the pressures of both the nitrogen pentoxide and the ozone, but for any given experiment the pressure of the pentoxide is constant, and the function is therefore dependent only on the ozone pressure, say proportional to some simple power, n, of it. This would give

$$F(P_{N_2O_5}, P_{O_3}) = (P_{N_2O_5}) \times P_{O_3}^n$$
 (11)

The problem of determining the dependence of F on the partial pressures thus divided itself into two parts, the determination of the order,

first with respect to ozone, and second with respect to the pentoxide.

The Order of the Secondary Reaction with Respect to Ozone: Assuming that the rate of the secondary reaction, which is given by F in
expression (4) is proportional to the first power of the ozone pressure
one obtains

$$-d P_{O_3} / d t = \alpha + \beta P_{O_3},$$
 (12)

where and 3 are independent of the ozone concentration.

Integrating with respect to Poz,

$$\log \left(\frac{\alpha}{3} + P_{03}\right) = -\beta t + \log \frac{\alpha}{3}, \qquad (13)$$

where the integration constant is evaluated from the fact that $P_{03} = 0$ when t = 0. Equation (6) can be put in the form

$$\log \frac{\alpha + \beta P_{2} o_{3}}{\alpha + \beta P_{1} o_{3}} = -\beta (t_{2} - t_{1}) = \beta T$$
 (14)

au being the time interval corresponding to a change in ozone pressure from P_{103} to P_{203} .

For any given run the value <, = $k_1P_{N_2O_5}$ is known from a knowledge of the initial pressure of nitrogen pentoxide. The value of (3 was first determined as follows. From the pressure-time curve for a given experiment was read off the time corresponding to a change of 5 mm. in the ozone pressure. For the experiments at 25° four intervals, corresponding to ozone pressure changes from 5 to 0 mm., 10 to 5 mm., and 20 to 15 mm. were used, provided the initial pressure of the ozone permitted. At 35° only the first two intervals were used. The values thus obtained were then substituted in (14), and the resulting equation was solved for (3 by a graphical method.

The results thus obtained are given in Table VI. Subscripts refer to the interval number.

TABLE VI
Temperature = 25°C

| | | | | | • | | |
|---|---|---|---|--|---|---------------------------------------|--|
| Exp. | PN205 mm | Po 03 | G, min-1 | G _{min} -1 | (3 _s min ⁻¹ | (3, min-1 | $\beta_{\text{Av.}}$ |
| 5 8 9 10 11+ 12 25 26 27 28 29+ 32 | 23.7 139 46 17.8 35.2 9.5 6.4 14.4 89 18 | 12 3 21 29 22 28 19 21 15 19 41 | .065 .193 .113 .059 .114 .041 .0305 .065 .160 | .086 .120 .064 .123 .042 .029 .031 .059 .187 | .124 .059 .0915 .037 .027 .029 .045 .189 | .054 .088 .0375 .026 .027 | .076 .195 .119 .059 .104 .039 .028 .029 .057 .178 |
| | | | Temperatu | re = 35 | •C | | |
| 16 17 18 20 21 22 23 | 25.3 4.4 13.7 43.7 19.8 15.7 | | .253 .105 .148 .393 .238 .188 | .227 .084 .127 .198 .173 .690* | | | .240 .094 .138 .393 .218 .180 |

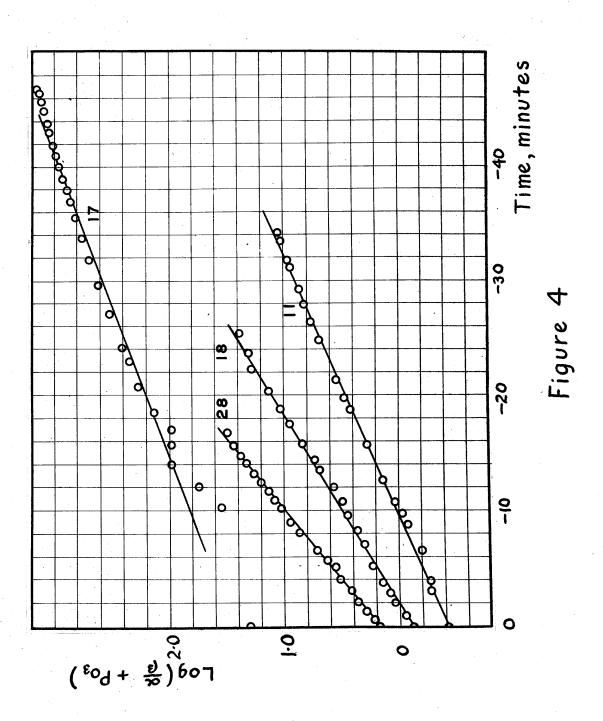
^{*}In these experiments the end of the ozone curve was very indefinite.

