

PART I

The Kinetics of the Fast Reaction  
between Ozone and Nitrogen Dioxide

PART II

A Mechanism for the Formation of Red Phosphorus from  
White Phosphorus In Solution

Thesis by

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## SUMMARY

### Part I.

1. A system has been designed and constructed which will mix two gaseous reactants, isolate them in a reaction cell, and follow the entire course of the reaction photoelectrically in one-tenth of a second. The output of the photoelectric tube is recorded by a time-exposure photograph of the screen of an oscilloscope.

2. The kinetics of the fast reaction between ozone and nitrogen dioxide was studied over a ten-fold range of each reactant. The rate law was found to be

$$- d(O_3)/dt = k (NO_2)(O_3)$$

over the entire course of the reaction. As expected from the speed of the reaction, the energy of activation was found to be low, 6.4 kilocalories per mole. A simple two-step mechanism is proposed to account for the observations.

### Part II.

1. In an effort to obtain information about the mechanism of the formation of red phosphorus from white phosphorus in a solution of phosphorus tribromide, a radioactive tracer study was made of that system. Tentative explanations are advanced for certain features of the process.

2. A great variety of colors of polymerized phosphorus were observed in this study, and correlations between presumed size and color are discussed.

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PART I

The Kinetics of the Fast Reaction  
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Ozone and Nitrogen Dioxide

## PART I

# The Kinetics of the Fast Reaction Between Ozone and Nitrogen Dioxide

### A. Introduction

The purpose of this investigation was two-fold: first, to develop a general method for the study of fast reactions in the gaseous phase; and, second, to study the kinetics of the oxidation of nitrogen dioxide by ozone.

Methods of studying the kinetics of fast reactions in the gaseous phase have been developed for several types of systems. The measurement of steady state properties of a stream of gases flowing down a reaction tube is a widely used technique. This constant pressure flow method for gases gives data difficult to interpret because of questions concerning diffusion and mixing<sup>(1)</sup>, and a change in the volume or the temperature during the reaction also complicates the calculations<sup>(2)</sup>. Fast atomic reactions have been studied in the gaseous phase by the methods of the diffusion flame and the highly dilute flame<sup>(3)</sup>, and fast reactions of organic free radicals have been followed by the Paneth mirror technique<sup>(4)</sup>. Also, other special techniques have been employed. The method desired for this study was one in which the reacting gases could be rapidly mixed, isolated, and followed in a static system by a fast analytical procedure free of lag.

The oxidation of nitrogen dioxide-tetroxide was described by Wulf, Daniels, and Karrer<sup>(5)</sup> as "practically instantaneous" in the gas phase and quantitative as written:



This reaction thus gave promise of yielding a clear-cut kinetic study.

## B. The Apparatus

### 1. Brief Description of the Entire Method

Three streams of oxygen, flowing at rates known from calibrated flowmeters, were used (1) to pick up  $\text{NO}_2$ - $\text{N}_2\text{O}_4$  in a saturator containing cold liquid  $\text{N}_2\text{O}_4$ , (2) to make ozone by passing through a silent electrical discharge tube, and (3) to dilute the nitrogen dioxide stream to the desired final concentration. The two resulting streams were mixed in about 0.01 seconds in a mixing chamber and passed into a small reaction cell. Through the reaction cell passed a filtered beam of light which fell on an electron multiplier photoelectric tube. The light source was interrupted by a slotted disk turned by a synchronous motor. The output of the photoelectric tube was put across the deflection plates of an oscilloscope, which, however, was not firing its beam. The temperature of the reacting gases was measured by a fine copper-advance thermocouple just below the outlet of the reaction cell. After a steady state was obtained, a weight was dropped which threw a lever which closed a stainless steel stop gate and



stopped the flow of the gases, cutting off a portion just above and just below the reaction cell. The stop gate upon closing made electrical contact with a brush which caused the oscilloscope to give a single sweep of its beam. During this single sweep the shutter of a camera was open catching all of the sweep on one film. The final data appeared on the photographic negative as a wave packet whose width was simply related to the  $\text{NO}_2$  concentration and whose wave period was known precisely from the speed of the synchronous motor.

Each of these features will be described, first as to construction and again as to calibration.

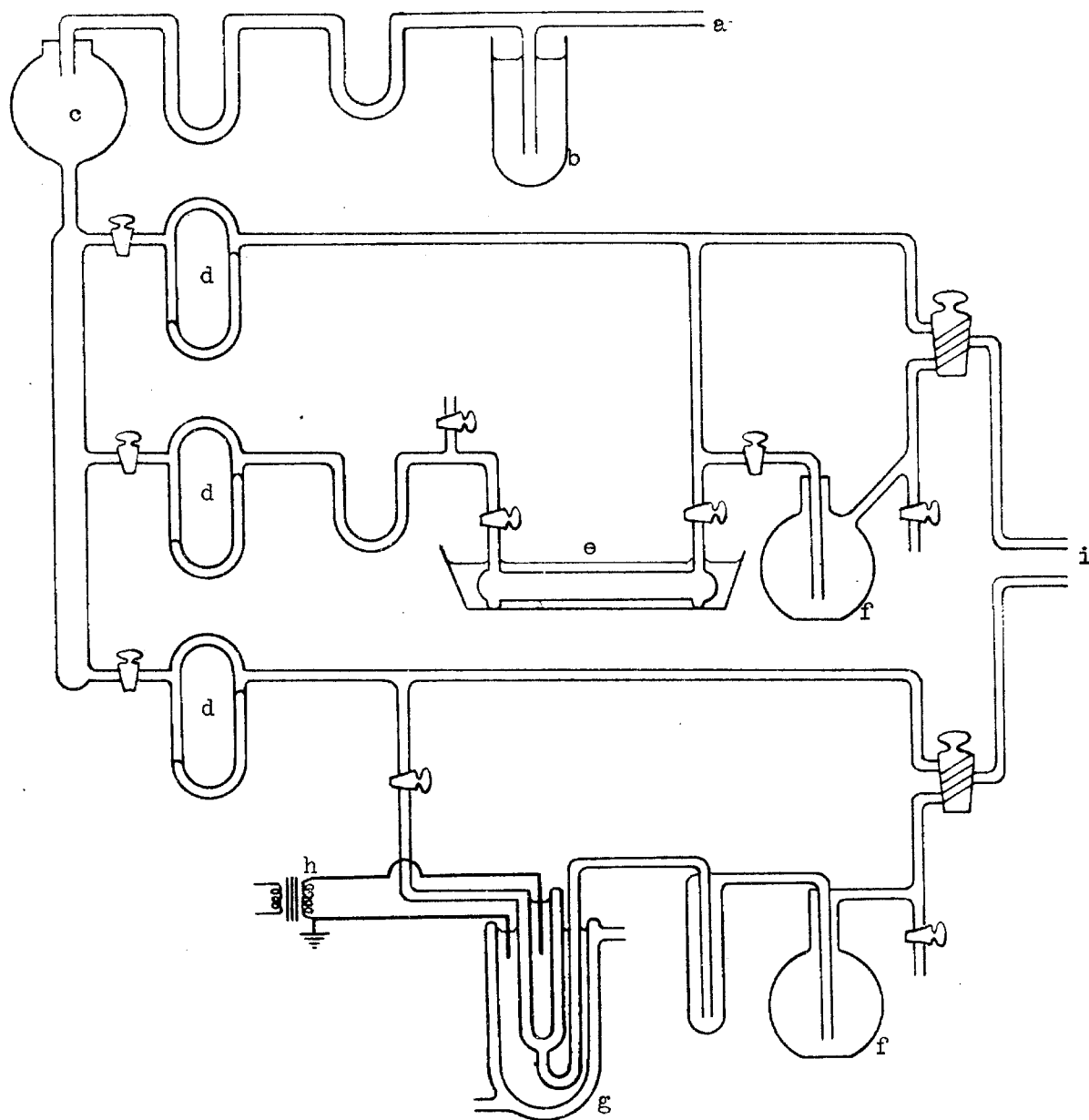
## 2. The Flowmeter System

### (a) Construction

The flowmeter system including the ozonizer and the saturator is shown schematically in Figure 1. To a commercial (Linde Corporation) tank of oxygen was attached a pressure reducing unit and a needle valve outlet. The oxygen from the tank came through a rubber tube to a T-joint in 8 millimeter internal diameter glass tubing. Down one side of the T-joint, the oxygen flowed out of the glass tube under about 300 millimeters of water, thereby maintaining a constant pressure inside the system up to the flowmeters.

The system of traps to remove suspected impurities consisted of a charcoal trap to pick up any organic matter from the rubber tubing and a calcium chloride U-tube and a

Figure 1. Schematic Drawing of the Flowmeter Circuit



- a. From tank of oxygen
- b. Overflow tube to maintain constant pressure
- c.  $P_2O_5$
- d. Capillary flowmeters with dibutylphthalate as manometer fluid
- e.  $N_2O_4$  saturator in ice bath
- f. Gas storage bulbs
- g. Ozonizer
- h. 15,000 volt transformer
- i. To mixing chamber (Figure 2)

one-liter flask full of  $P_2O_5$  and glass chips to remove water. As a double protection of the  $N_2O_4$  saturator, a charcoal tube (to remove manometer fluid vapors) and then a  $P_2O_5$  tube were placed between the flowmeter and the saturator. No attempt was made to remove the nitrogen in the oxygen except such of it as was converted to  $N_2O_5$  in the ozonizer. To take out such nitrogen pentoxide, a trap chilled in the dry ice and acetone mixture was placed in the ozone line. This flow system was of all glass construction from the flowmeters to the stop gate. The only material, except glass and the stainless steel stop gate, exposed to the corrosive action of the reactants was Dow Corning silicone stopcock grease, which was attacked only slowly and slightly by these gases.

The method of determining the flow rate of oxygen down each of the three lines was to measure the drop in pressure produced as the oxygen flowed through a long capillary tube. Different flow rates were obtained by the use of capillaries of various lengths and internal diameters. The pressure drop was measured by a manometer using dibutylphthalate as the manometer fluid. This fluid was placed in a vacuum line and volatile impurities were pumped off by a vacuum pump which was run for 5 hours.

Large reservoir bulbs, 2-liters on the  $NO_2$  line and 1-liter on the  $O_3$  line, were included for two reasons: first, to smooth out any instantaneous fluctuations in the output

of the ozonizer or saturator, and second, to cushion the effect of suddenly stopping the flow just as readings were being made. In order to make calibrations it was necessary to be able to bypass the ozonizer and the ozone reservoir bulb or the saturator and the nitrogen dioxide bulb.

(b) Calibration of the Flowmeters

The flowmeters were calibrated by measuring the time required to collect a given amount of oxygen over water for one value of the manometer reading. The oxygen was dried over  $P_2O_5$  before it passed through the flowmeters. The usual corrections were applied for the vapor pressure of the water, the height of the final water column, and the barometric pressure. During the calibration and during the course of the experiments, the room temperature was always between 19 and 21 degrees Centigrade and the barometric pressure was  $745 \pm 3$  millimeters of mercury. The calibration curves so prepared gave the rate of flow of dry oxygen at  $20^{\circ}C.$  and 745 mm. pressure as a function of the manometer reading.

Seventeen capillaries were calibrated, spaced over roughly equal factors in the range of 4 cubic centimeters per minute to 4 liters per minute at a manometer reading of 300 millimeters of dibutylphthalate. The reproducibility of the calibration points reveals errors of the order of 1/2 to 1 percent in the flowmeter method.

### 3. The Ozonizer

#### (a) Construction

The ozonizer used in this study was of the usual type. It was an exact copy of the auxiliary ozonizer shown in Figure 1 of a paper by Shultz and Wulf<sup>(6)</sup>. The transformer which was used is rated at 15,000 volts when 110 volts of 60 cycle alternating current is applied across the primary coil.

#### (b) Calibration

The ozone in the oxygen stream was removed by absorption in a neutral solution of potassium iodide. This solution was then acidified with dilute sulfuric acid and titrated with standardized sodium thiosulfate solution<sup>(5)</sup>. The yield of the ozonizer at 20°C. for various voltages across the primary coil and at various flow rates of dry oxygen at 745 mm. pressure is given in Table 1.

Table 1. Yield of the Ozonizer

| Ozone in milli-atmospheres                        |     | Voltage across primary coil |    |    |    |    |    |
|---|-----|-----------------------------|----|----|----|----|----|
|   |     | 90                          | 80 | 70 | 60 | 50 | 40 |
| Flow rate in cc. per minute of dry O <sub>2</sub> | 15  | 55                          |    |    |    |    |    |
|   | 44  | 58                          | 55 | 50 | 49 | 48 | 38 |
|   | 76  | 59                          | 54 |    | 48 |    | 35 |
|   | 135 | 56                          | 53 |    | 43 |    | 27 |
|   | 260 | 50                          |    |    |    |    |    |

During the course of the kinetics experiments, the voltage across the primary coil was set at 80 volts. The yield of the ozonizer is almost independent of the flow rate at this voltage.

#### 4. The $N_2O_4$ Saturator

##### (a) Construction

The saturator was an all-glass vacuum-tight apparatus which consisted of nine glass tubes, each 6 inches long and 12 millimeters in internal diameter. The nine tubes were mounted parallel to each other and in the horizontal plane. They were connected from below by glass tubes which permitted liquid to flow freely from one to another, and at the ends they were alternately joined above by glass tubes which, when the apparatus was half full of liquid, forced the oxygen to pass back and forth from one tube to the next until it had moved over the surface of the liquid for the entire  $4\frac{1}{2}$  feet. Thus the oxygen to be saturated moved freely over the surface without bubbling through the liquid.

The apparatus was mounted in an insulated pan which was filled with a well-stirred mixture of water and ice. Nitrogen dioxide (from a tank prepared by the Matheson Company) was passed through a tube of  $P_2O_5$  and through an all glass system into the ice cooled saturator until it was half full of liquid. At first the liquid had a trace of greenish color due to  $N_2O_3$ . This color changed to straw orange at zero degrees Centigrade after the liquid had been exposed to an atmosphere of oxygen for a few hours, presumably, as the  $N_2O_3$  was oxidized to  $N_2O_4$ .

(b) Calibration

In the calibration of the saturator a stream of oxygen was blown over the liquid  $N_2O_4$ , and the vapors picked up were absorbed in a known volume of standardized base by the method described in section B-9. The excess base was titrated to the end point of phenolphthalein. Two equivalents of acid were assumed to be equal to one formula weight of  $N_2O_4$ .

Though the calculations are all elementary, for convenience of reference there is recorded in detail here the steps taken in going from known flow rates, times of flow, and titrations to a table of  $NO_2$  concentrations at various temperatures.

Under ordinary conditions of temperature and pressure, nitrogen dioxide exists as an equilibrium mixture of the red  $NO_2$  and the colorless  $N_2O_4$ , each present in considerable amounts. A chemical analysis gives the total amount of  $NO_2$  and  $N_2O_4$ , and an optical method of analysis using blue light gives only the amount actually present as  $NO_2$ . The following terms are defined as an aid in describing this system:

- x = concentration of  $NO_2$  in milli-atmospheres
- y = concentration of  $N_2O_4$  in milli-atmospheres
- z = concentration of  $O_3$  in milli-atmospheres
- c = formal concentration of  $N_2O_4$  in milli-atmospheres  
=  $x/2 + y$
- K = equilibrium constant for the reaction  $N_2O_4 = 2NO_2$   
=  $x^2/y$

$n_x, n_y, n_o$  = number of gram molecular weights respectively of  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ , and  $\text{O}_2$  in a given volume under discussion

$v_o$  = volume of dry  $\text{O}_2$  at 745 mm. and  $0^\circ\text{C}$ . passed into the saturator

$v$  = volume of the  $\text{O}_2$  plus the  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  after equilibrium is established in the saturator

$R$  = the gas constant

$T$  = the absolute temperature = 273.1 in the saturator

$p$  = the partial pressure of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the saturator, that is, the vapor pressure of liquid  $\text{N}_2\text{O}_4$ .

Assuming the perfect gas law to apply inside the saturator, there are at once obtained the following relations:

$$K = x^2/y = n_x^2 RT/vn_y$$

$$v = v_o(n_x + n_y + n_o)/n_o$$

$$p = (n_x + n_y)RT/v$$

$$n_x/2 + n_y = n_o$$

These four equations contain four unknowns,  $n_x$ ,  $n_y$ ,  $v$ , and  $p$ . The solution for  $n_x/2$  is:

$$n_x/2 = \frac{-A + \sqrt{A^2 + 4A(n_o^2/n_o + n_o)}}{2}$$

where  $A = K v_o n_o / (4 n_o RT + K v_o)$ .

