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A STUDY OF THE KINETICS OF THE UNIMOLECULAR REACTION BETWEEN NITROGEN-PENTOXIDE AND NITROSYL CHLORIDE

NICHOLAS ZEVOS

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**A STUDY OF THE KINETICS OF THE UNIMOLECULAR REACTION
BETWEEN NITROGEN PENTOXIDE AND NITROSYL CHLORIDE**

BY

NICHOLAS ZEVOS

B. A., St. Anselm's College, 1954

A THESIS

**Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
Doctor of Philosophy**

**Graduate School
Department of Chemistry
November, 1963**

TO

MOTHER AND FATHER

This thesis has been examined and approved.

Walter R. Small

A. F. [unclear]

Kenneth K. Anderson

Charles W. [unclear]

R. J. [unclear]

DATE

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INTRODUCTION

HISTORICAL

The oxides of nitrogen have been referred to as a "Happy Hunting Ground" of gas phase kinetics.¹ If this is true then nitrogen pentoxide might seem to represent a field that has been gleaned of game. This is hardly the case, for although the experimental work on this compound is vast, there are still a few questions about the mechanism of the reaction which are unanswered.

Daniels and Johnston² first studied the kinetics of the gas phase decomposition of nitrogen pentoxide. In this classical study they demonstrated clearly that the reaction was unimolecular and homogenous. This was true over a large temperature and pressure range.

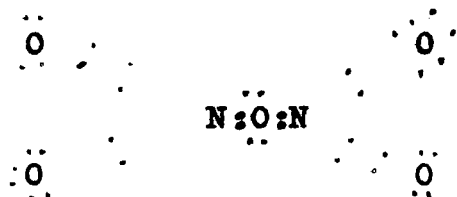
This work was carried out at a time when the science of kinetics was still young and consequently a great amount of work was done on what variables might effect the reaction. Also, at this time, the mechanism whereby molecules obtain energy in a unimolecular reaction was under careful consideration. Using this decomposition reaction, Daniels³ demonstrated the validity of the collision theory or the Lindemann process⁴ over the radiation theory.⁵

It was also found that the rate of decomposition was not affected by various impurities. Quantities of phosphorous

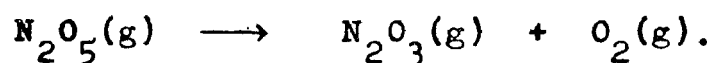
pentoxide⁶ and oxygen⁷ did not change the decomposition rate.

Further studies on the effect of foreign gases were carried out by Busse and Daniels.⁸ They found that hydrogen, carbon monoxide, bromine and chlorine did not affect the decomposition rate, but certain organic vapors such as diethyl ether and acetone did undergo very fast reactions with nitrogen pentoxide. A very important reaction which Busse and Daniels described as immeasurably fast was noticed between NO and N₂O₅.

Although Daniels and Johnston showed that the reaction was first order, the stoichiometry indicates a bimolecular reaction. This implies that the decomposition must take place by a complex mechanism. From electron diffraction studies⁹ it has been shown that nitrogen pentoxide has the following structure:



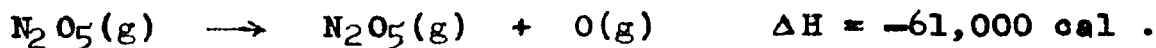
Considering this structure, several possibilities exist for the initial step in the decomposition reaction. An initial step suggested by Bodenstein¹⁰ was



This reaction was discarded because molecular oxygen was formed which is paramagnetic. In order to do this a spin change in one of the electrons would be required. It has been shown

that reactions of this type¹¹ have a very small probability of occurring.

Another possibility would involve:

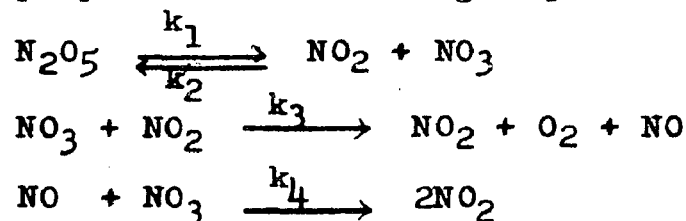


Thermochemically this reaction requires 61,000 calories.