^{*}The time interval from which this value is obtained is only .9 min.

It will be seen that the values of \$\mathref{G}\$ fall off as the pressure of ozone increases indicating an order with respect to ozone slightly lower than the first. This falling off is greatest where the initial pressure of the nitrogen pentoxide is low, and hence where the reaction rate is slow. Experiment 27 with an initial nitrogen pentoxide pressure of 14.4 mm. shows the greatest effect where \$\mathref{G}\$ falls off by 1/3 its value.

However, the value of β obtained from the first interval is not as good as that determined from the other intervals, first, because at low ozone pressures the rate is largely determined by α , and second, because of the difficulty in determining the time at which the ozone reaction ends. An error made in this determination especially in the experiments where the rate is slow would not lead to appreciable error in the pressure at this point and hence would not greatly affect the values of β for the other intervals.

In order to obtain a better average of \Im , the following method of calculation was also used. The average value of \Im as determined by the interval method was substituted into the left-hand side of (6), and the quantity $\log\left(\frac{\alpha}{\beta} + P_{0_3}\right)$ was then plotted against -t. The average slope of this line was then taken as giving a corrected value of \Im . At higher values of P_{0_3} , $\frac{\alpha}{\Im}$ becomes small in comparison so an error in the selection of \Im becomes negligible in the sum. The values of \Im thus obtained are tabulated in the succeeding section. Figure 4 illustrates graphically the results of 4 experiments of which 11 and 25 were carried out at 25° and 17 and 18 at 35°. The decrease in the value of \Im with increasing ozone pressure is again shown in



the experiments at lownitrogen pentoxide pressures. In experiment 17 the initial pressure of the pentoxide was only 4.4 mm. The irregularity of the points at the lower end of this curve is due to the large experimental error in determining the time corresponding to a given ozone pressure for these slow rates.

The Order with Respect to Nitrogen Pentoxide: - The next step in determining the form of F was to investigate the dependence of on the nitrogen pentoxide pressure. As was done in the case of ozone, assume 3 proportional to some power of the pentoxide pressure

$$\beta = k_2 P_{N_2 O_5}^n . \tag{15}$$

Since the value of β was determined over nearly the same ranges of ozone pressures the order, n, found in this way is almost independent of any small deviation of the order assumed with respect to ozone from the true order of the reaction.

To determine the value of n the logarithm of β was plotted against that of $P_{N_2O_5}$, the slope of the line obtained giving the value of n. Figure 5 represents a plot made in this way. The lines, drawn in with slopes equal to 2/3, fit the data fairly well at both 25° and 35°. β then takes the form,

$$\beta = k_2 P_{N_2 O_5}^{2/3} \tag{16}$$

 k_2 was then calculated from this expression and its value for the various experiments together with the value of β found in the preceding section is given in Table 7.

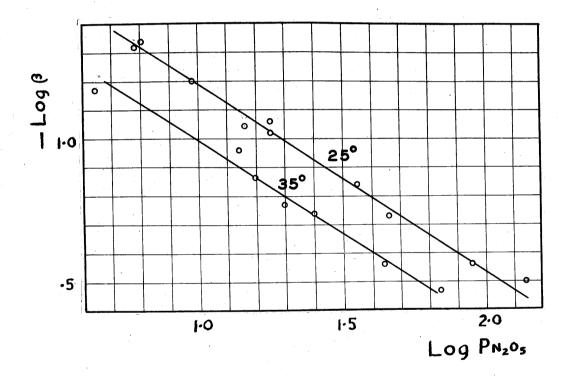


Figure 5

TABLE VII

| Tempera | ture = | 25°C |
|---------|--------|------|
|---------|--------|------|