Extrapolating the work of Verhoek and Daniels<sup>(7)</sup> to  $0^\circ\text{C}$ . at the total formal concentration of  $\text{N}_2\text{O}_4$  observed here, the value of  $K$  was found to be 0.0159 atmospheres. Substituting



numerical values for this K and for one liter of air through the flowmeters, A is found to be  $1.646 \times 10^{-4}$  moles per liter, and  $n_0$  is 0.0407 moles per liter.

Table 2 gives a summary of the values of  $n_0$  found on various titrations. The average value of  $n_0$  is  $0.0211 \pm 0.0007$  (the double standard deviation of the mean) formula weights of  $N_2O_4$  per liter of dry  $O_2$  as measured by the flowmeters.

Table 2. Calibration of the  $N_2O_4$  Saturator

| Rate of flow of dry $O_2$ through the flowmeters liters per minute $\times 10^3$ | Equivalents of base neutralized by $NO_2^-$ $N_2O_4$ per minute $\times 10^3$ | Formula weights of $N_2O_4$ per liter of $O_2$ |
|--|---|--|
| 3.60   | 0.1498  | 0.0208   |
| 3.72   | 0.1600  | 0.0215   |
| 3.78   | 0.1611  | 0.0213   |
| 4.22   | 0.1772  | 0.0210   |
| 4.13   | 0.1780  | 0.0215   |
| 4.22   | 0.1791  | 0.0212   |
| 6.27   | 0.263   | 0.0210   |
| 6.35   | 0.266   | 0.0210   |
| 6.40   | 0.271   | 0.0212   |

AVERAGE 0.0211

Introducing the value of  $n_0 = 0.0211$  in the equations above, the numerical answers for the various quantities are:

$$n_x/2 = 2.23 \times 10^{-3} \text{ moles per liter of } O_2$$

$$v = 1.465 \text{ liters}$$

$$p = 0.356 \text{ atmospheres}$$

Solution of the vapor pressure equation for the  $\text{NO}_2\text{-N}_2\text{O}_4$  mixture above the liquid as given by Giaugue and Kemp<sup>(8)</sup> yields at  $273.1^\circ\text{A}$ . the value of 26.28 cm. of mercury or 0.346 atmospheres. Although the difference in 0.356 and 0.346 lies outside the experimental error of the analysis, this difference could easily be due to gas imperfections or to an error in the extrapolation of K. Thus the check on the vapor pressure is to be considered as probably satisfactory.

In the calculation of the pressure of  $\text{NO}_2$  in the final stream after dilution with a large excess of oxygen, certain simplifications can be introduced. It is also desirable to express this quantity in terms of the measured flow rates rather than in terms of mole fractions. In the calculation of the final volume of the highly diluted stream at room temperature, the association of the  $\text{NO}_2$  may be ignored. In the range of pressures used, this simplification introduces an error ranging from 0.05% to 0.5%. Using previous values of  $n_c$  and  $n_o$ , it is seen that the ratio of the flow rate out of the saturator to the flow rate of the entering  $\text{O}_2$ ,  $f_s$ , is  $1 + 2n_o/n_c = 2.04 \approx 2$ . The formal pressure of  $\text{N}_2\text{O}_4$  in the final stream in milli-atmospheres is

$$c = nRT/v = 1000n_oRTf_s / (2f_s + f_c) \approx 507f_s / (2f_s + f_c)$$

where  $f_c$  is the flow of the carrier  $\text{O}_2$  expressed in the same units as  $f_s$ , the flow rate of dry  $\text{O}_2$  at  $20^\circ\text{C}$ . and 745 mm.

pressure, and  $v$  is the general volume of the perfect gas equation, not  $v$  defined on page 9.

With this convenient way of finding  $c$  the equilibrium equation can be readily solved.

$$K = x^2/y = x^2/(c - x/2)$$

$$x^2 + Kx/2 - Kc = 0$$

$$x = \frac{-K/2 + \sqrt{K^2/4 + 4Kc}}{2}$$

$$F = (x/2)/c = \frac{-K + \sqrt{K^2 + 16Kc}}{8c}$$

$F$  is the fraction of the total formal amount of  $N_2O_4$  which is in the form of  $NO_2$ . The equilibrium constant  $K$  is a function of the temperature and of the value of  $c$ .<sup>(7)</sup> For the low concentrations in the final diluted streams the dependence of  $K$  on  $c$  may be neglected entirely.

As an aid to calculation, three graphs were prepared which allow immediate translation to be made from  $x/2$  to  $c$  or from  $c$  to  $x/2$  at any temperature. The first was a plot of the logarithm of the equilibrium constant against the reciprocal of the absolute temperature from the data of Verhoek and Daniels<sup>(7)</sup>. Next there was plotted on one sheet of paper the relation of  $F$  to  $c$  for each of four values of  $K$ , 0.05, 0.10, 0.15, and 0.25 atmospheres. From this second graph was prepared a third of  $1/F$  versus  $x/2$  for the same set of equilibrium constants. For other values of the equilibrium constant, interpolation between the lines could be made.

## 5. The Mixing Chamber

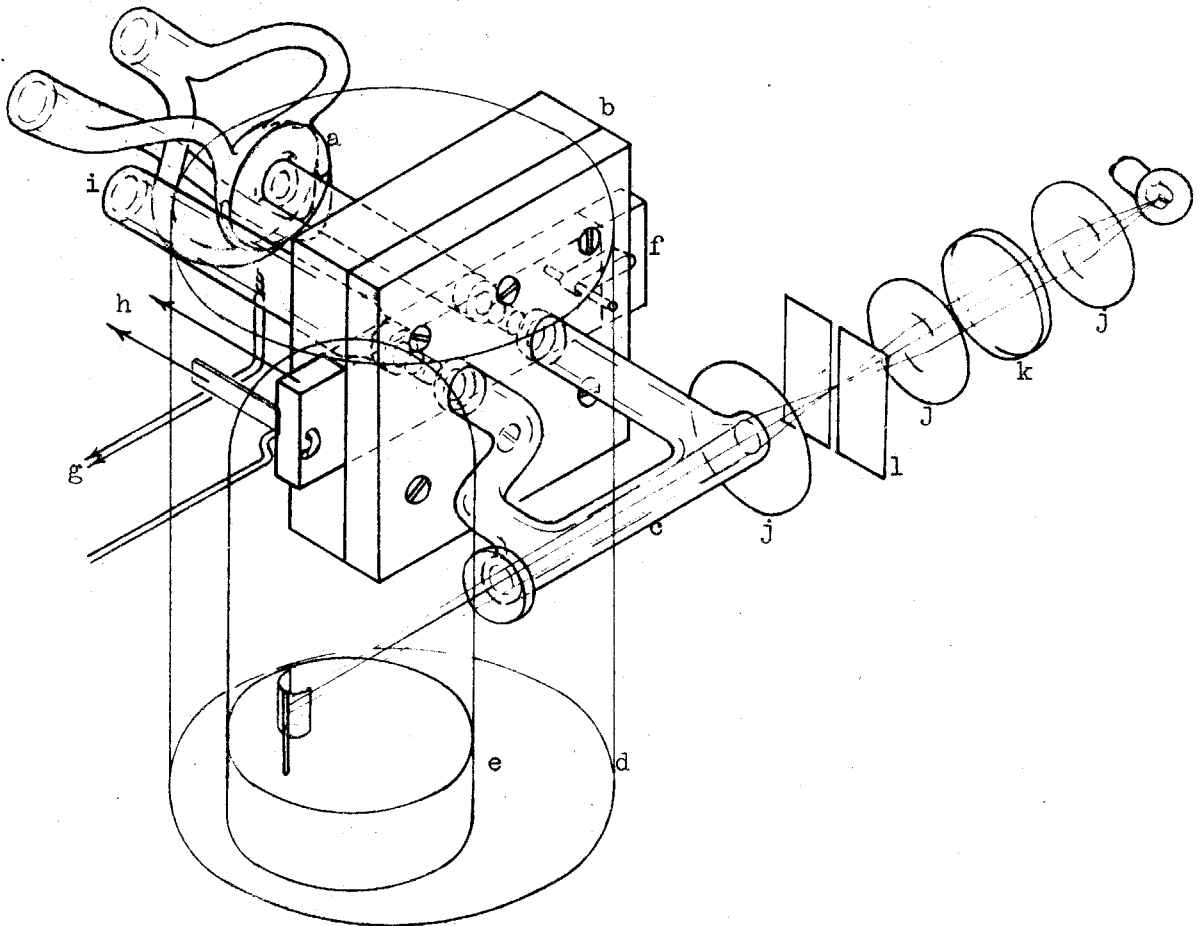
### (a) Construction

The mixing chamber was designed after those of Hartridge and Roughton<sup>(9)</sup>. The chamber is shown in Figure 2. Each of the two streams to be mixed is split in two and introduced tangentially from one-millimeter jets into the flat cylindrical mixing chamber. Around the perimeter of the flat cylinder the four jets were evenly spaced, and a given stream from the flow system came in from opposite sides of the chamber. The chamber was of all glass construction. Its internal dimensions were one millimeter in thickness and 18 millimeters in diameter. The mixed gases flowed out of a two-millimeter tube co-axial with the mixing cylinder. From the weight of mercury required to fill the cylinder and exit tube, the total volume was found to be 0.20 cubic centimeters. At the flow rate usually used of 1.2 liters per minute, the time lost on mixing was about 0.01 second.

### (b) Calibration

In this study it is not necessary to know exactly how soon mixing is satisfactorily complete. All that must be known is that the gases are thoroughly mixed by the time they flow into the reaction cell. The calibration of the mixing chamber consists of a demonstration that mixing is at least 99.5% complete by the time the gases reach the reaction cell. A stream of oxygen carrying one-third of an atmosphere of

Figure 2. Isometric Projection of Mixing Chamber, Stop Gate, and Reaction Cell and Schematic Drawing of Light Source



- a. Mixing chamber
- b. Stop gate
- c. Reaction cell
- d. Housing for photoelectric tube
- e. Photoelectric tube
- f. Movable plunger for stop gate
- g. Thermocouple leads
- h. Contact for external synchronization of the oscilloscope
- i. Gas exit tube
- j. Lenses
- k. Filters
- l. Small circular "slit" for point source of light

$\text{NO}_2\text{-N}_2\text{O}_4$  and flowing at 100 milliliters per minute was diluted in the mixing chamber with a stream of pure oxygen at one liter per minute. Before dilution the  $\text{NO}_2\text{-N}_2\text{O}_4$  mixture would be about 80% in the form of the colorless  $\text{N}_2\text{O}_4$ , and after dilution  $\text{N}_2\text{O}_4$  would constitute only about 15% of the total material. It is well known that at room temperature the rate of attainment of the  $\text{NO}_2\text{-N}_2\text{O}_4$  equilibrium is exceedingly rapid; <sup>(10)</sup> when the pressure of  $\text{N}_2\text{O}_4$  is atmospheric the specific reaction rate is estimated at  $10^5$  per second. If mixing was complete in the 0.01 seconds the gases are in the mixing chamber, no evidence of the dissociation of  $\text{N}_2\text{O}_4$  should have been detected in the reaction cell. On the other hand if mixing was not complete and as mixing finally did occur due to diffusion, intensification of color should be observable in the issuing gases. No such intensification was observed with the photoelectric and photographic method of analysis to be described later. Considering the sensitivity of the apparatus (section B-7), this fact means that less than  $1 \times 10^{-4}$  atmospheres of  $\text{N}_2\text{O}_4$  had failed to be mixed and converted to  $\text{NO}_2$ . In terms of the final concentrations, 0.02 atmospheres of  $\text{N}_2\text{O}_4$  had been diluted and reacted, and less than  $1 \times 10^{-4}$  atmospheres or less than 0.5% had failed to be mixed.

#### 6. The Stop Gate and the External Synchronization Circuit

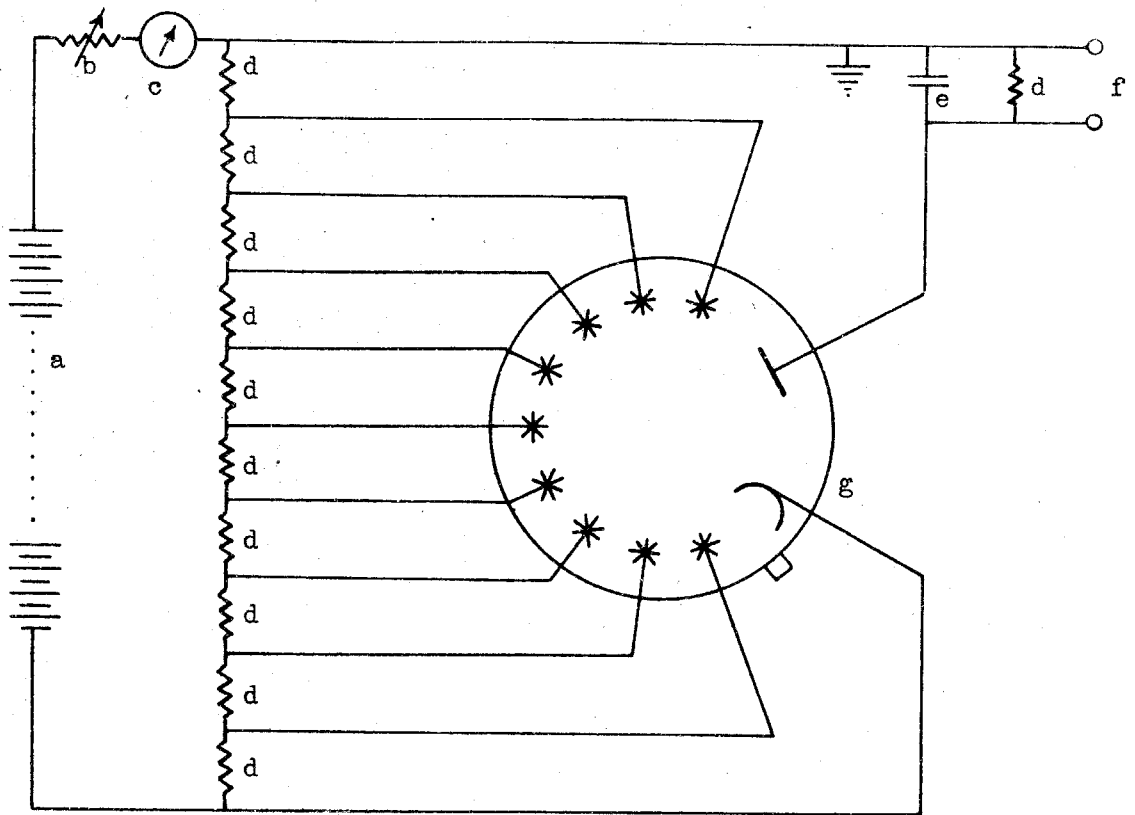
The stop gate, Figure 2, was such that by suddenly moving its flat plunger about  $3/16$  of an inch, two channels of flow were simultaneously cut off. The slot in one of the two squares

of stainless steel which held the plunger and the plunger itself were highly polished and lubricated with a bare minimum of silicone stopcock grease. The channels through the blocks of steel were two millimeters in diameter and countersunk to take the glass fittings from the mixing chamber and the reaction cell.

The stop gate was actuated by a unit efficiency, L-shaped lever which was constrained to move only one quarter of an inch. To one end of the lever was attached an 8-ounce lead weight by means of a strong fishing cord. The other arm of the lever was connected to the plunger of the stop gate by means of a 12-inch brass rod  $1/16$  inches in diameter. When the lever was raised without the weight, friction just held it up. The weight was then dropped 30 centimeters to throw the lever and close the stop gate in less than 0.001 seconds. The lever was mounted on a separate table from the stop gate, and it absorbed essentially all of the violent mechanical shock which occurred as the sinker came to the end of its rope.

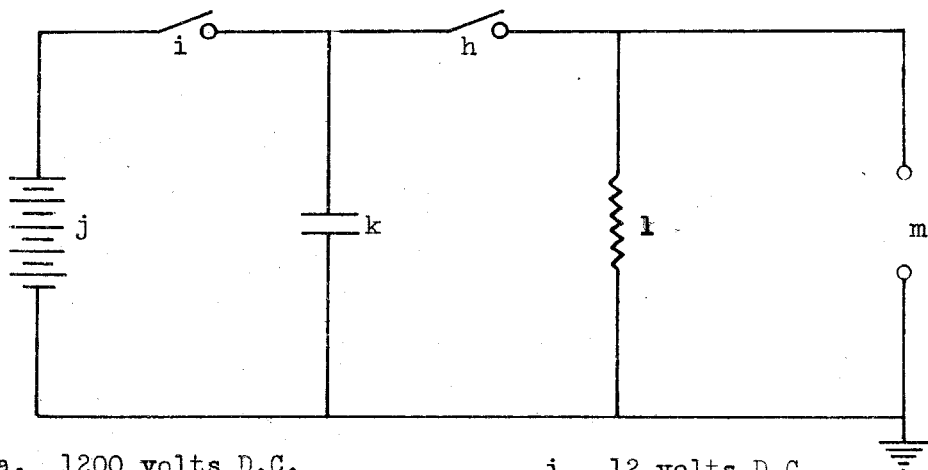
The external synchronization circuit, as is shown in Figure 3, was simply a battery which charged up a condenser when a key was closed and a resistor through which the condenser discharged when the plunger in the stop gate, upon being closed, touched a phosphor bronze brush. The voltage developed across the resistor caused the oscilloscope beam to begin its single trip across the screen at the exact time when the sample of gas had been isolated in the reaction cell.