This is much greater than the energy of activation which is 24 K cal² for the decomposition reaction.

Busse and Daniels⁸ proposed that $\text{N}_2\text{O}_5(\text{g}) \longrightarrow \text{NO}(\text{g}) + \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$. This initial step was eliminated because it is the reverse of a three-body collision. In this case three bonds have to be broken simultaneously.

Perhaps the most logical initial step to propose after one inspects the structure of nitrogen pentoxide, would be a fission of a nitrogen oxygen bond. Smith and Daniels¹² did propose such an initial step in order to explain the reaction between nitric oxide and nitrogen pentoxide. However, this was modified by R. A. Ogg¹³ in a very clever way to give what is now the generally accepted mechanism for the decomposition reaction. Ogg proposed the following sequence of steps:



According to Ogg step three is the rate determining step.

Then application of the steady state assumption to (NO) and (NO₃) should give the observed rate equation:

$$R = \frac{-d(N_2O_5)}{dt} = -k_1 (N_2O_5) + k_2 (NO_2) (NO_3) \quad (1)$$

$$\frac{d(NO_3)}{dt} = k_1 (N_2O_5) - k_2 (NO_2) (NO_3) - k_3 (NO_3) (NO_2) - k_4 (NO) (NO_3) \quad (2)$$

$$\frac{d(NO)}{dt} = k_3 (NO_3) (NO_2) - k_4 (NO) (NO_3) \quad (3)$$

After a short induction period the intermediates will reach their steady state value. Hence, we may equate equations (2) and (3) to zero and solve for the concentrations of the intermediates:

$$\begin{aligned} k_3 (NO_2) &= k_4 (NO) \\ (NO) &= \frac{k_3}{k_4} (NO_2) \end{aligned}$$

Substituting into eq. 2

$$\begin{aligned} k_1 (N_2O_5) &= k_2 (NO_2) (NO_3) + k_3 (NO_3) (NO_2) + \\ & k_3 (NO_2) (NO_3) \\ &= [k_2 (NO_2) + 2k_3 (NO_2)] (NO_3) \end{aligned}$$

$$\frac{k_1 (N_2O_5)}{(k_2 + 2k_3) (NO_2)} = (NO_3)$$

$$\begin{aligned} \therefore R &= k_1 (N_2O_5) + \frac{k_2 k_1 (N_2O_5)}{(k_2 + 2k_3)} \\ &= \left(\frac{k_2}{k_2 + 2k_3} - 1 \right) k_1 (N_2O_5) \end{aligned}$$

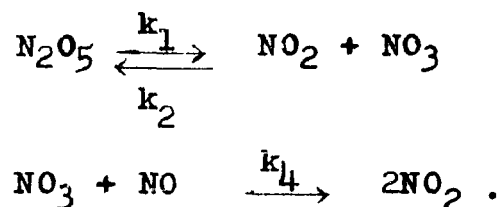
$$R = \frac{-2k_3 k_1}{k_2 + k_3} (N_2O_5) = -k_{obs} (N_2O_5)$$

From this treatment we see that the observed rate constant is a complex rate constant composed of three elementary rate constants.

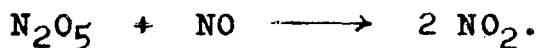
Three methods have been used to demonstrate the validity of the Ogg mechanism. They are

1. A study of the decomposition in the presence of a strong reducing agent.
2. Isotopic exchange.
3. A study of the decomposition at elevated temperatures by the shock tube technique.