| Exp. | P _{N2} 05 | P _{N2} 05 | β | I | K ₂ m-2/3 t-1 |
|-------------|--------------------|--------------------|--------------|-----------------|-----------------------------|
| 5 8 9 | 23.7 | 8.25 | 0.080 | | 0.0097 |
| g | 139 | 26.8 | .210 | | .0078 |
| 9 | 46 | 12.8 | .117 | | .0091 |
| 10 | 17.8 | 6 .8 3 | •060 | | .0088 |
| 11 | 35.2 | 10.8 | .102 | | •0094 |
| 12 | 9.5 | 4.49 | .040 | | •00 89 |
| 25 | 6.05 | 3.32 | .030 | | •0090 |
| 26 | 6.4 | 3-46 | .029 | | .0084 |
| 27 | 14.4 | 5•93 | •05 8 | | .0098 |
| 28 | 89 | 20.0 | .174 | | .0087 |
| 29 | 18.0 | 6.88 | •055 | | .0080 |
| 32 | 5-75 | 3.21 | • 0,4 | | .012+ |
| | | | | Averag e | 2 089 |
| | | Temperatu | re = 35°C | | |
| 16 | 25.3 | 8.60 | .197 | | .023 |
| 17 | 4.4 | 2.92 | .086 | | .030 |
| 18 | 13.7 | 5.72 | .138 | | .024 |
| 20 | 43.7 | 12.4 | • 35 | | .028 |
| 21 | 19.8 | 7.32 | .22 | | .030 |
| 22 | 15.7 | 6.28 | .172 | | .027 |
| 23 | 69 | 1.59 | .43 | | .027 |
| | | · | | Average | .027 |

Experiment 32 was carried out at a total pressure of one-quarter atmosphere. This value of k_2 is not included in the average.

The Effect of Oxygen: - If the secondary reaction involves some chain mechanism it was conceivable that the oxygen might inhibit the reaction by deactivating thru collisions the activated molecules participating in the chain, thus decreasing the number of ozone molecules decomposed per chain. However, no increase in the rate was observed in three experiments in which the oxygen pressure was approxi-

mately halved. One experiment in which the total pressure was 1/4 atmosphere showed a 1.35-fold increase in the rate as shown in Table 7. In this experiment the initial pressures of both ozone and nitrogen pentoxide were low, 8, 3, and 5.75 millimeters, respectively, making it difficult to determine the point of inflection, and hence, the value of k_2 . From the above results it can be definitely concluded that the rate does not have any large dependence on the oxygen pressure, as is the case in the thermal decomposition of ozone, where the rate is inversely proportional to the first power of the oxygen pressure.

DISCUSSION OF RESULTS

The rate of decomposition of ozone in the presence of nitrogen pentoxide may hence be given by the equation

$$-d P_{03} / d t = k_1 P_{N_2 O_5} + k_2 P_{N_2 O_5}^{2/3} P_{03}$$
 (17)

over a range of nitrogen pentoxide pressures from 6 to 129 mm. at 25° and from 4.4 to 69 mm. at 35°, and for ozone pressures up to 25 mm. At high ozone and low pentoxide pressures the rate falls off from that first order with respect to the ozone. The value of k_2 increases 3.3 fold for the 10° rise in temperature as compared to the increase of 3.9-fold for k_1 over this range.

No theoretical interpretation has been made to account for the 2/3 power with respect to the pentoxide. The fact that the order with respect to both the ozone and pentoxide falls below unity when the rate is slow suggests inhomogeneity of the reaction, a wall reaction of lower order taking place. However, the fact that changing the surface-to-volume ratio three-fold in the reaction vessels used had no effect on the rate, and also that the order with respect to nitrogen pentoxide is lowered the same amount at the two temperatures are arguments against any appreciable reaction taking place on the walls.

It might be possible to fit the data over the range of pressures studied with an expression of the form

- d P_{03} / d t = $k_1 P_{N_2 O_5} + (P_{N_2 O_5})(P_{03})/(aP_{N_2 O_5} + bP_{03} + cP_{02} + d)$ (18) where the presence of $P_{N_2 O_5}$ and of P_{03} in the denominator would lower the order with respect to these variables, and the term cP_{02} would lead to an inhibiting effect of oxygen for which there is some evidence in

experiment 32. The relative values of a, b, c, and d would then determine the amount by which the order with respect to the various pressures is lowered.

An expression of this type can be derived from the following mechanism.

This gives a chain mechanism which is almost certainly necessary to account for the large increase in the rate of ozone decomposition over that at low pressures (approximately 15-fold at 20 mm. ozone pressure). In step (a) ozone oxidizes the nitrogen tetroxide, formed in the pentoxide decomposition, with the formation of an active oxygen molecule. From the heat of dissociation of ozone

$$0_3 \rightarrow 3/2 \ 0_2 + 34,000 \ cal.,$$
 (20)

and the heat of formation of nitrogen pentoxide from the tetroxide and oxygen

$$N_2O_4 + \frac{1}{2}O_2 \longrightarrow N_2O_5 + 2690 \text{ cal.},$$
 (21)

it is seen that there is available approximately 37,000 calories for the activation. In the next step (b) an activated oxygen molecule collides with an ozone molecule resulting in an interchange of the energy of activation. The excited ozone molecule thus formed can collide with a normal ozone molecule giving again an activated oxygen molecule (c). This molecule can then collide with another ozone molecule with a repetition of the above process, or it can become deactivated by collision with any of the molecules present, as shown by steps (d), (e), and (f), or by a unimolecular decay, as in (g).