Figure 3. Circuit Diagrams



Electron multiplying photoelectric tube

External synchronization of oscilloscope



- |  |                      |
|--|----------------------|
| a. 1200 volts D.C.   | j. 12 volts D.C.     |
| b. 200,000 ohms  | k. 1.0 microfarad    |
| c. Zero to one milliampere                                   | l. 1000 ohms         |
| d. 100,000 ohms  | m. "External synch." |
| e. 0.01 microfarad   |                      |
| f. y deflector plates of the oscilloscope                    |                      |
| g. RCA 931-A   |                      |
| h. Contact for external synchronization (Same as Figure 2-h) |                      |
| i. Key for charging the condenser                            |                      |



7. The Photoelectric Method of Following the Reaction in the Reaction Cell

(a) Construction

(1) The Reaction Cell

The reaction cell was glass of 2 millimeters internal diameter and 37 millimeters length. The ends of the glass walls of the reaction cell were covered with black tygon paint before the windows were sealed on in order to prevent light from trans- versing the glass walls and hitting the photoelectric tube. On one end of the cell was fastened a small lens of 13 milli- meter focal length, and on the other end was fixed a square of glass cut from a microscope cover glass. These windows were secured by several layers of tygon paint baked on. The out- side walls of the reaction chamber were heavily coated with black paint.

The reaction cell was fastened to the stop gate by squar- ing and polishing the ends of the leads until they conformed to the countersunk portion. The polished ends were very thinly coated with sealing wax and stuck to the heated stop gate. After it cooled, the seal was reinforced by liberal quantities of 50-50 beeswax and rosin wax on the outside.

One end of the reaction cell was put through a small circular hole in the metal cylinder which housed the photo- electric tube. This end was sealed inside the cylinder by black sealing wax, thus giving good mechanical support and completely shutting off foreign sources of light.

The total volume of the reaction cell was calculated to be about 0.1 cubic centimeters. At the usual flow rate of 1.2 liters per minute, the gas in one end of the cell had been reacting 0.005 seconds longer than that in the other end. In the oxidation of  $\text{NO}_2$  by  $\text{O}_3$  at the concentrations usually used, the half times of the reaction were of the order of magnitude of 0.1 seconds, and so no corrections were made for this effect. In a study of much faster reaction, either much faster flow rates or a shorter cell should be used.

(ii) The Light Source

A 500-watt General Electric projection bulb, operated from storage batteries at 80.0 volts (according to the voltmeter across the bulb), was used as the source of light. It was housed in a metal box and cooled by a fast stream of compressed air which was blown through the housing. The light was roughly collimated by a pair of condensing lenses and brought away from the hot light source. A one-centimeter path of 6% cupric sulfate solution was used to remove the heat rays.<sup>(11)</sup> The light beam was further filtered by a blue and a yellow filter whose transmission curves as obtained on the Beckman spectrophotometer are shown in Figure 4. The light was focused by a second pair of lens on a hole 0.2 millimeters in diameter in a piece of aluminum foil glued over a 2-millimeter hole in a plate of brass. The light, lenses, filters, and housing including the brass plate were all mounted firmly on

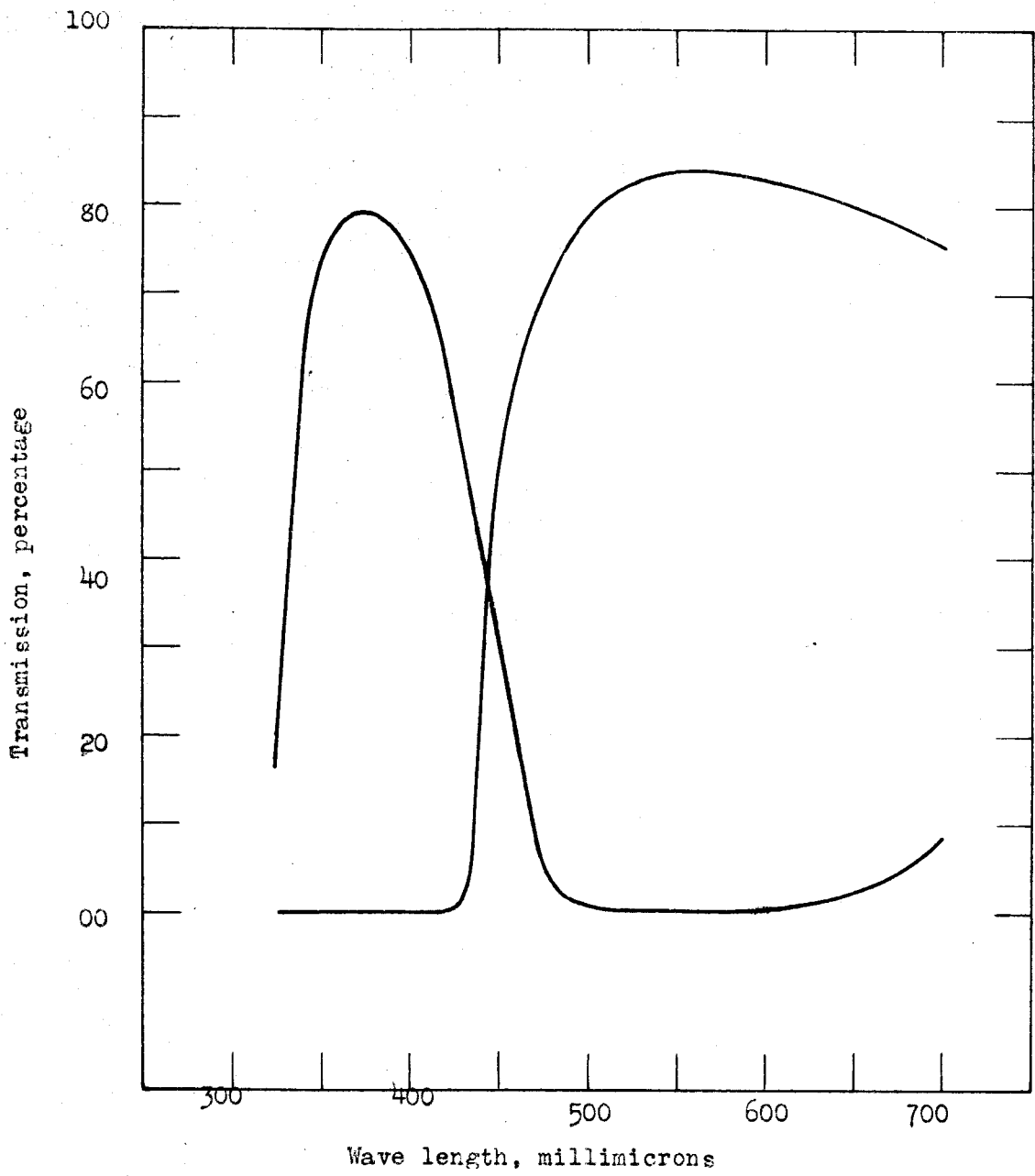


Figure 4. Transmission Curves for Filters

a lead brick. After the rest of the apparatus was installed this unit was moved to the proper position and screwed down to the common base board. The lens on the reaction cell focused the image of the 0.2 millimeter point source about a centimeter beyond the light sensitive surface of the photoelectric tube, so that the light in the reaction cell was slightly convergent and should have missed the walls entirely.

(iii) The Rotating Slotted Disk

The outer edge of a dural disk,  $9\frac{1}{8}$  inches in diameter and  $1/16$  inches thick, was machined into ten equally spaced holes which were 18 degrees in width between diameters of the disk. The 10 teeth in the disk were also 18 degrees in angular width. The disk was mounted on a  $1/15$  horse power synchronous motor which ran at 1800 revolutions per minute. Thus the disk turned at 30 revolutions per second, and the light beam was interrupted 300 times each second. The disk was mounted so that its teeth were just in front of the 0.2-millimeter hole which was the source of light for the reaction cell.

(iv) The Photoelectric Tube and its Circuit

Figure 3 shows the circuit diagram for the RCA 931-A electron multiplying photoelectric tube. The source of voltage was 16 mini-max batteries rated at  $67\frac{1}{2}$  volts each. Selected pairs of 50,000-ohm wire wound resistors were combined to make a voltage divider of 10 equal steps. The maximum variation in resistance between different pairs was about one per cent. A 200,000-ohm potentiometer was adjusted so that at all times during the experiments the ammeter in series with

the voltage divider read 0.920 milli-amperes when no light fell on the photoelectric tube. A resistor and condenser were put in parallel across the output of the photoelectric tube in order to short out the high frequency components of the "noise" in the photoelectric tube. The tube was completely unusable at the low intensities employed without this condenser. At these low intensities the width of the wave packet on the screen was proportional to the intensity of the light, as was seen in a fairly rough experiment in which calibrated screens were put in the collimated beam of light.

(v) The Oscilloscope

The oscilloscope was the DuMont type 247 with a 5 inch screen. The screen gave a blue light to which photographic film is quite sensitive.

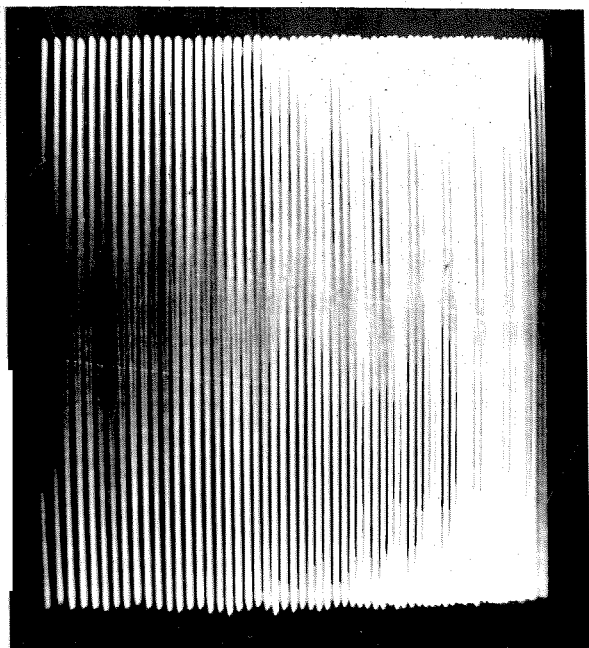
(vi) The Camera

An Argus A-2 camera with its lens remounted and set forward was used for this work. The position of the camera relative to the screen remained fixed at all times.

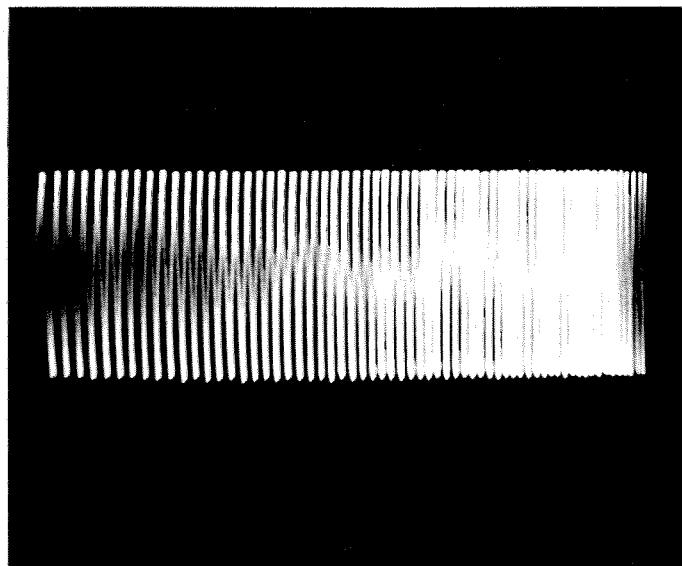
(b) Calibration of the Photoelectric Method of Following the Reaction in the Reaction Cell

Streams of different known  $\text{NO}_2$  concentrations were made up after the method described above in Section B-4. Before a calibration run was made, the streams flowed for a time which, on the assumption of perfect mixing in the bulb, was sufficient to fill the storage bulb to 99.9% of the concentration of the stream itself. The voltage across the light bulb was set to 80.0 volts D. C. by a variable resistor in

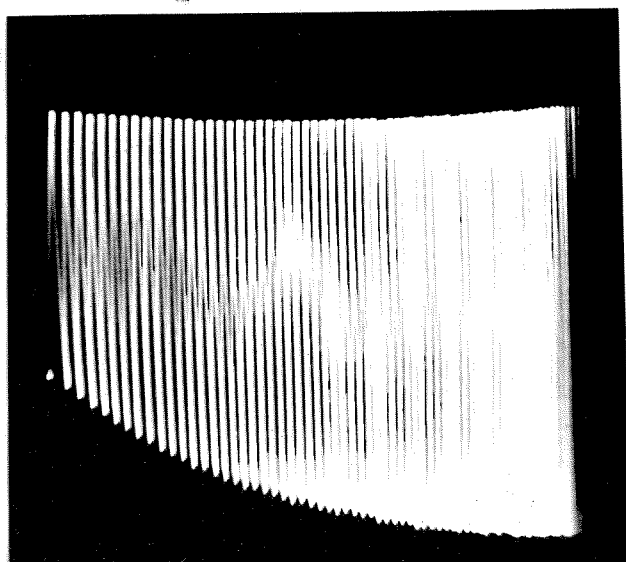
Figure 5. Photographs of the Oscilloscope Trace