The first method involves studying the decomposition reaction in the presence of nitric oxide. The reaction sequence would then be



Under these conditions the rate of reaction (4) is increased to effectively cope with reaction (2). Upon addition of these elementary reactions the stoichiometric equation is obtained:



Thus step (1), the true unimolecular step, is the rate determining step. Application of the steady state assumption to the above sequence gives the following expressions.

$$\begin{aligned} \frac{d(\text{N}_2\text{O}_5)}{dt} &= -k_1 (\text{N}_2\text{O}_5) + k_2 (\text{NO}_2) (\text{NO}_3) \\ \frac{d(\text{NO}_3)}{dt} &= k_1 (\text{N}_2\text{O}_5) - k_2 (\text{NO}_2) (\text{NO}_3) - k_4 (\text{NO}_3) (\text{NO}) = 0 \end{aligned}$$

$$\frac{d(\text{NO})}{dt} = -k_4 (\text{NO}_3)(\text{NO}) = 0$$

$$(\text{NO}_3) = \frac{k_1 (\text{N}_2\text{O}_5)}{k_2 (\text{NO}_2) + k_4 (\text{NO})}$$

$$\therefore \frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1 \text{N}_2\text{O}_5 \left[1 - \frac{k_2 \text{NO}_2}{k_2 (\text{NO}_2) + k_4 (\text{NO})} \right]$$

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = \frac{k_1 (\text{N}_2\text{O}_5)}{1 + \frac{k_2 (\text{NO}_2)}{k_4 (\text{NO})}}$$

Hence, one can measure directly the rate constant for the true unimolecular step which is, in this case, the rate determining step. Smith and Daniels¹² studied the above reaction in the pressure range 0.1 mm to 20 mm and found a first order dependence on nitrogen pentoxide and a 0.1 order dependence on nitric oxide which they attributed to a heterogeneous reaction.

If the rate determining step is preceded by a rapid equilibrium, then one should be able to demonstrate that an isotopic exchange takes place. The initial attempts were taken by Ogg,¹⁴ using the ¹³N isotope and carbon tetrachloride as a solvent. Ogg also studied the equilibrium $\text{N}^{15}\text{O}_2 + \text{N}^{14}\text{O}_5 \rightleftharpoons \text{N}^{14}\text{N}^{15}\text{O}_5 + \text{N}^{14}\text{O}_2$.

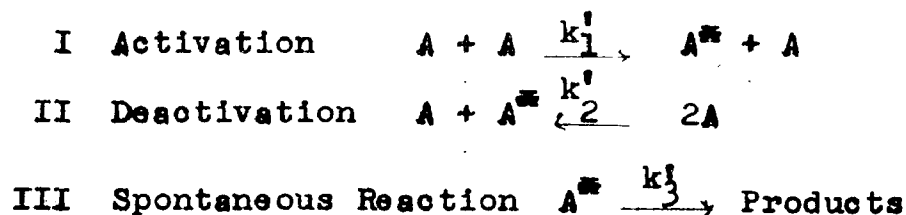
Amell and Daniels¹⁵ also studied the same exchange reaction, but by an entirely different method. They were able to determine values for k_1 from the exchange reaction

at three temperatures. The values obtained agreed within experimental error with previous values obtained for k_1 by other experimental methods.

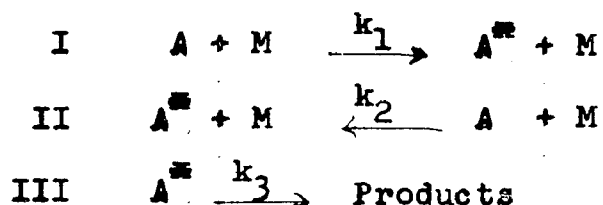
The final method¹⁶ involves a direct study of the dissociation of N_2O_5 and a determination of the equilibrium constant involving reactions one and two at elevated temperatures. In order to attain the high temperatures, a shock tube technique was employed. The high temperature results were then extrapolated to lower temperatures. The results obtained agreed with the results at room temperature. In addition to this a direct study was made on the reaction $NO_2 + NO_3 \longrightarrow NO + O_2 + NO_2$ which is the rate determining step in the Ogg mechanism.

No study of unimolecular reactions is complete without a discussion of the "falling off" of the rate constant as the pressure is decreased. The region where this "falling off" occurs is often called the "Lindemann region" and reactions which display this phenomenon are often called "quasi unimolecular" reactions.