Equation (18) can be derived from the above as follows: Let k_1 , k_2 , k_3 , etc. be the rate constants for the reactions (a), (b), (c), etc.

Ozone is used up in steps (a), (b), and (c) the rate being given by

 $- d(O_3)/dt = k_1(N_2O_5) + k_2(O_3)(O_2) + k_3(O_3)(O_3), \qquad (22)$ where (O₃), (N₂O₅), etc. are concentrations of the ozone, pentoxide, etc., respectively.

The rate of change of 031 is

$$d(0_3!)/dt = k_2(0_2!)(0_3) - k_3(3!)(0_3), \qquad (23)$$

and that of 021,

$$d(O_2!)/dt = k_1(N_2O_5) - k_2(O_2!)(O_3) + k_3(O_3!)(O_3) - k_4(O_2!)(O_3) - k_5(O_2!)(N_2O_5) - k_6(O_2!)(O_2) - k_7(O_2!).$$
(24)

Since (0_2) and (0_3) are very small, their rates of change can be put equal to zero. From (23) we then obtain the equation

$$\mathbf{k}_{2}(0_{2}^{1})(0_{3}) - \mathbf{k}_{3}(0_{3}^{1})(0_{3}) = 0,$$
 (25)

or

$$(0_3^1) = \frac{k_2}{k_3}(0_2^1). \tag{26}$$

and from (24), after substituting for (0_3^1) its value in terms of (0_2^1) given by (26),

 $k_1(N_2O_5) - k_4(O_2^1)(D_3) - k_5(O_2^1)(N_2O_5) - k_6(O_2^1)(O_2) - k_7(O_2^1) = 0$ Solving for (O_2^1)

$$(0_2') = \frac{k_1(N_2O_5)}{k_4(O_3) + k_5(N_2O_5) + k_6(O_2) + k_7}.$$
 (28)

Substituting (26) and (28) in equation (22) there results

$$-\frac{d(0_3)}{dt} = k (N_2O_5) + \frac{2k_1k_2(N_2O_5)O_3)}{k_4(O_3) + K_5(N_2O_5) + k_6(O_2) + k_7}$$
which can easily be put in the form (18).

If any of the last four steps in (19) were ineffective in deactivating the 0_2 ' the rate for that reaction would become zero and the term corresponding to it would drop out of the denominator of the last term of (29).

Other mechanisms might be worked out, possibly involving the ozone-nitrogen pentoxide complex, reported by Warburg and Leithauser to be present in very small concentrations in mixtures of ozone and the pentoxide, as an intermediate product of the reaction; but no attempt in this direction has been successful.

This research was suggested and supervised by Dr. Richard C. Tolman, to whom the author is greatly indebted. The author also wishes to extend his thanks to Mr. William. Ure, who started the research, working out the general method of procedure, and to Mr. Warren P. Baxter for his assistance in carrying out the experiments.

SUMMARY

A method of determining the rate of decomposition of ozonenitrogen pentoxide mixtures, which consists of following the pressure change by means of an all glass "click" gauge, is given.

The decomposition curves were found to consist of two parts, the first representing the decomposition of ozone and the second that of the pentoxide. A sudden 3-fold increase in the rate marks the start of the pentoxide decomposition.

The specific reaction rates for the first order decomposition of nitrogen pentoxide at 25° and 35° were found to agree well with the results of Daniels and Johnston.

At high ozone pressures the decomposition of ozone was found much faster than that required for the oxidation of nitrogen dioxide formed in the decomposition of nitrogen pentoxide, but approached this predicted rate as the ozone pressure approached zero. An expression for the rate in which the reaction was divided into two parts, one depending on the pentoxide pressure alone, and the other on both the pentoxide and ozone pressures was worked out. In the expression giving the second reaction rate the order is found to be 2/3 with respect to the pentoxide, and approximately first order with respect to ozone, falling off where the pentoxide pressure is low.

The total pressures were reduced to 1/2 atmosphere with no appreciable effect. One experiment at 1/4 atmosphere shows a slightly increased rate.

Another form of rate expression, for which a mechanism is given, is suggested.

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