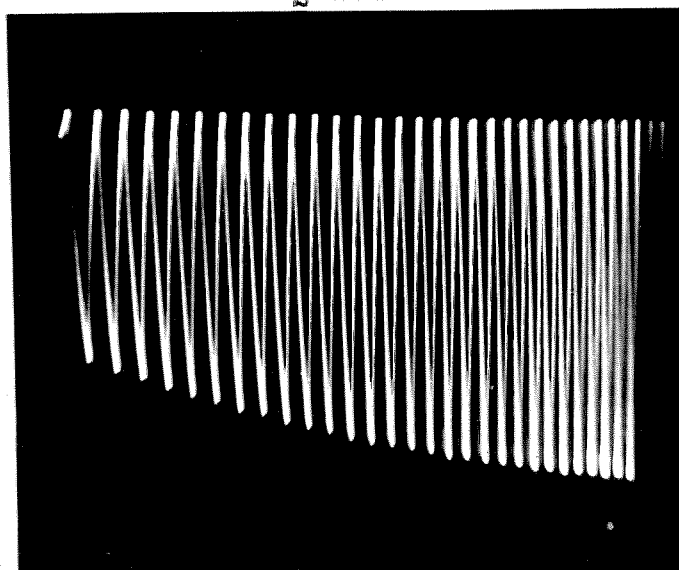
O<sub>2</sub> Blank



NO<sub>2</sub> Blank



Reaction, Slow Sweep



Reaction, Fast Sweep

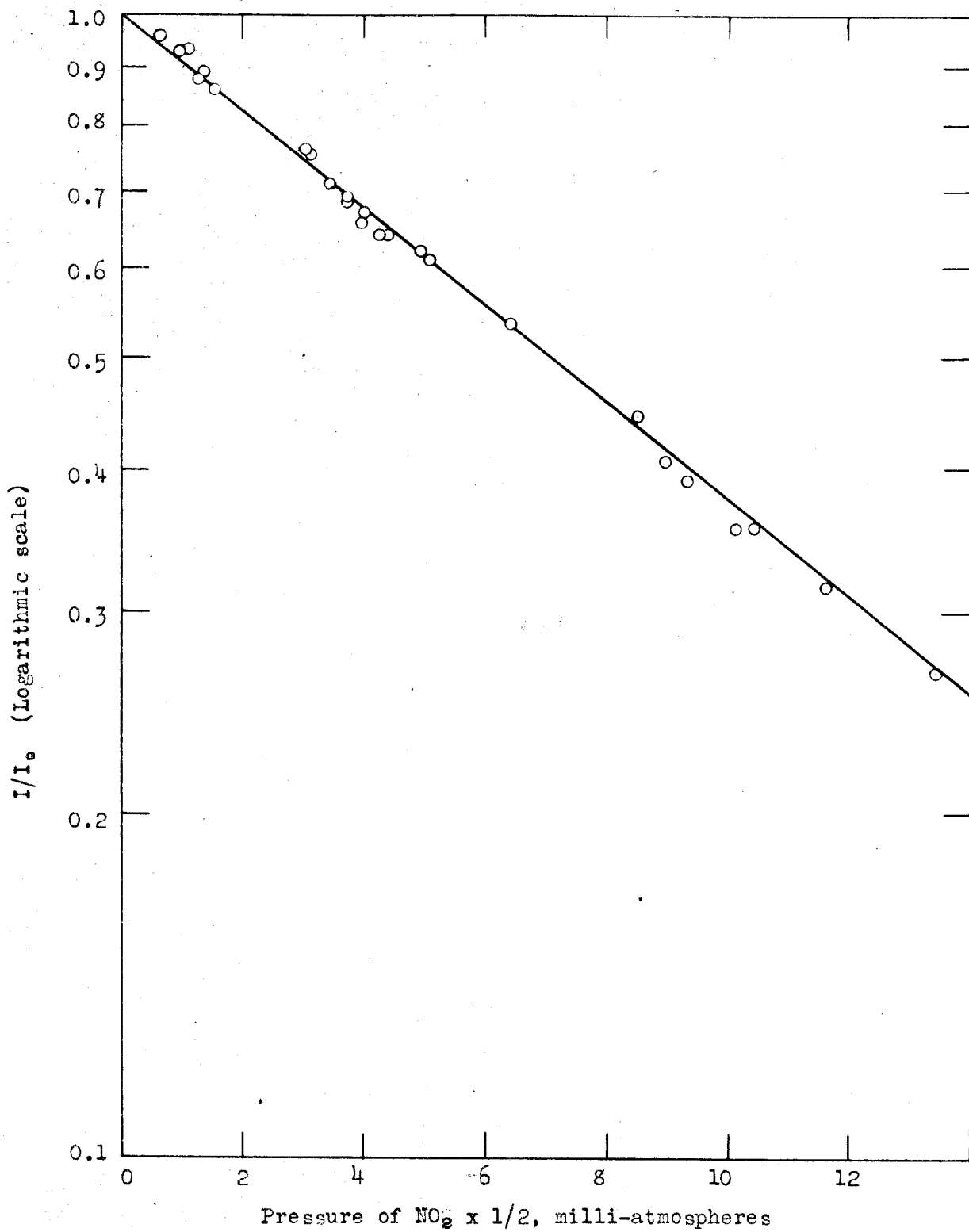


Figure 6. Calibration of the Reaction Cell and the Photoelectric Circuit

series with the bulb, and the current through the voltage divider for the photoelectric tube was set at 0.920 milliamperes when the tube was in the dark. With pure oxygen being blown through the reaction cell, the camera shutter was opened, and the weight was dropped, starting the beam across the oscilloscope screen. The light beam of frequency 300 cycles per second actuated the photoelectric tube whose output was registered on the oscilloscope screen and photographed. The width of the trace on the photographic film, as read in a microfilm projector, was called  $I_0$ . Immediately afterward the stream of  $\text{NO}_2$  from the storage bulb was passed through the reaction cell, and after one minute or more another oscilloscope trace was photographed whose width was called  $I$ . The temperature of the stream was observed by means of the thermocouple. The bypass stopcocks were turned and another measure of  $I_0$  was taken.

If  $I_0$  changed during the run, the value used was interpolated linearly with respect to the time. The values of  $I/I_0$  obtained for various concentrations of  $\text{NO}_2$  are given in Table 3. The same data are plotted as the logarithm of  $I/I_0$  against one half the  $\text{NO}_2$  concentration in Figure 6. It can be seen, somewhat surprisingly, that with the filters and concentrations of  $\text{NO}_2$  used, Beer's law is obeyed by  $\text{NO}_2$ .

This calibration curve, Figure 6, was the basis of all further work. Using the nomenclature defined on page 8, it



can be seen the experimentally determined quantities give the pressures of all components of the gas mixture:

$I/I_0$  (observed) gives  $x/2$

The thermocouple reading (observed) gives the temperature from which the equilibrium constant  $K$  can be found<sup>(7)</sup>

The graph of  $1/F$  against  $x/2$  for various values of  $K$  gives the value of  $1/F$

$$c = (1/F)(x/2)$$

$$y = (1/F - 1)(x/2)$$

From the calibration curve the sensitivity of the apparatus can be seen to be about  $1 \times 10^{-4}$  atmospheres of  $\text{NO}_2$ . The most efficient working range is between 1 and 10 milliatmospheres.

### 8. Temperature Measurement

In the study of the fast reaction between ozone and nitrogen dioxide, the temperature was measured rather than controlled. A chamber was built around the mixing chamber and reaction cell, and the air inside was heated or cooled to bring the cell to about the desired temperature. Also before entering the chamber the gases passed through glass coils in a water bath of approximately the right temperature. With this arrangement the desired temperature was only very slowly obtained in the reaction cell and the method was not a desirable one. The leads to the mixing chamber, the mixing chamber, and the reaction cell should all be in a liquid bath in order to have satisfactory temperature control.

Table 3.

Calibration of the Photoelectric System  
Against NO<sub>2</sub>

| Film Roll | Film Frame | o<br>Milli-atmospheres | Temp.<br>°C | F     | x/2<br>Milli-atmospheres | I/I <sub>0</sub> |
|-----------|------------|------------------------|-------------|-------|--------------------------|------------------|
| III       | 1-7        | 1.10                   | 21.0        | 0.957 | 1.05                     | 0.935            |
|           | 7-10       | 0.60                   | 20.5        | 0.975 | 0.58                     | 0.960            |
|           | 11-14      | 0.98                   | 20.1        | 0.960 | 0.94                     | 0.931            |
|           | 14-17      | 1.65                   | 19.2        | 0.928 | 1.53                     | 0.858            |
|           | 18-21      | 4.41                   | 19.1        | 0.845 | 3.73                     | 0.692            |
|           | 21-24      | 11.9                   | 19.6        | 0.712 | 8.49                     | 0.443            |
|           | 25         | 8.07                   | 20.1        | 0.785 | 6.34                     | 0.537            |
|           | 26         | 6.10                   | 20.1        | 0.820 | 5.00                     | 0.618            |
|           | 27         | 5.19                   | 20.2        | 0.840 | 4.36                     | 0.642            |
|           | 28         | 4.37                   | 20.2        | 0.858 | 3.75                     | 0.686            |
|           | 29         | 3.87                   | 20.6        | 0.876 | 3.39                     | 0.712            |
|           | 30         | 3.48                   | 20.6        | 0.884 | 3.08                     | 0.756            |
|           | 31-32      | 3.37                   | 20.4        | 0.887 | 2.99                     | 0.759            |
|           | IV         | 1-8                    | 1.23        | 12    | 0.917                    | 1.13             |
| 35-36     |            | 1.37                   | 20.6        | 0.947 | 1.30                     | 0.890            |
| V         | 1-8        | 5.00                   | 20.4        | 0.851 | 4.26                     | 0.643            |
|           | 9-16       | 4.55                   | 21.1        | 0.867 | 3.95                     | 0.671            |
|           | 34-35      | 5.75                   | 21.4        | 0.845 | 4.86                     | 0.622            |
| VI        | 1-8        | 5.05                   | 12          | 0.767 | 3.87                     | 0.653            |
|           | 21-28      | 21.0                   | 20.2        | 0.640 | 13.4                     | 0.267            |
|           | 29-34      | 17.5                   | 20.1        | 0.665 | 11.6                     | 0.319            |
|           | 37         | 14.9                   | 21.5        | 0.695 | 10.4                     | 0.352            |
| VII       | 4-6        | 12.3                   | 20.5        | 0.725 | 8.92                     | 0.403            |
|           | 8-14       | 13.8                   | 22.5        | 0.729 | 10.1                     | 0.353            |
|           | 18-20      | 12.6                   | 21.3        | 0.739 | 9.32                     | 0.390            |

The temperature of the gases leaving the reaction cell was measured by a thermocouple made of 36-gauge copper and 30-gauge advance wire. It was coated with three coats of wire enameling fluid, baked on for 12 hours at 120°C, in order to protect it from the corrosive reactants. The reference junction was sealed with wax inside a thin-wall test tube and immersed in a well-stirred ice bath. With the other junction in a stirred bath in a Dewar flask, whose temperature was read by a mercury in glass thermometer, the thermocouple was calibrated over the range that it was used. As can be seen in Figure 2, the thermocouple junction was mounted inside the flow line where the gas from the reaction cell had just gone through the stop gate. The potential developed by the thermocouple was read with a Leeds and Northrup portable precision potentiometer, No. 8662.

#### 9. The Gas Washing Device Used for Calibrations

The ozone or NO<sub>2</sub> was washed free of its carrier oxygen by passing it down a co-flowing washing column. A 4-foot length of 3 millimeter internal diameter capillary tube was made into a helix of about 4 inches internal diameter and one inch between turns. At the top there was a T-tube made of the same capillary material. The proper solution to absorb the gas flowed at a constant rate, set by a constricting capillary, down one arm of the T-tube, and the oxygen solution of gases flowed down the other. The gas stream was

broken into small bubbles separated by a piston of liquid. In this way prolonged intimate contact between the gas and washing solution was obtained. This method works when the ratio of gas to liquid is less than 10, and with a glass column this small the total flow could not be much over 100 cubic centimeters per minute.

#### 10. Remarks concerning Trouble with Mechanical Vibrations

The apparatus was found to be exceedingly sensitive to mechanical vibrations. The motor which turned the slotted disk had to be mounted on a separate table. Vibrations from the sudden closing of the stop gate were eliminated only after 50 pounds of lead were mounted so that the weight bore down on the stop gate itself. Even with these precautions some of the final data showed some vibrations to have been present.

#### C. The Reaction between Ozone and Nitrogen Dioxide

##### 1. The Procedure in Carrying out an Experiment

The power on the oscilloscope was turned on for about an hour before use. The proper capillaries were installed on the flowmeters, and the streams were passed through the saturator and the ozonizer for an hour, or longer if necessary to sweep out the storage bulbs to 99.9% of the desired concentrations. The current through the voltage divider in the photoelectric circuit was adjusted to 0.920 milliamperes while the tube was dark. The voltage across the light was set at 80.0 volts D.C., and the rotating sector

was turned on and started in motion. The turning of the bypass stopcocks isolated the  $\text{NO}_2$  and  $\text{O}_3$  storage bulbs, and pure  $\text{O}_2$  was blown through the cell. A photograph was taken in the manner previously described to give an  $\text{O}_2$  blank. The  $\text{NO}_2$  bulb and saturator was then cut into the stream, the  $\text{O}_3$  bulb still being bypassed. After at least a minute, a picture was taken of the oscilloscope trace to give a  $\text{NO}_2$  blank. The ozone bulb was finally turned into the stream, and after another minute or so the weight was dropped again, isolating a sample of the reacting gases in the cell and taking a picture of the oscilloscope screen. Three or more duplicates were made, sufficient time being allowed between runs for the steady state to be restored. The duplicates were usually made with different velocities of the beam across the oscilloscope screen. The temperature of the thermocouple junction was read at each stage of the run. The calibration procedure was reversed at the end of a series of runs. The ozonizer and the  $\text{O}_3$  storage bulb were bypassed to give a  $\text{NO}_2$  calibration. The saturator and  $\text{NO}_2$  storage bulb were next bypassed to give another  $\text{O}_2$  blank.

## 2. The Method of Calculating the Data

### (a) Taking the Data from the Film

The film, plus-X, was developed in Defender 777 fine grain developer to a gamma of 1.2. The traces on the film were projected in a microfilm reader on a sheet of white paper

taped in place. The details of the upper and lower edges were lightly drawn with a soft lead pencil, and the time scale marked and labeled. The paper was removed and a smooth curve was drawn through the slightly ragged edges. The edges were ragged in some cases due to mechanical vibrations from the falling weight or the rotating sector, and some scatter was due to random variation in the output of the photoelectric tube. The paper with the smoothed tracing was taped to a rigid board. The vertical distance from one side of the envelope to the other side was taken as the measure of I at that particular time.

An example of the form of the data on the film is given in Figure 5. There are shown an O<sub>2</sub> blank, a NO<sub>2</sub> blank, and two runs at different rates of sweep of the oscilloscope beam.

(b) Correction for Distortion and for Drift  
in the Calibration

A portion of the data was found to have as much as two percent distortion by an analysis of the O<sub>2</sub> and NO<sub>2</sub> calibration pictures. The distortion was found to be markedly dependent on the position on the screen along the time axis, and much less so a function of the height of the trace. For each such run two distortion correction curves were plotted against the time coordinate, one from the O<sub>2</sub> calibrations and the other from the NO<sub>2</sub> calibrations.

Where these two curves were not identical, values were interpolated between them to get a correction factor for each point of the actual run. In view of the fact that correction curves for distortion were reproduced almost identically for different blank runs, it can be stated that distortion was not an important source of error in the final results.

The principal source of error in this work was due to drift in the value of  $I_0$  and uncertainties in the interpolation of this quantity between the initial and final calibration points. An arbitrary procedure was devised to make this interpolation. The time of making the initial and final calibrations and the time of the run in question were known, and so the interpolation of  $I_0$  was made linearly with respect to these times. Much of this drift appeared to be due to the oscilloscope, which was not in its best condition during these experiments. After the experiments were completed, it was decided that  $O_2$  calibration blank runs should be made between every individual run, rather than merely before and after a set of three or four identical runs.

Sample numerical calculations were made on a few examples of the runs, in which a value of  $I_0$  was chosen other than that obtained by the arbitrary interpolation method but within the range of the initial and final calibration

points for that set of runs. The nature of the rate law was very little influenced by this change of  $I_0$ , but the value of the rate constant was markedly altered. The entire scatter shown by the final tabulation of the rate constants could have been due to this cause. Thus it appears that the precision of this method can be improved by much more careful attention to this point.

(c) Calculation of the Pressures of the Various Gases

The pressure of  $\text{NO}_2$  divided by two,  $x/2$ , was obtained directly from the corrected value of  $I/I_0$  and Figure 6. As was shown on pages 21 and 22, a knowledge of  $x/2$  and the temperature permits the calculation of the actual pressure of  $\text{N}_2\text{O}_4$ ,  $y$ , and the total formal pressure of  $\text{N}_2\text{O}_4$ ,  $c$ . The pressure of ozone,  $z$ , can then be found by difference.

Wulf, Daniels, and Karrer<sup>(5)</sup> showed that the reaction ozone and nitrogen dioxide is given quantitatively by the chemical equation:



Thus at any time, the amount of  $\text{O}_3$  which had reacted was equal to the formal amount of  $\text{N}_2\text{O}_4$  which had been consumed, or

$$c_0 - c = z_0 - z$$

$$z = c + (z_0 - c_0)$$

where  $c_0$  and  $z_0$  are respectively the formal pressure of  $\text{N}_2\text{O}_4$  and the pressure of  $\text{O}_3$  at zero time. The value of  $c_0$  was

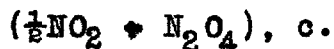


calculated from the calibration of the saturator, the flow rates, and the equilibrium constant. The value of  $z_0$  was calculated from the calibration of the ozonizer and the flow rates.

Thus there was tabulated opposite the time, a column for the pressures of  $\text{NO}_2/2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{O}_3$ , and  $(\text{NO}_2/2 + \text{N}_2\text{O}_4)$ . A typical example is given in Table 4.

(d) Calculation of the Rate of the Reaction

Since the equilibrium between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is established at an exceedingly high rate,<sup>(10)</sup> the rate of the reaction of interest is that of the disappearance of



By this method of following the reaction, there is obtained a large number of closely spaced experimental points. As a good approximation, the difference between two successive points may be treated like a differential, and the rate considered to be the difference in  $c$  between two points divided by the duration of the time interval. The next to the last column in Table 4 gives the rate of the reaction for experiment VI-9, calculated in this manner. In a similar manner the rate of the reaction was calculated for the other 42 runs made in this study.

3. Analysis of the Data

(a) The Differential Rate Equation

An inspection of the tables of the reaction rate quickly lead to an hypothesis that the rate law is simply

Table 4.