Lindemann was the first to postulate the general mechanism for a unimolecular reaction. His proposal consisted of the following sequence for the overall unimolecular process $A \longrightarrow$ Products, where A represents a reactant molecule.



A^{\ddagger} represents an activated molecule. The mechanism has been generalized so that it includes any molecule (M) which is capable of activating a reactant molecule (A). In the latter form it is usually written as



This mechanism has been the fundamental basis for all the theories of unimolecular reactions, including the Hinshelwood¹⁷, Rice and Ramsperger¹⁸, Kassel^{19,20} and the new approach which has been proposed by Slater.^{21,22}

Application of the steady state assumption to the above mechanism will show that the observed rate constant is a complex rate constant composed of elementary rate constants.

$$\frac{d(A^{\ddagger})}{dt} = k_1 (A) (M) - k_2 (A^{\ddagger}) (M) - k_3 (A^{\ddagger}) = 0 \quad (1)$$

$$R = \frac{d(P)}{dt} = k_3 (A^{\ddagger}) \quad (2)$$

$$(A^{\ddagger}) = \frac{k_1 (A) (M)}{k_2 (M) + k_3}$$

on substitution into (2)

$$R = \frac{k_3 k_1 (A) (M)}{k_2 (M) + k_3}$$

There are two regions of importance.

Case I The high pressure region where (M) is very large therefore $k_2 (M) \gg k_3$ and the rate of reaction is given by

$$R = \frac{k_3 k_1}{k_2} \quad (A) \quad \text{hence} \quad k_{\text{obs}} = \frac{k_3 k_1}{k_2}$$

Case II The low pressure region here $k_3 \gg k_2 (M)$; i.e., (M) is very, very small. Under these conditions the rate of reaction is given by

$$R = k_1 (A) (M)$$

Early low pressure work on nitrogen pentoxide was hampered by experimental difficulties in using very small quantities of nitrogen pentoxide. The best work was done by Linhorst and Hodges²³ on pure nitrogen pentoxide. They reported at pressures below 0.004 mm a rate constant of 3.2×10^5 cc mole⁻¹ sec⁻¹.

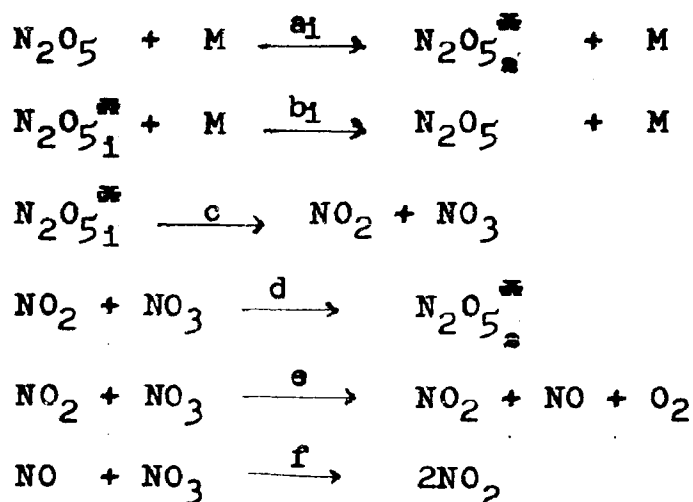
H. S. Johnston^{24,25,26,27} has studied the decomposition of N₂O₅ in the presence of nitric oxide as a function of the total pressure over a pressure range of 7×10^{-2} mm to 7×10^3 mm. It was found that k_1 varied as a function of the pressure and although neither the maximum high pressure or the minimum low pressure region was reached experimentally values for both rate constants were obtained by extrapolation. In the low pressure region it was found at $t = 27^\circ\text{C}$ that the second order rate constant had a value of 230 liters/mole/sec. This value compares quite well to the value of Linhorst and Hodges who reported a value of 320 liter/mole/sec. Johnston

and his coworkers also were able to reproduce the rate constants of Smith and Daniels at the same pressure and temperature.

It was also found that various inert gases (M) can activate the N_2O_5 molecules with various efficiencies. The various gases were H_2 , He, Ar, Xe, SF_4 , N_2 and CO_2 .

The above work forms the basis of the experimental work on the unimolecular decomposition of nitrogen pentoxide. All the results have been summarized by H. S. Johnston²⁸ and the results have been used to write mechanisms for four complex reactions, namely the decomposition of pure nitrogen pentoxide, the decomposition of nitrogen pentoxide in the presence of nitric oxide, the decomposition of ozone in the presence of nitrogen pentoxide and the formation of nitrogen pentoxide from ozone and nitrogen dioxide.

The mechanism for the decomposition reaction of nitrogen pentoxide according to H. S. Johnston consists of the following steps.



This method takes into consideration that any molecule M can activate a reactant molecule. It also considers that the reactant molecule can be excited to various energy states. For the sake of consistency this notation will be used throughout this thesis.

It appears that the Ogg extension of the decomposition reaction is valid and it explains most of the experimental work reasonably well. If the mechanism is valid then nitric oxide should not be unique in minimizing reaction (2). That is, a reducing agent of similar strength should allow one to measure the rate of the primary step. In fact this was first attempted by Weston²⁹ who studied the reaction between nitrogen pentoxide and nitrosyl chloride.

The reaction between the two gases has the following stoichiometry $N_2O_5 + NOCl \longrightarrow NO_2Cl + N_2O_4$. Weston studied the reaction between 0°C and 25°C in glass vessels by measuring the increase in nitrogen dioxide concentration. He found that the reaction was affected by the surface of the reaction vessel and by moisture. By applying the Arrhenius equation to the experimental rate constants, a small negative activation energy of about five kcal is found. Kinetically the reaction was found to be of second order. Weston proposed a mechanism which involved a simple bimolecular collision between the two reacting species.

Later Amell and Ricci³⁰ reinvestigated the reaction and confirmed the fact that the reaction on an ionic surface was indeed heterogenous. The reaction takes place by two

reaction paths, one being a heterogenous path and the other being a homogenous path. The rate equation for the entire process is given by

$$R_{\text{total}} = R_{\text{heterogenous}} + R_{\text{homogenous}} .$$

In the presence of an ionic type surface $R_{\text{heterogenous}}$ $R_{\text{homogenous}}$ and the rate expression reduced to Weston's equation, namely

$$R_{\text{heterogenous}} = k_{\text{obs}} (N_2O_5) (NOCl).$$

The reaction was also studied with the surface partially covered with beeswax. The kinetics changed drastically so that the reaction was no longer dependent on the concentration of nitrosyl chloride, but only on the concentration of nitrogen pentoxide. Thus it appeared that the surface reaction was eliminated and a measurement was obtained of the true homogenous reaction.

EXPERIMENTAL

PART A - MATERIALS

I. Purification of the Sulfur Dioxide

The sulfur dioxide used in the experiments was obtained conveniently from a small tank supplied by the Matheson Company. An anhydrous grade of the gas was used. This was then treated in the manner prescribed by J. R. Bright and W. C. Fernelius³¹, which consists of passing the gas through concentrated sulfuric acid, then over phosphorous (V) oxide. The gas was finally condensed, using a dry ice and trichloroethylene freezing mixture. The trap containing the solid sulfur dioxide was then transferred to the vacuum system and the SO₂ was distilled into a storage vessel. The SO₂ was kept under vacuum until it was used.

II. Preparation of Nitrogen Pentoxide

The nitrogen pentoxide used in all the experiments was prepared by the reaction of nitrogen dioxide (2) in a stream of ozone.³² The nitrogen dioxide used was obtained from the Matheson Company. The gas was dried by passing it through a U-tube filled with phosphorous (V) oxide. The oxygen was obtained from the Linde Air Products Company. The oxygen was dried by passing it through columns filled with glass wool and phosphorous (V) oxide. The nitrogen pentoxide obtained in this manner is very pure and crystalline.