An Example of the Method Used to Analyse the Data

Run VI-9. Total flow rate 0.594 liters per minute, temperature 12°C.,  
 $z_0 = 7.28$  milli-atmospheres,  $c_0 = 5.05$  milli-atmospheres.

| Time<br>unit<br>1/300<br>sec. | $I_0$ (obs.)<br>$O_2$<br>blank<br>mm. | $I$ (obs.)<br>mm. | $I/I_0$ | Pressure of Gases in Milli-atmospheres |                 |                |              |            |                            |               |  |
|-------------------------------|---------------------------------------|-------------------|---------|--|-----------------|----------------|--------------|------------|----------------------------|---------------|--|
|                               |                                       |                   |         | $NO_2/2$<br>$x/2$                      | $N_2O_4$<br>$y$ | $x/2+y$<br>$c$ | $O_3$<br>$z$ | $\Delta c$ | $\Delta c/\Delta t$<br>$R$ | $R/xz$<br>$k$ |  |
| 0                             | 243 1/2                               | 183 1/4           | 0.752   | 2.93                                   | 0.67            | 3.60           | 5.83         |            |                            |               |  |
| 1                             | 244                                   | 185 3/4           | 0.762   | 2.79                                   | 0.61            | 3.40           | 5.63         | 0.20       | 60                         | 1.83          |  |
| 2                             | 244 3/4                               | 188 1/4           | 0.769   | 2.70                                   | 0.60            | 3.30           | 5.53         | 0.10       | 30                         | 0.98          |  |
| 3                             | 245                                   | 190               | 0.776   | 2.61                                   | 0.55            | 3.16           | 5.39         | 0.14       | 42                         | 1.45          |  |
| 4                             | 245 1/4                               | 191 3/4           | 0.782   | 2.53                                   | 0.51            | 3.04           | 5.27         | 0.12       | 36                         | 1.32          |  |
| 5                             | 245 1/2                               | 193 1/4           | 0.787   | 2.47                                   | 0.49            | 2.96           | 5.19         | 0.08       | 24                         | 0.92          |  |
| 6                             | 246 1/4                               | 195               | 0.792   | 2.40                                   | 0.44            | 2.88           | 5.11         | 0.08       | 24                         | 0.96          |  |
| 7                             | 246                                   | 196 1/4           | 0.798   | 2.33                                   | 0.44            | 2.77           | 5.00         | 0.11       | 33                         | 1.38          |  |
| 8                             | 246 1/2                               | 198               | 0.804   | 2.25                                   | 0.41            | 2.66           | 4.89         | 0.11       | 33                         | 1.46          |  |
| 9                             | 246 1/4                               | 199 1/4           | 0.809   | 2.18                                   | 0.39            | 2.57           | 4.80         | 0.09       | 27                         | 1.26          |  |
| 10                            | 246 1/4                               | 200 1/4           | 0.813   | 2.13                                   | 0.38            | 2.51           | 4.74         | 0.06       | 18                         | 0.88          |  |
| 11                            | 246 1/2                               | 201 3/4           | 0.818   | 2.06                                   | 0.35            | 2.41           | 4.64         | 0.10       | 30                         | 1.52          |  |
| 12                            | 247                                   | 203               | 0.822   | 2.02                                   | 0.34            | 2.36           | 4.59         | 0.05       | 15                         | 0.66          |  |
| 13                            | 247 1/4                               | 204               | 0.825   | 1.98                                   | 0.32            | 2.30           | 4.53         | 0.06       | 18                         | 0.81          |  |
| 14                            | 247 1/4                               | 205 1/4           | 0.830   | 1.92                                   | 0.31            | 2.23           | 4.46         | 0.07       | 21                         | 1.20          |  |
| 15                            | 247 1/4                               | 206 1/4           | 0.834   | 1.87                                   | 0.28            | 2.15           | 4.38         | 0.08       | 24                         | 1.43          |  |
| 16                            | 247 1/4                               | 207 3/4           | 0.840   | 1.80                                   | 0.27            | 2.07           | 4.30         | 0.08       | 24                         | 1.51          |  |
| 17                            | 247 1/4                               | 209               | 0.846   | 1.73                                   | 0.24            | 1.97           | 4.20         | 0.10       | 30                         | 2.00          |  |
| 18                            | 247 1/4                               | 210               | 0.850   | 1.68                                   | 0.24            | 1.92           | 4.15         | 0.05       | 15                         | 1.05          |  |
| 19                            | 247 1/4                               | 211               | 0.854   | 1.63                                   | 0.23            | 1.86           | 4.09         | 0.06       | 18                         | 1.32          |  |
| 20                            | 247 1/4                               | 212               | 0.858   | 1.59                                   | 0.21            | 1.80           | 4.03         | 0.06       | 18                         | 1.38          |  |
| 21                            | 247 1/4                               | 213               | 0.862   | 1.54                                   | 0.20            | 1.74           | 3.97         | 0.06       | 18                         | 1.44          |  |
| 22                            | 247 1/4                               | 214               | 0.866   | 1.49                                   | 0.18            | 1.67           | 3.90         | 0.07       | 21                         | 1.76          |  |
| 23                            | 247 1/4                               | 215               | 0.870   | 1.44                                   | 0.17            | 1.61           | 3.84         | 0.06       | 18                         | 1.58          |  |
| 24                            | 247 1/4                               | 215 3/4           | 0.873   | 1.41                                   | 0.17            | 1.58           | 3.81         | 0.03       | 9                          | 0.82          |  |
| 25                            | 247 1/4                               | 216 1/2           | 0.876   | 1.37                                   | 0.16            | 1.53           | 3.76         | 0.05       | 15                         | 1.42          |  |
| 30                            | 246 3/4                               | 220               | 0.892   | 1.18                                   | 0.12            | 1.30           | 3.53         | 0.23       | 13.8                       | 1.48          |  |
| 35                            | 246                                   | 223               | 0.906   | 1.01                                   | 0.08            | 1.09           | 3.32         | 0.21       | 12.6                       | 1.68          |  |
| 40                            | 245 1/2                               | 224 3/4           | 0.915   | 0.91                                   | 0.06            | 0.97           | 3.20         | 0.12       | 7.2                        | 1.10          |  |
| 45                            | 245 1/2                               | 226               | 0.922   | 0.83                                   | 0.06            | 0.89           | 3.12         | 0.08       | 4.8                        | 0.88          |  |
| 50                            | 245                                   | 227 3/4           | 0.929   | 0.75                                   | 0.05            | 0.80           | 3.03         | 0.09       | 5.4                        | 1.11          |  |

Average in (Atm.  $\times 10^{-3}$  x sec.)<sup>-1</sup>

1.29

$$- dc/dt = kxz$$

that is, the rate of disappearance of formula weights of  $N_2O_4$  is proportional to the product of the pressures of  $NO_2$  and  $O_3$ . The simplest way to test this hypothesis is to divide the average rate obtained for a short interval by the average value of  $x$  and  $z$  observed at the beginning and end of the interval. The last column of Table 4 gives an illustration of the result obtained when this test is made. The average of 30 instantaneous values of  $k$  is 1.29 (milli-atmospheres x seconds)<sup>-1</sup>. Though the individual, instantaneous values scatter fairly badly, there is no trend in the value of  $k$  down the column. Thus it can be safely said that in experiment VI-9 the differential equation shown above describes the results.

In a similar fashion to that shown in Table 4, the values of  $k$  for the other experiments were computed. For each of these runs the value of  $k$  was about as constant with respect to the time as the values shown in Table 4, until the pressure of a reactant became so low that the normal scatter of the points exceeded the value of the pressure. One additional rule was adopted for the method of calculating the average value of  $k$ . Since the reaction is exothermic and in order to reduce the uncertainty in the temperature reading, the convention was adopted of averaging only those values of  $k$  observed in the first tenth of a second after the stop gate was closed for runs in which  $c_0$  or  $z_0$  exceeded 10 milli-atmospheres.

The average value of  $k$  and the initial formal pressure of  $O_3$  and  $N_2O_4$  are given in Table 5 for all experiments carried out at room temperature which could be interpreted. (Some runs were made with such small pressures of the reactants or with such a small ratio of one to the other that much less change in  $x/2$  was observed than corresponds to the errors of the method.) Though the measured temperature varied by  $2^\circ C.$ , in Table 5 the values of  $k$  at room temperature are considered a homogeneous group, because the measurement of the temperature itself is uncertain to about a degree or two, and furthermore the value of  $k$  changes very slowly with a change in temperature.

Omitting from Table 5 experiment V-28 which is uncertain, the initial values of  $c$  and  $z$  each vary over a factor of 10. The ratio of  $c_0$  to  $z_0$  varies from 0.21 to 2.4, or more than a factor of 10. Over this range of conditions it can be seen that, with some scatter, essentially the same value is obtained for the rate constant. The average value found for  $k$  at  $21^\circ C.$  is  $1.51$  (milli-atmospheres seconds) $^{-1}$ , the standard deviation is 0.14 or about 10%, and the standard error of the mean is only 0.02. The deviations do not appear to be correlated with any of the quantities listed in Table 5. It is felt that the principal source of scatter in the values of  $k$  lies in uncertainties in the interpolation of  $I_0$ , as discussed in Section C-2-b.

From Table 5 it must be concluded that the differential equation

$$- dc/dt = kxz$$

does describe all of the observed data at room temperature. There remains the question as to whether some other equation would do equally as well. Inspection of the data shows that no other product of integral powers of the pressures of the reactants gives a satisfactory rate law, with a possible exception of  $2kxz$ . During most runs  $2c$  and  $x$  are on the average within 5% of each other, and no choice could be made. In experiments V-10, 11, 12, and 13, with the large excess of  $\text{NO}_2$ ,  $2c$  averages 123% of  $x$ , and the values of  $k$  found from the equation

$$- dc/dt = 2kxz$$

would be 1.14, 1.22, 1.20, and 1.08, all far below the average value expected for this case. On this basis the second differential equation may be rejected. Though there is the possibility of some complex law being even better than the one tested, the not inconsiderable quantity of evidence on hand indicates that the assumed simple differential equation describes the rate of the reaction between  $\text{NO}_2$  and  $\text{O}_3$ .

Table 5

Summary of Rate Constants Observed at Room Temperature

| Film Roll | Film Frame | Temp. °C | $c_0$             | $z_0$ | Rate Constants<br>(Milli-atmospheres seconds) <sup>-1</sup> |         |
|-----------|------------|----------|-------------------|-------|---|---------|
|           |            |          | Milli-atmospheres |       | k   | k(ave.) |
| IV        | 18         | 20       | 1.23              | 1.92  | 1.33  | 1.54    |
|           | 19         | 20       | 1.23              | 1.92  | 1.68  |         |
|           | 20         | 20       | 1.23              | 1.92  | 1.60  |         |
| IV        | 23         | 20       | 1.28              | 3.68  | 1.26  | 1.45    |
|           | 24         | 20       | 1.28              | 3.68  | 1.65  |         |
| IV        | 26         | 20       | 1.21              | 5.70  | 1.50  | 1.46    |
|           | 27         | 20       | 1.21              | 5.70  | 1.45  |         |
|           | 28         | 20       | 1.21              | 5.70  | 1.42  |         |
| V         | 28         | 21       | 5.72              | 1.08  | 1.5 (?)   |         |
| V         | 19         | 21       | 5.35              | 4.69  | 1.49  | 1.61    |
|           | 20         | 21       | 5.35              | 4.69  | 1.74  |         |
| V         | 4          | 20       | 5.00              | 7.52  | 1.65  | 1.64    |
|           | 5          | 20       | 5.00              | 7.52  | 1.61  |         |
|           | 6          | 20       | 5.00              | 7.52  | 1.77  |         |
|           | 7          | 20       | 5.00              | 7.52  | 1.54  |         |
| V         | 11         | 21       | 4.55              | 11.35 | 1.37  | 1.39    |
|           | 12         | 21       | 4.55              | 11.35 | 1.38  |         |
|           | 13         | 21       | 4.55              | 11.35 | 1.36  |         |
|           | 14         | 21       | 4.55              | 11.35 | 1.45  |         |
| VII       | 10         | 22       | 13.4              | 5.60  | 1.40  | 1.43    |
|           | 11         | 22       | 13.4              | 5.60  | 1.50  |         |
|           | 12         | 22       | 13.4              | 5.60  | 1.48  |         |
|           | 13         | 22       | 13.4              | 5.60  | 1.33  |         |
| VI        | 36         | 22       | 14.9              | 18.0  | 1.65  | 1.72    |
|           | 37         | 22       | 14.9              | 18.0  | 1.79  |         |
| VII       | 4          | 20       | 12.3              | 23.8  | 1.50  | 1.50    |
|           | 5          | 20       | 12.3              | 23.8  | 1.51  |         |
|           | 6          | 20       | 12.3              | 23.8  | 1.50  |         |

Average 1.51

$c_0$  is the initial pressure of  $N_2O_4$  plus  $NO_2/2$ .

$z_0$  is the initial pressure of  $O_3$ .

(b) The Integrated Rate Equation

Using again the terms defined on page 8, the differential equation is expressed in terms of  $x$  alone, and this equation is then integrated.

The observed differential equation is

$$- dc/dt = kxz$$

The equilibrium equation is

$$K = x^2/y = x^2/(c-x/2)$$

which on solution for  $c$  gives

$$c = x/2 + x^2/K$$

Differentiating this expression with respect to time, there results

$$- dc/dt = -(\frac{1}{2} + 2x/K)dx/dt$$

It was shown on page 28 that

$$z = c + (z_0 - c_0) = (z_0 - c_0) + x/2 + x^2/K$$

Substitution of these expressions into the differential equation and separation of variables gives

$$\frac{(\frac{1}{2} + 2x/K)dx}{[(z_0 - c_0) + x/2 + x^2/K]x} = -k dt$$

By breaking this expression into two parts, there is obtained

$$\frac{1}{2} \int \frac{dx}{(z_0 - c_0) + x/2 + x^2/K x} + 2/K \int \frac{dx}{(z_0 - c_0) + x/2 + x^2/K} = -k \int dt$$

These integrals are No. 67 and No. 78 in Pierce's table.<sup>(12)</sup>

When  $4(z_0 - c_0)/K$  is less than  $\frac{1}{4}$ , which was true for all of the experiments carried out in this study, the solution is

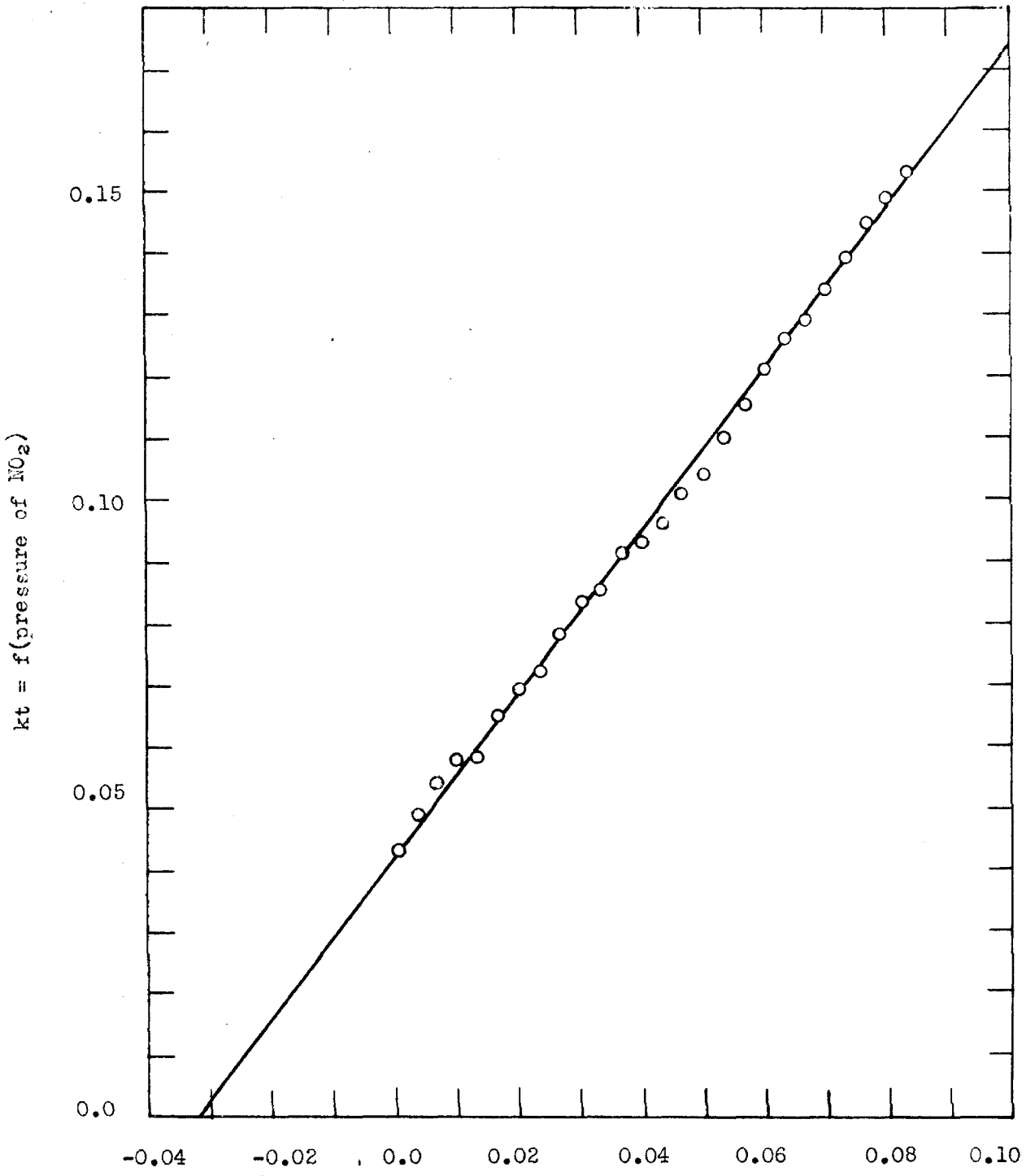
$$kt = C - \left[ \frac{1/4(z_0 - c_0) \log x^2 / (z_0 - c_0 + x/2 + x^2/K)}{2(z_0 - c_0) \log \frac{2x/K + \frac{1}{2} + \sqrt{\frac{1}{4} - 4(z_0 - c_0)/K}}{2x/K + \frac{1}{2} - \sqrt{\frac{1}{4} - 4(z_0 - c_0)/K}}} \right]$$

where C is the value of the terms in the bracket when x is replaced by  $x_0$ .

An example of a test of the integrated equation is shown in Figure 7, in which the data given in Table 4 for run VI-9 are substituted into the integrated equation. The values of kt computed from the integrated equation are plotted against the time. The expected linear relation is obtained in a satisfactory manner, even though the points can be seen to drift slightly around the line. The slope of the line shown in Figure 7 is 1.32 (milli-atmospheres seconds)<sup>-1</sup> which is in satisfactory agreement with the average value of k, 1.29 in the same units, found from the same data by use of the differential equation.

The intercept on the time axis of the line found by the integrated equation is -0.032 seconds. The total flow rate during this experiment was 589 cubic centimeters per minute or 9.8 cubic centimeters per second. These facts imply a volume of 0.31 cubic centimeters in front of the cell after mixing has occurred. The volume in cubic centimeters of the mixing chamber was 0.20, the leads to the reaction cell another 0.10, and the reaction cell itself about 0.10. From the center of the mixing cell to the jets of the mixing





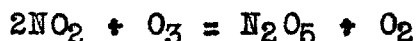
Time, seconds from start of observations (Experiment VI-9)

Figure 7. Test of the Integrated Equation

chamber was thus about 0.35 cubic centimeters. It appears then that mixing is essentially complete early in the stage of the mixing process.

(c) The Energy of Activation

The measurement of the temperature was uncertain because of the temperature rise resulting from the heat of reaction. At 18°C. the reaction



liberates 50 kilocalories per mole of  $\text{N}_2\text{O}_5$  which is formed. (13)  
If the reaction occurred adiabatically, the temperature would rise about 8°C. when one milli-atmosphere of  $\text{O}_3$  reacted in the presence of one atmosphere of oxygen. Actually, the reaction occurred neither adiabatically nor isothermally. In the small tubes and reaction cell, considerable heat interchange occurred between the gas and the walls. It required from 10 to 20 minutes for the temperature of the thermocouple to reach its steady state value when the reactants flowed through the reaction cell, and the maximum increase in temperature observed was about 10% of that calculated on the assumption of adiabatic conditions. Also at the flow rate of 1.2 liters per minute the reaction was only about 5 to 25% complete inside the reaction cell when the streams were still flowing. Thus it was felt that before the stop gate closed the temperature of the walls and the gas inside of the reaction cell was within about a

degree of that of the entering gases. After the stop gate was closed the walls could easily absorb the heat of reaction for the small quantity of gas entrapped in the cell. The gases would warm up, however, because of the time required for the flow of heat. It was further thought that when the gate was first closed the turbulence of the air stream would persist for a short time giving more rapid heat transfer than mere diffusion. On the basis of these arguments, the temperature assigned for a run was that of the gases before reaction started, as measured by the thermocouple for a  $\text{NO}_2$  blank. Also, for high concentrations of reactants only the data for the first tenth of a second were retained.

To try to eliminate these uncertainties of the study of the effect of temperature on the rate of the reaction, these runs were made with low pressures of the reactants. A summary of the values of the rate constant for different temperatures is given in Table 6. In the series of experiments recorded on film roll IV, the pressure of the reactants is low, and the maximum temperature rise due to the heat of reaction was less than one degree Centigrade. In the second set of conditions shown in Table 6, the maximum temperature rise was about  $2\frac{1}{2}$  degrees. In the cold and the warm runs, the temperature of the air space around the reaction cell was within two degrees of that of the thermocouple inside the glass line. Thus though the temperature control was far

from ideal, the errors in the temperature reported in Table 6 should be no more than about two degrees. Also there is no reason to think that the errors are systematic in the sense of giving too great or too small a range in temperature, which would invalidate the measurement of the energy of activation.

The energy of activation  $E$  was calculated from the Arrhenius equation,

$$\ln k = -E/RT + \text{constant}$$

by that method of least squares which recognizes the possibility of error in both variables,<sup>(14)</sup>  $\ln k$  and  $1/T$ . The standard error of estimate of  $E$ , however, was calculated on the assumption that  $1/T$  is an arbitrary independent variable.<sup>(15)</sup> The standard error so found should be a good estimate of that quantity, and at any rate this method of calculation will certainly not underestimate the error. The value found for the energy of activation was 6400 calories per mole; the standard error of estimate was found to be 570 calories per mole. Thus as expected for this reaction, which is fast at room temperature, the energy of activation is quite low. The points which appear in Table 6 are plotted in Figure 8, and the least squares line is drawn on the figure.

Table 6

Summary of Rate Constants Observed at Various Temperatures

| Film Roll | Film Frame | Temp. °C. | $c_0$<br>Milli-atmospheres | $z_0$<br>Milli-atmospheres | Rate Constants<br>(Milli-atmospheres<br>seconds) <sup>-1</sup><br>k | k(ave.) |
|-----------|------------|-----------|----------------------------|----------------------------|---|---------|
| IV        | 4          | 13        | 1.23                       | 1.92                       | 1.23  | 1.21    |
|           | 5          | 13        | 1.23                       | 1.92                       | 1.11  |         |
|           | 6          | 13        | 1.23                       | 1.92                       | 1.22  |         |
|           | 7          | 15        | 1.23                       | 1.92                       | 1.27  |         |
| IV        | 18         | 20        | 1.23                       | 1.92                       | 1.33  | 1.54    |
|           | 19         | 20        | 1.23                       | 1.92                       | 1.68  |         |
|           | 20         | 20        | 1.23                       | 1.92                       | 1.60  |         |
| IV        | 11         | 29        | 1.23                       | 1.92                       | 1.74  | 2.02    |
|           | 12         | 29        | 1.23                       | 1.92                       | 2.06  |         |
|           | 13         | 29        | 1.23                       | 1.92                       | 2.26  |         |
| VI        | 3          | 15        | 5.05                       | 7.28                       | 1.20  | 1.26    |
|           | 4          | 15        | 5.05                       | 7.28                       | 1.27  |         |
|           | 5          | 14        | 5.05                       | 7.28                       | 1.29  |         |
|           | 6          | 14        | 5.05                       | 7.28                       | 1.30  |         |
|           | 9          | 12        | 5.05                       | 7.28                       | 1.29  |         |
|           | 10         | 12        | 5.05                       | 7.28                       | 1.25  |         |
|           | 13         | 13        | 5.05                       | 7.28                       | 1.20  |         |
|           | 14         | 14        | 5.05                       | 7.28                       | 1.28  |         |
| V         | 4          | 20        | 5.00                       | 7.52                       | 1.65  | 1.64    |
|           | 5          | 20        | 5.00                       | 7.52                       | 1.61  |         |
|           | 6          | 20        | 5.00                       | 7.52                       | 1.77  |         |
|           | 7          | 20        | 5.00                       | 7.52                       | 1.54  |         |

$c_0$  is the pressure of  $N_2O_4$  plus  $NO_2/2$  (initial).

$z_0$  is the pressure of  $O_3$  (initial).

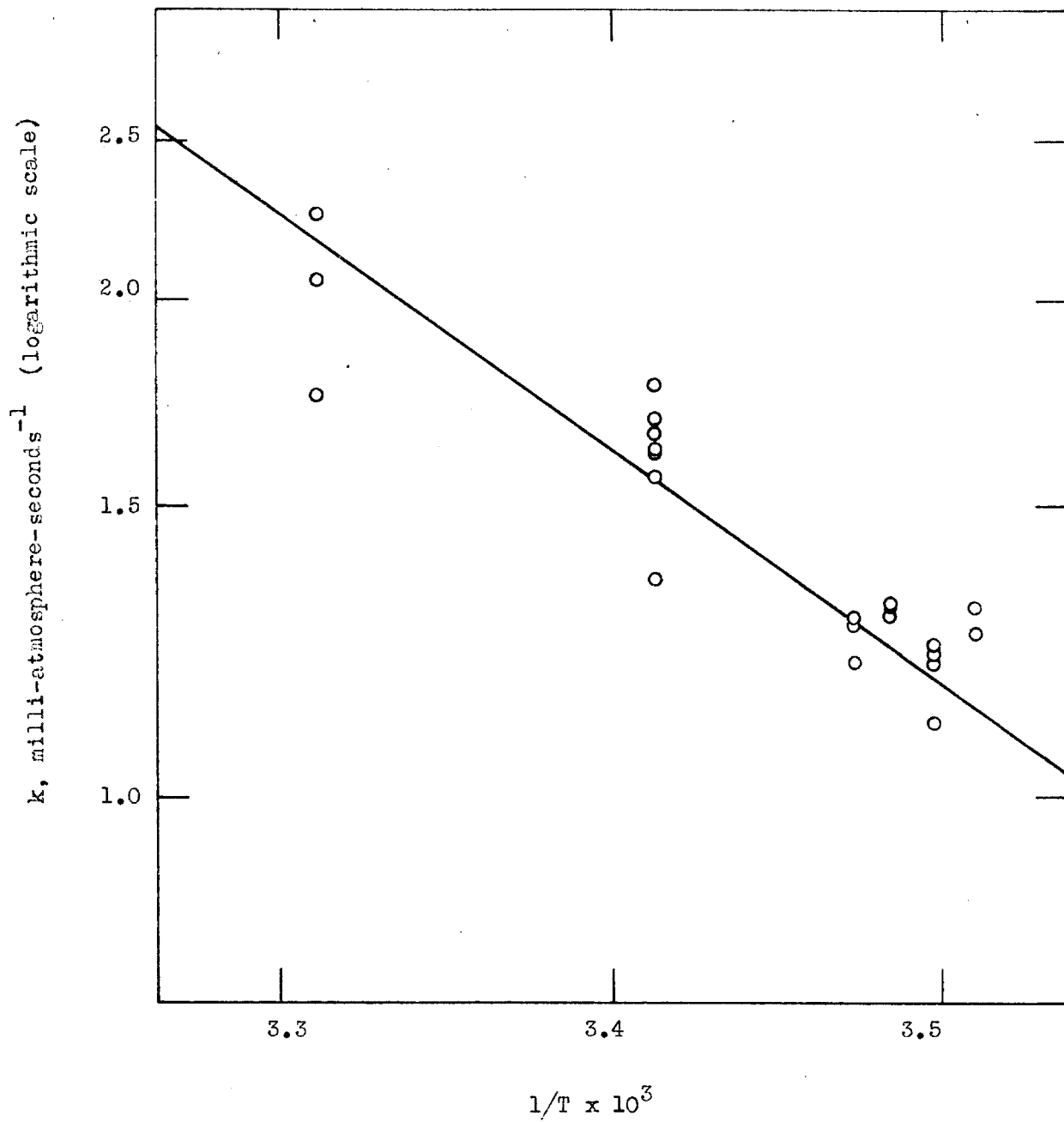


Figure 8. Temperature Dependence of the Rate Constant

#### 4. Discussion of Results

##### (a) Implications as to Mechanism

The rate law for the reaction between ozone and nitrogen dioxide has been shown in this investigation to be first order with respect to each of the two reactants. This fact makes it reasonable to believe that the first and rate determining step is the reaction.

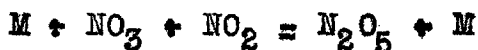


$\text{NO}_3$  is a substance regularly postulated to explain the mechanism of reactions of the higher oxides of nitrogen. (16,17,18)

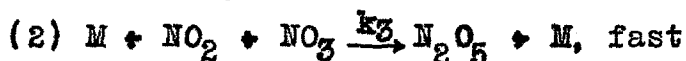
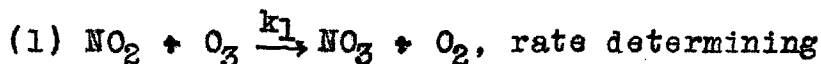
Since its absorption spectrum has been obtained (most recently by Jones and Wulf), (19)  $\text{NO}_3$  is more nearly a substantiated compound than a postulated intermediate.

In this study it was noticed repeatedly that in runs with excess ozone the same rate law was followed as far as the data could be analyzed and until the  $\text{NO}_2$  was virtually all gone. For example, in Table 4 it can be seen that by the end of the observations 84% of the initial  $\text{NO}_2$  had disappeared; in experiment VI-4. 97% of the initial amount of  $\text{NO}_2$  had been consumed before observation ceased. Similarly in experiments using an excess of  $\text{NO}_2$ , VII-11 for example, the same rate law was followed until 96% of the  $\text{O}_3$  had reacted, and almost twice as much  $\text{NO}_2$  had been observed to disappear as there had been  $\text{O}_3$  in the original stream in agreement with Wulf, Daniels, and Karrer. (5) Thus, either with a

large excess of  $O_3$  or of  $NO_2$ , within the limit of errors of the method the same rate law is followed as far as observations can go, and twice as much  $NO_2$  reacts as  $O_3$ . These facts demand that as fast as one  $NO_2$  reacts with  $O_3$  another  $NO_2$  also disappears. The assumptions are made, then, that the second step in the reaction is

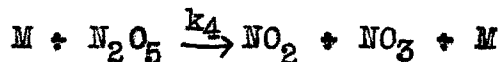


where  $M$  is any third body, and that this reaction is fast compared to the first step. Thus the proposed mechanism is



Four other possible reactions of these materials, including the intermediate  $NO_3$ , are rejected from consideration, for various reasons. In all cases except (ii) the fact that ozone is quantitatively consumed in a one-to-two ratio with  $NO_2$  applies toward rejecting a given step.

(i) The reverse of the second step,



is not considered because it can be shown that  $k_4$  is very small compared to  $k_3$ . If the reaction occurs rapidly there exists the equilibrium

$$K = k_4/k_3 = (NO_2)(NO_3)/(N_2O_5)$$

Though the visible absorption spectrum of  $NO_3$  is well known<sup>(19)</sup>.



no trace of  $\text{NO}_3$  could be observed<sup>(19)</sup> in a two-meter path of  $\text{N}_2\text{O}_5$  at 98 millimeters of mercury pressure of pure  $\text{N}_2\text{O}_5$ . Thus the equilibrium constant above is small, and  $k_3$  is much larger than  $k_4$ .

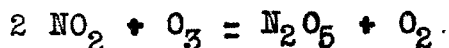
A second reason is found from an examination of the work of Smith and Daniels<sup>(18)</sup> on the reaction between  $\text{NO}$  and  $\text{N}_2\text{O}_5$ . Their results can be explained much more fully than they were willing to do so by assuming the mechanism which they tentatively propose and deriving the rate law which it implies. When this is done, their observed initial rate constant is  $k_4$ . Numerically  $k_4$  so found is much less than  $k_1$  which is considered to be much less than  $k_3$ . Thus again it is concluded that  $k_4$  is much smaller than  $k_3$ .

(11) The reverse of the first step



can be rejected from consideration of the chemical energies involved. Using the value of the heat of formation of  $\text{NO}_3$  given by Bichowsky and Rossini<sup>(13)</sup> the reaction above is found to be endothermic by 29.5 kilocalories per mole. Thus the energy of activation of the reaction must be at least 29.5 kilocalories per mole which is vastly greater than the value of 6.4 observed in this study for the reaction,  $\text{NO}_2 + \text{O}_3$ . Thus the rate of the above reaction is negligible even in the presence of one atmosphere of oxygen.

The heat of formation of  $\text{NO}_3$  as given by Bichowsky and Rossini is itself based on kinetic work and an assumed mechanism. A more direct argument can be given from the work of Smith and Daniels.<sup>(18)</sup> The overall reaction



is exothermic to the extent of 50 kilocalories per mole. The reaction

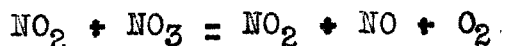


assuming Smith and Daniels' mechanism, cannot be more endothermic than their observed activation energy of 16 kilocalories per mole. Thus the reaction,



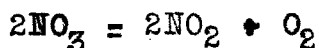
must be endothermic by at least 34 kilocalories per mole, as compared with 29.5 kilocalories per mole by the other method. By either argument the conclusion is the same that this reaction may be ignored.

(iii) Ogg<sup>(17)</sup> has suggested the reaction



as being the rate determining step in the slow first-order decomposition of  $\text{N}_2\text{O}_5$ . If so, it is negligibly slow compared to the fast rates under discussion.

(iv) Schumacher and Sprenger<sup>(16)</sup> deduced from their work on the catalysis of the decomposition of  $\text{O}_3$  by  $\text{N}_2\text{O}_5$  that the reaction



has a fairly large rate constant. The principal evidence against believing that this reaction, or the first-order decomposition of  $\text{NO}_3$ , is important in the system studied is that in the reaction one mole of  $\text{O}_3$  was observed to be equivalent to two moles of  $\text{NO}_2$ . If much  $\text{NO}_3$  decomposed before reacting with  $\text{NO}_2$ , an excess of ozone would have been used.

After eliminating these four reactions from the mechanism of this system, it remains to be shown just what differential equation the assumed mechanism implies. The net rate of disappearance of  $\text{NO}_2$  is:

$$- d(\text{NO}_2)/dt = k_1 (\text{NO}_2)(\text{O}_3) + k_3 (\text{NO}_2)(\text{NO}_3)(M)$$

The net rate of appearance of  $\text{NO}_3$  is:

$$d(\text{NO}_3)/dt = k_1 (\text{NO}_2)(\text{O}_3) - k_3 (\text{NO}_2)(\text{NO}_3)(M)$$

Since the second  $\text{NO}_2$  disappeared as rapidly as the first, no  $\text{NO}_3$  accumulated, and thus the  $\text{NO}_3$  would have a small steady state value with  $d(\text{NO}_3)/dt = 0$ .

In this case.

$$k_1 (\text{NO}_2)(\text{O}_3) = k_3 (\text{NO}_2)(\text{NO}_3)(M)$$

which when substituted into the equation for the disappearance of  $\text{NO}_2$  shows that:

$$- d(\text{NO}_2)/dt = 2k_1 (\text{NO}_2)(\text{O}_3)$$

This rate law is the one observed. The observed rate constant

is  $k_1$  because the rate of disappearance of formula weights of  $N_2O_4$  is one-half the rate of disappearance of  $NO_2$ .

(b) Comparison of Results with Simple Kinetic Theory

The two steps in the mechanism proposed for the rate of the reaction between  $NO_2$  and  $O_3$  are each fast, and it becomes a matter of interest to see if simple collision theory together with the observed energy of activation can account for the speed of the reaction or whether extra quadratic terms must be included.

According to the simplest possible picture from kinetic theory, the rate of a bimolecular reaction is the product of the total number of collisions and that fraction of the molecules which in two square terms have an energy in excess of a value  $E$ . Hinshelwood<sup>(20)</sup> gives as the expression for this product

$$N_a N_b (\sigma_{ab})^2 \left[ 8\pi RT (1/M_a + 1/M_b) \right]^{\frac{1}{2}} \exp(-E/RT)$$

where  $N_a$  and  $N_b$  are the numbers of molecules of the reacting species,  $a$  and  $b$ , per cubic centimeter,  $\sigma_{ab}$  is the mean kinetic diameter,  $M_a$  and  $M_b$  are the gram molecular weights of  $a$  and  $b$ ,  $T$  is the absolute temperature,  $R$  is the gas constant in ergs per mole-degree, and  $E$  is the energy of activation found from the Arrhenius equation. If  $NO_2$  and  $O_3$  are each present at a pressure of one milli-atmosphere

$N_a = N_b = N pv/RT = 2.5 \times 10^{16}$  molecules per  $\text{cm.}^3$ , where  $N$  is Avogadro's number. Since the kinetic diameters of  $\text{NO}_2$  and  $\text{O}_3$  are not known, the value of  $3.5 \times 10^{-8}$  cm. is assumed for this calculation. The collision rate between  $\text{O}_3$  and  $\text{NO}_2$  is then found to be  $1.2 \times 10^{23}$  per  $\text{cm.}^3$  per second. The value of the exponential factor is  $1.7 \times 10^{-5}$  at  $21^\circ\text{C}$ . when the experimental value of 6400 calories per mole is used. The rate is thus calculated to be  $2.0 \times 10^{18}$  molecules per  $\text{cm.}^3$  per second. The observed rate was  $3.75 \times 10^{16}$  molecules per  $\text{cm.}^3$  per second, or about 1/50 of the rate permitted by the simple theory. Thus there is no difficulty in explaining the existence of this fast rate.

The second step in the mechanism requires a three-body collision, and it must still be very fast. Thus its activation energy must not be greatly different from zero. Hinshelwood gives a factor of  $10^{-3}$  between three-body collisions and two-body collisions at room temperature and atmospheric pressure. Since only about one collision in  $10^7$  resulted in reaction in the first step, a factor of a thousand in the second step still leaves open the possibility that it is very fast.

In the reaction cell the ratio of the number of surface collisions to gas phase collisions was calculated to be  $4 \times 10^{-5}$ . Though no measurement of surface effect was made, it can be seen to be negligible in this reaction, for there were not enough surface collisions of sufficient energy to give the observed rate of reaction.

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PART II

A Mechanism for the Formation of Red Phosphorus  
from White Phosphorus In Solution



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## PART II

### A Mechanism for the Formation of Red Phosphorus from White Phosphorus In Solution

#### A. Introduction

When white phosphorus dissolved in  $PBr_3$ ,  $PI_3$ , or molten  $P_4S_3$  is heated or exposed to light, it is converted to red phosphorus, which precipitates from the solution.<sup>(1)</sup> The colored precipitate is not identical with ordinary red phosphorus in that it is more brightly colored and somewhat more reactive. Schenck<sup>(1)</sup> argued that the scarlet substance was the same allotropic form as ordinary red phosphorus, but that it was a much more finely divided form. He cited as supporting evidence his kinetic study which showed a first order (and thus, he presumed, mono-molecular) rate of precipitation of phosphorus from the solution. The solvents which were used catalyzed the reaction, and they all contained phosphorus atoms. There are numerous questions as to the nature of this catalysis and the effect of the solvent on the allotropic transformation. It was with a view of following separately the phosphorus atoms from the white phosphorus and those from the solvent  $PBr_3$  that a radioactive tracer study was made of this system.

In a study seeking information on the mechanism of the allotropic transformation, it is well to recognize

the nature of the two allotropic forms of interest. White phosphorus is a tetrahedron of four phosphorus atoms, each bonded to each of the other three. Red phosphorus is a fairly amorphous polymer with about the same interatomic distances, though substantially different bond angles, to its three nearest neighbors as are found in  $P_4$ .<sup>(2)</sup> Thus, the allotropic transformation of white to red phosphorus involves a breaking up of the tetrahedral phosphorus molecule and the synthesis of polymers. Since the phosphorus atom is trivalent in red phosphorus, the polymers are not long chains, but would be expected to be intertangled loops, chains, and crumpled sheets.

## B. The Experimental Procedure

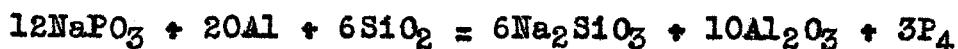
### 1. Brief Description of the Experimental Procedure

Purified radioactive  $P_4$  and inactive  $PBr_3$  were distilled in a high vacuum into the same bulb, from which small glass ampules extended like fingers. The bulb was sealed off under vacuum and tilted to run the solution into the ampules, which were then separately sealed off. These ampules were exposed to a high temperature in the vapors of boiling liquid for the desired time, removed, chilled, and opened. The reactants and products were separated, oxidized to phosphoric acid, and precipitated. The radioactivity of the precipitates was determined by a Geiger-Mueller counter, and the quantities of material later found gravimetrically.

## 2. Materials

Commercial  $PBr_3$  was distilled with an initial excess of bromine. It was then fractionally distilled in an all glass apparatus in an atmosphere (743 mm.) of carbon dioxide dried with  $P_2O_5$ . The distilling column was packed with glass helices to a height of 15 inches. The delivery tube went through a rubber stopper into a large desiccator filled with dry  $CO_2$ . The fore and middle samples were collected by sliding the base of the desiccator so that the distillate fell into the appropriate bottle which was inside the desiccator. The middle sample boiling at  $171.8-172.0^\circ C$ . was collected in a dark glass bottle. At the end of the distillation it was stoppered by remote control and stored in the dark in a desiccator using  $Mg(ClO_4)_2$  in an atmosphere of  $CO_2$ . The  $PBr_3$  was removed from this system by means of a pipet inside a dry box.  $PBr_3$  prepared and stored in this way was water white. (In spite of this white color  $PBr_3$  must be protected from light, for it absorbs very strongly and continuously in the ultra-violet region just below the visible range. Ordinary glass, which is opaque to most ultraviolet light, is of no protection against the very near ultra-violet light around .380 microns.)

Radioactive white phosphorus was prepared by the reduction of <sup>radioactive</sup> sodium metaphosphate with aluminum powder and silica according to Rossel and Franck<sup>(3)</sup>:



at red heat in an oxygen free atmosphere. The sodium metaphosphate was formed by heating  $\text{NaH}_2\text{PO}_4$  to about  $900^\circ\text{C}$ . in a platinum crucible and suddenly cooling the melt. The glass that formed was crushed and mixed with the equivalent amounts of powdered Al and  $\text{SiO}_2$  in a small porcelain crucible. The crucible was placed in a small electric furnace formed by nichrome wires wrapped vertically around a notched bottomless porcelain crucible. The furnace was suspended by heavy nickel leads inside an all glass apparatus which was slowly evacuated. The tungsten and glass seals were insulated electrically and the outside of the glass bulb was cooled in a stream of water. As the furnace reached a dull red heat, the highly exothermic reaction took over, and at once the entire apparatus was filled with white, yellow, orange, and red phosphorus. The white phosphorus was distilled over into a trap, and most of the colored phosphorus was similarly recovered as white P by the application of a hot flame to the outside of the flask. Purified carbon disulfide was distilled on top of the white phosphorus in the trap. The solution was transferred in a dry box filled with  $\text{CO}_2$  into a bottle and stored tightly stoppered in a dry atmosphere of  $\text{CO}_2$  in the dark.

### 3. Preparation of samples

Into one arm of an all glass system filled with slowly streaming dry  $\text{CO}_2$  was put a measured volume of  $\text{PBr}_3$ , and into the other bulb was put a measured volume of the solution of  $\text{P}_4$  in  $\text{CS}_2$ . The arms were sealed off closing

the system which was joined to a high vacuum line. The  $\text{CS}_2$  was pumped off, leaving the  $\text{P}_4$  as a white solid. The  $\text{PBr}_3$  was vacuum distilled at room temperature into a U-trap at the temperature of dry ice. The white phosphorus was similarly distilled except that a steam hood was used to speed the distillation. The entire system, still evacuated, was sealed off so that it could be tilted. In a dark room with a small red light the solution of  $\text{P}_4$  in  $\text{PBr}_3$  was thoroughly mixed by shaking and it was poured in roughly equal amounts into the small ampules. To avoid pyrolysis when sealing off, the upper portions of the ampules were steamed until all of the solution had distilled out of these upper portions. When the ampules were sealed off with a flame, the reactants were protected from the light of the flame by a right angle bend in the ampules and by a rubber tube which was pulled over the outside of the ampules. The solutions prepared this way were found to be colorless and water clear. Exposure to light, however, would produce first a foggy turbidity and later a precipitate colored yellow, orange, or orange red.

#### 4. The Runs

The ampules were suspended by wires in the vapors of boiling aniline in a large boiler during one run, in boiling  $\text{PBr}_3$  in another, and in the liquid of boiling aniline in a third. A thermometer in the vapor with the ampules showed constancy of temperature within  $\pm 0.2^\circ\text{C}$ . In the

boiling liquid, the temperature varied over a range of one degree, and the liquid was hotter than the vapors. The ampules were singly removed and cooled in cold dilute HCl solution at specified times. The runs were carried out in the dark, a small flashlight being used at the time of removal of the ampules.

The ampules were opened, washed out repeatedly with CS<sub>2</sub>, and the solution was filtered through a micro sintered glass funnel. The colored polymer was left on the filter and on the walls of the ampule. The clear colorless filtrate was extracted repeatedly with water, the PBr<sub>3</sub> hydrolyzing and going to the water phase and the P<sub>4</sub> staying in the CS<sub>2</sub>. With solutions of pure P<sub>4</sub> or pure PBr<sub>3</sub> the errors of this separation were found to be approximately 2%.

The three separated substances were treated with bromine water to get each of them in water as a mixture of phosphorous and phosphoric acids. Complete oxidation to phosphoric acid was carried out by sealing the aqueous solution in an ampule with liquid bromine and heating on a water bath for two hours. After cooling and opening the ampules, the excess bromine was boiled off. The phosphoric acid solutions were precipitated in the standard manner as magnesium ammonium phosphate.

By filtering the solution through a small square of ashless filter paper which was backed by a sintered glass funnel base and held in place by means of a glass chimney

clamped to the base, the precipitate was spread over a reproducible area. After the precipitate was washed and dried, it had clamped over it another small square of paper, and the edges were sealed by scotch tape. This "sandwich" was mounted on a thin aluminum plate which slid into a rack in a lead chamber containing a Geiger-Mueller counter tube. The counts were scaled down by means of a scale of 32 circuit and were registered on a Cenco counter and on neon light interpolators. After being counted the sample and its ashless filter paper covers were ignited and weighed as  $Mg_2P_2O_7$  in the standard gravimetric manner.

### C. Discussion of Results

#### 1. Some Deductions as to the Mechanism of Precipitation and Exchange

The data for the three complete runs which were carried out are given in Table 1. The first fact to be emphasized is that the results show a surprisingly low precision. The discussion of results, therefore, is concerned solely with first order effects.

The results of these experiments are in agreement with Schenck<sup>(1)</sup> as to the rate of disappearance of white phosphorus from the solution. The reaction appears to be first order with respect to  $P_4$ . The rate constants found by the method of least squares, considering time to be the independent variable, are given in Table 2 along with the standard error of estimate.



Table 1

The Data Obtained on the Rates of Precipitation and Exchange

| Run No. | Time Min.        | Sample           | Weight of $Mg_2P_2O_7$ mg. | Counts per Minute | Counts per Milligram | Atom fraction of Phosphorus |
|---------|------------------|------------------|----------------------------|-------------------|----------------------|-----------------------------|
| 3       | 0                | PBr <sub>3</sub> | 170.2                      | 6                 | 0.03                 | 0.916                       |
|         |                  | P <sub>4</sub>   | 15.6                       | 102               | 5.5                  | 0.084                       |
|         |                  | polymer          | 0                          | 0                 | ---                  | 0                           |
|         | 10               | PBr <sub>3</sub> | 145.2                      | 35                | 0.24                 | 0.933 ?                     |
|         |                  | P <sub>4</sub>   | 10.3                       | 51                | 5.0                  | 0.067 ?                     |
|         |                  | polymer          | lost                       | ---               | ---                  | ---                         |
|         | 30               | PBr <sub>3</sub> | 175.2                      | 83                | 0.47                 | 0.878                       |
|         |                  | P <sub>4</sub>   | 8.9                        | 40                | 4.5                  | 0.045                       |
|         |                  | polymer          | 15.4                       | 13                | 0.84                 | 0.077                       |
|         | 55               | PBr <sub>3</sub> | 215.3                      | 123               | 0.57                 | 0.898                       |
|         |                  | P <sub>4</sub>   | 13.6                       | 53                | 2.7                  | 0.057                       |
|         |                  | polymer          | 10.8                       | 16                | 1.5                  | 0.045                       |
| 210     | PBr <sub>3</sub> | 154.1            | 98                         | 0.64              | 0.860                |                             |
|         | P <sub>4</sub>   | 3.2              | 3 ?                        | 1                 | 0.018                |                             |
|         | polymer          | 22.1             | 24                         | 1.1               | 0.122                |                             |
| 2       | 0                | PBr <sub>3</sub> | 88.9                       | 29                | 0.3                  | 0.878                       |
|         |                  | P <sub>4</sub>   | 11.4                       | 520               | 46.7                 | 0.113                       |
|         |                  | polymer          | 0                          | 0                 | ---                  | ---                         |
|         | 10               | PBr <sub>3</sub> | 107.1                      | 280               | 2.6                  | 0.897                       |
|         |                  | P <sub>4</sub>   | 8.9                        | 332               | 37.3                 | 0.074                       |
|         |                  | polymer          | 3.5                        | 18                | 5.1                  | 0.029                       |
|         | 30               | PBr <sub>3</sub> | 135.5                      | 609               | 4.5                  | 0.805                       |
|         |                  | P <sub>4</sub>   | 11.2                       | 278               | 24.8                 | 0.066                       |
|         |                  | polymer          | 21.9                       | 128               | 5.8                  | 0.129                       |
|         | 50               | PBr <sub>3</sub> | 130.1                      | 736               | 5.6                  | 0.773                       |
|         |                  | P <sub>4</sub>   | 5.8                        | 80                | 13.8                 | 0.034                       |
|         |                  | polymer          | 32.5                       | 208               | 6.4                  | 0.193                       |
|         | 70               | PBr <sub>3</sub> | 117.0                      | 609               | 5.2                  | 0.856                       |
|         |                  | P <sub>4</sub>   | 5.8                        | 81                | 13.9                 | 0.042                       |
|         |                  | polymer          | 13.9                       | 83                | 6.0                  | 0.102                       |
|         | 100              | PBr <sub>3</sub> | 114.5                      | 588               | 5.1                  | 0.807                       |
|         |                  | P <sub>4</sub>   | 5.9                        | 58                | 9.8                  | 0.042                       |
|         |                  | polymer          | 21.4                       | 107               | 5.0                  | 0.151                       |
| 900     | PBr <sub>3</sub> | 114.1            | 630                        | 5.5               | 0.815                |                             |
|         | P <sub>4</sub>   | 0                | 0                          | ---               | ---                  |                             |
|         | polymer          | 26.1             | 79                         | 3.0               | 0.185                |                             |
| 1       | 0                | PBr <sub>3</sub> | 66.4                       | 8                 | 0.1                  | 0.815                       |
|         |                  | P <sub>4</sub>   | 15.1                       | 651               | 43.2                 | 0.185                       |
|         | 10               | PBr <sub>3</sub> | 110.0                      | 250               | 2.3                  |                             |
|         |                  | P <sub>4</sub>   | 16.7                       | 652               | 39.0                 |                             |
|         | 40               | PBr <sub>3</sub> | 89.4                       | 472               | 5.3                  |                             |
|         | 100              | PBr <sub>3</sub> | 108.1                      | 775               | 7.1                  |                             |
| 960     | PBr <sub>3</sub> | 111.0            | 921                        | 8.3               |                      |                             |

Table 2

Rate Constants for the Precipitation of White  
Phosphorus from Phosphorus Tribromide

| Run No.   | Initial Mole Fraction of P <sub>4</sub> | Temperature | Rate $k_1$ Constant (Minutes) <sup>-1</sup> |
|-----------|---|-------------|---|
| 3         | 0.028                                   | 181         | (6.1 ± 0.3) × 10 <sup>-3</sup>              |
| 2         | 0.021                                   | 185         | (8.2 ± 1.4) × 10 <sup>-3</sup>              |
| Schenck's | 0.039                                   | 184         | (8.00 ± 0.03) × 10 <sup>-3</sup>            |
| Work      | 0.040                                   | 172         | (3.8 ± 0.5) × 10 <sup>-3</sup>              |

There are postulated here four extreme, idealized mechanisms, and the equations written down which describe these cases. The experimental results will be fitted, with further assumption, into the pattern set by these idealizations. The following terms consistent with the nomenclature previously used in exchange kinetics,<sup>(4)</sup> are defined as an aid in describing the extreme cases:

- a = concentration in moles per liter of PBr<sub>3</sub>
- x = concentration in moles per liter of radioactive PBr<sub>3</sub>
- b = four times the concentration in moles per liter of P<sub>4</sub>
- y = four times the concentration in moles per liter of radioactive P<sub>4</sub>

- $z/c$  = specific activity of the precipitate expressed as a mole fraction
- $R$  = the rate of exchange of phosphorus atoms between  $P_4$  and  $PBr_3$
- $k_1$  = the first order rate constant for the precipitation of red phosphorus from the solution
- $k_2$  =  $R/b$ , the rate constant for the assumed first order exchange reaction

Case 1. If the white and colored phosphorus never exchanged phosphorus atoms with the  $PBr_3$ , the specific activity of the  $P_4$  and of the precipitate would have a constant value at all times.

$$dx/dt = 0, y/b = z/c = \text{a constant.}$$

Case 2. If the white phosphorus exchanged atoms of phosphorus with  $PBr_3$  and in a completely separate reaction precipitated red phosphorus without exchange, the rate of appearance of radioactive  $PBr_3$  would be

$$dx/dt = R(y/b - x/a)$$

and the rate of disappearance of radioactive white phosphorus would be

$$- dy/dt = R(y/b - x/a) + k_1 y.$$

The activity of the precipitate is given by  $z/c = y/b$  when  $t$  is small.

Case 3. If the  $P_4$  and  $PBr_3$  did not exchange at all, but if the precipitate exchanged rapidly and completely with

$PBr_3$  during the process of precipitation, one would expect the following equations to be true:

$$y/b = \text{constant}$$

$$dx/dt \approx k_1 y, \text{ when } t \text{ is small.}$$

Case 4. If  $P_4$  and  $PBr_3$  exchanged with each other in solution, and if upon formation the red phosphorus exchanged completely with the  $PBr_3$ , the movement of radioactivity would be described by:

$$dx/dt = R(y/b - x/a) + k_1 y, \text{ when } t \text{ is small}$$

$$- dy/dt = dx/dt$$

$$z/c = x/a, \text{ when } t \text{ is small.}$$

In the actual runs the specific activity of the white phosphorus decreased with time in every case. Thus there existed an interchange of phosphorus atoms between  $P_4$  and  $PBr_3$ , and cases 1 and 3 must be ruled out. After corrections were made for solvation of the precipitate, it was found that the activity of the initial precipitate lay approximately two-thirds of the way between case 2 and case 4, that is, two-thirds of the activity of the phosphorus which precipitated went into the  $PBr_3$ . For the initial conditions the following differential equation is assumed:

$$dx/dt = R(y/b - x/a) + 0.64K_1y$$

or in terms of measured quantities

$$d(x/a)/dt = R/a(y/b - x/a) + 0.64 k_1(y/b) b(1/a).$$

It is difficult to integrate this equation because  $b$  is not constant ( $b = b_0 e^{-k_1 t}$ ), and the relation between  $x$  and  $y$  is complicated. It is simple, however, to substitute the observed values of  $y/b$ ,  $x/a$ ,  $a$ , and  $b$  into the differential equation and to solve for  $R$ .

The value of  $R$  was computed from the data for the first ten minutes of each of the three runs. At this point it was necessary to introduce an assumption as to the nature of the dependence of  $R$  on the concentration of  $P_4$  and  $PBr_3$ . Since  $PBr_3$  is present in excess, the assumption was made that the empirical rate law would be

$$R = k_2(P_4)$$

that is, a first order dependence on the white phosphorus concentration was assumed. When this procedure was carried through, three values of  $k_2$  were found and are given in Table 3.

Table 3

Rate Constants for the Exchange of Phosphorus Atoms  
between Phosphorus and Phosphorus Tribromide

| Run No. | Initial Mole Fraction of $P_4$ | Temperature | Rate Constant $k_2$ (Minutes) <sup>-1</sup> × 10 <sup>3</sup> | $k_2/k_1$ |
|---------|--------------------------------|-------------|---|-----------|
| 3       | 0.028                          | 181         | 45  | 7.4       |
| 2       | 0.021                          | 185         | 50  | 6.1       |
| 1       | 0.046                          | 172         | 27  | 7.1       |

The energy of activation calculated from the Arrhenius equation for the three values of  $k_2$  was 18.3 kilocalories per mole. This value is suggestively close to the phosphorus-phosphorus single bond energy of 18.9 kilocalories per mole.<sup>(5)</sup> In view of the assumptions involved and the fact that so many reactions have about this calculated activation energy anyway, no emphasis should be placed on this numerical agreement. It does, however, suggest that the rate determining step in the exchange is the rupture of a single bond in  $P_4$ . Since the ratio of  $k_2$  to  $k_1$  appears to be constant, Table 3, there is the further suggestion that this bond rupture is also the rate determining step for the precipitation.

A reasonable account of the events occurring in this system can be given, though it is to be emphasized that this is speculation in agreement with limited observations, not a mechanism demanded by facts. A  $P_4$  molecule in the  $PBr_3$  solution eventually suffers a collision of such energy that a bond is broken. While it limps around in this condition three alternatives are open:

(1) It may collide with another phosphorus molecule (or it may require another ruptured molecule) initiating polymerization into red phosphorus.

(2) It may react with  $PBr_3$ , the relatively unbound atoms exchanging with the phosphorus in  $PBr_3$ .

(3) It may heal itself of its injury, reforming a  $P_4$

molecule and giving up the energy of formation to the ever present solvent molecules.

By this picture, exchange results from (2) followed by (3). Partial exchange with the solvent upon precipitation is caused by (2) followed by (1). The catalytic action of the solvent could be due to its inhibition of the healing process (3) by virtue of its attack (2) on the broken molecule, which, however, could still initiate polymerization.

## 2. Observations on the Nature of Elementary Phosphorus and a Possible Explanation of the Colors

There is advanced here an opinion which has grown out of qualitative observations made in the formation and handling of elementary phosphorus under various conditions. The allotropes of phosphorus with which we are concerned are the alpha white and the polymerized or "red" phosphorus which may take on many appearances depending on the mode of preparation.

The alpha white form of phosphorus is a clear colorless substance. Large white crystals may be formed by slow vacuum sublimation. The molten phosphorus (melting point  $44.1^{\circ}\text{C}.$ ) readily supercools and may exist indefinitely as a liquid at room temperature. This supercooled liquid phosphorus may freeze with an audible click to a soft white glass. True white phosphorus kept in the dark exists only as a colorless liquid, colorless glass, or colorless crystals.

The clear solution of white phosphorus in  $\text{PBr}_3$  formed a white foginess when first heated to about  $170^\circ\text{C}$ . The white fog soon turned yellow and precipitated from the solution, and the color of the precipitate later changed to a bright orange, orange red, and finally to a bright scarlet. The colored intermediates were isolated and found to be heavily contaminated with bromine, as Schenck had observed. The light colored substances were prepared in several other ways, for example, from dilute solutions of  $\text{P}_4$  in  $\text{CS}_2$ ,  $\text{CCl}_4$ , or ligroin by the action of light. A similar looking yellow powder stable in air could be recovered from each solvent, but they were found to contain only 50% to 75% of phosphorus by weight. By the action of light on more concentrated solutions, orange and orange-red powders could be obtained which appeared to be similar to those recovered from  $\text{PBr}_3$ . By the contact of hot glass of the right temperature on dilute vapors of pure white phosphorus in a vacuum line, a small amount of a yellow powder stable in air was obtained. When any of these yellow, orange, or scarlet products were heated at about  $250^\circ\text{C}$ ., each of them turned into a dark red powder. From the nature of the preparation of the colored products, from the fact that continued application of the same method or the application of increasingly severe methods caused the transition from yellow to orange to red, and from the known polymerized structure<sup>(2)</sup> of red phosphorus, it appears that these substances differ as to polymer



size; and the contamination with the solvent is due to the action of the solvent as a terminating group for the polymer chains.

If these precipitates differ as postulated in polymer size, there is an interesting correlation between their size and their color. It is well known that with a carbon chain of conjugated double bonds the upper wave length limit of the electronic absorption spectrum is an increasing function of the number of units in the conjugated chain.<sup>(6)</sup> If the electronic structure of polymerized trivalent phosphorus is written down, it can be seen that there are two electrons left over on each atom. If it is considered possible for these pairs of electrons occasionally utilizing the d orbitals to form double bonded structures which resonate with the single bonded ones, then in an analogous fashion to the conjugated double bond system a mechanism can be shown whereby an electron appears to vibrate from one side of the polymer to the other, though actually it may move only a very short distance. As the distance over which this type of resonance can occur becomes larger, the longer becomes the wave length of the light which can be absorbed inducing this transition. The progression of colors of white, yellow, orange, red, and even violet and black is just that of the upper limit of a continuous absorption curve moving across the visible spectrum. This is likewise the series of colors of polymerized phosphorus found upon increasingly powerful and prolonged action of formation, and presumably it parallels an increase in size.

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- (5) L. Pauling, The Nature of the Chemical Bond, p. 53, Cornell Univ. Press (1940).
- (6) G. N. Lewis and M. Calvin, Chem. Rev., 25, 273 (1939).

## PROPOSITIONS

### A. The Minor Subject

1. For laboratory uses of an interferometer in which a large number of fringes are expected to pass, I propose the use of an electron multiplying photoelectric tube behind a slit. By this method one could count fringes at almost any rate if the pulses from the photoelectric tube were scaled and recorded in a Geiger tube counting circuit.

2. Text books in optics often state that the wave phenomenon of beats has not been demonstrated for light due to the difficulty--or impossibility--of obtaining two coherent sources of light of different frequencies. A method is proposed whereby one could get such a pair of light sources. Using high grade monochromatic canal rays, such as are obtained from Dempster's canal ray tube, and taking the light out at about 180 degrees from the same point by a proper system of mirrors and lenses similar to that used by Ives and Stilwell, one could obtain two rays which would be coherent because they are part of the same spherical wave train from a radiating atom, and they would have different frequencies because of the Doppler effect. By taking these two beams into an interferometer, in principle beats of light could be demonstrated, not by a change of intensity at a point with time, but by a distortion of an interference pattern in space.

Batho and Dempster, Astrophysical Journal, 75, 34 (1932).  
Ives and Stilwell, Jour. Opt. Soc., 28, 215 (1938)

3. A semi-classical way of thinking about the annihilation of electron-positron pairs is that annihilation occurs at the distance

$$r = e^2/2mc^2 = 1.4 \times 10^{-13} \text{ cm}$$

where the potential energy of attraction is equal and negative to the rest mass energy of the two particles.

#### B. General Chemistry

4. For those cases where the absorption spectrum of chemical substances is recorded by the photographic method, I propose a photoelectric and osciloscopic method which should be quite sensitive and give the data in a much more easily interpreted form.

Daly and Sutherland, Nature, 157, 547 (1946).  
Baker and Robb, Rev. Sci. Instr., 14, 362 (1943).

This method differs from previous similar ones.

5. Chemists should not call white phosphorus "yellow".

#### C. Chemical Kinetics

6. Ogg recently proposed a mechanism to account for the first order rate of decomposition of  $N_2O_5$ .

a. There are additional arguments in favor of this mechanism:

(1) The forward and reverse reactions of the equilibrium postulated have been independently proposed, respectively, by Smith and Daniels and by Johnston and Yost.

(2) The branching reactions whereby two reactants form two separate sets of products can be rationalized quite simply.

(3) It is possible to show that kinetic theory permits enough collisions of the right sort to maintain the observed rate to as low a pressure as  $10^{-6}$  atmospheres. Previously, it was impossible to explain the observed rate at low pressures in terms of the kinetic theory.

b. Experiments are proposed to check quantitatively the proposed mechanism.

7. Schumacher and Sprenger were able to explain the observed rate law for the catalytic decomposition of ozone by nitrogen pentoxide

$$-d(O_3)/dt = k(N_2O_5)^{2/3}(O_3)^{2/3}$$

by use of a complicated mechanism involving chain initiating and terminating reactions and a cyclic use of one intermediate. On the basis of recent work by Smith and Daniels and by Johnston and Yost, I propose a simple three step mechanism which in an immediate and straightforward manner gives the observed rate law.

Schumacher and Sprenger, Z. Phys. Chem., B2, 267 (1929).

8. Smith and Daniels studied the kinetics of the reaction between NO and  $N_2O_5$ . They were perplexed by certain features of their results:

- (1) The almost-but not quite-first order dependence of the rate on the concentration of  $N_2O_5$
- (2) The almost-but not quite-zero order dependence of the rate on the concentration of NO
- (3) The apparent zero effect of the concentration of  $NO_2$  on the initial rate of the reaction
- (4) The evidence of heterogeneity of the reaction

I propose to explain all of these features by using the mechanism tentatively proposed by the authors and following through its implications.

9. The field of the kinetics of fast reactions offers numerous opportunities for interesting investigations. The following three reactions are offered as illustrations, and to me each one is interesting for a different type of reason:

- (1)  $NO + NO_2 = N_2O_3$
- (2) The rate of exchange of bromine atoms between HBr and  $Br_2$
- (3) The oxidation of positive ions (ferrous, vanadous, europous) by ceric ion in perchloric solution.