No further purification was carried out. Purity was ascertained by determining the rate constant of the decomposition reaction and comparing this with the results of Daniels and Johnston.²

III. Preparation and Purification of Nitrosyl Chloride

Initially nitrosyl chloride was prepared by passing nitrogen dioxide gas through a column of moist KCl. The crude NOCl is dried over phosphorous (V) oxide. The NOCl obtained in this manner contains traces of NO₂. This impurity is eliminated by passing the crude NOCl through the moist KCl column several times.

Nitrosyl chloride in the latter experiments was obtained from the Matheson Company. The purity of the gas was stated to be 93%. Further purification was carried out on a vacuum system which was used strictly for gas purification.

A one liter vessel was filled with one atmosphere of the gas. The NOCl was condensed into a 50 ml flask containing glass wool and phosphorous (V) oxide, using a liquid nitrogen trap. The flask with the condensed gas was placed into a Dewar flask containing trichloroethylene and dry ice so that the more volatile impurities, nitric oxide and hydrogen chloride could be distilled off. This type of distillation was repeated several times. Each time the distillate was frozen out by using liquid nitrogen and discarded. The condensed NOCl was then placed in a chloroform slush bath. Two distillations were carried out under these conditions. Each time the center cut was kept.

IV. Purification of Nitrogen (II) Oxide

The nitric oxide obtained from the Matheson Company was of 99.0% purity. Further purification was carried out by condensing the gas with liquid nitrogen and distilling from an isopentane slush bath (-160.5°C). The product, after the above treatment, consisted of a pure white solid.

V. Purification of Ammonia

An anhydrous grade of ammonia gas (99.99%) obtained from the Matheson Company was used in all of the experiments. Further purification of the gas entailed condensing the gas with liquid nitrogen and distilling the condensed gas from an ethyl acetate slush bath (-83.0°C). Purity of the gas was checked by gas chromatography using a diethanolamine, sodium iodide, lauryl alcohol column with a fluorocarbon base.³⁴ No impurity peaks were detected.

VI. Purification of Hydrogen Chloride and Hydrogen Bromide

Both gases were obtained from the Matheson Company and both were of an anhydrous grade, the hydrogen bromide of a 99.8% purity and the hydrogen chloride of a 99.0% purity. Both gases were condensed using liquid nitrogen. The hydrogen chloride was distilled from a carbon disulfide slush bath and the hydrogen bromide from an ethyl acetate slush bath.

PART B - APPARATUS

I. Description of the Vacuum System

A schematic diagram of the vacuum system used in making the kinetic runs is given in Fig. I (numbers and letters on this diagram are used throughout the thesis). The following figures contain detailed description of the various components of the vacuum system. For example, Fig. II and Fig. III give dimensions of the housing for the wire strain gauge, and Fig. IV describes the wiring diagram involved.

The reaction vessel (G) and the calibrated pipet (F) were immersed in a constant temperature bath which could be controlled to $\pm 0.02^{\circ}\text{C}$. The nitrogen pentoxide was stored in vessel (H) immersed in a trichloroethylene-dry ice bath. The vapor pressure of the nitrogen pentoxide could be controlled very easily by immersing the storage bulb in a water bath at a selected temperature. The vapor pressure data for crystalline nitrogen pentoxide was obtained from Bright and Daniels.³⁵ Usually the nitrogen pentoxide crystals were immersed in an equilibrium mixture of ice and water. At this temperature the nitrogen pentoxide has a vapor pressure of 50 mm and decomposes with a half life of eleven days. Hence, decomposition was kept at a minimum, yet the quantities required for the kinetic runs could be obtained quite easily.

II. Glass Membranes

Due to the corrosive nature of the gases involved in the kinetic experiments special methods were required to measure the pressure changes during the kinetic runs. Several attempts were made to make glass membranes as described by Farrington Daniels³⁶, but they all proved unsuccessful for our purposes.

Finally, the required membranes were made by the Ryan & Velluto Company of Cambridge, Massachusetts (see Fig. I). The membranes were such that they could withstand a pressure differential of about one atmosphere and were sensitive enough to measure the pressure changes in the reactions involved. An increase in pressure causes the pointer to move in an outward direction, while a decrease in pressure causes movement in the opposite direction.

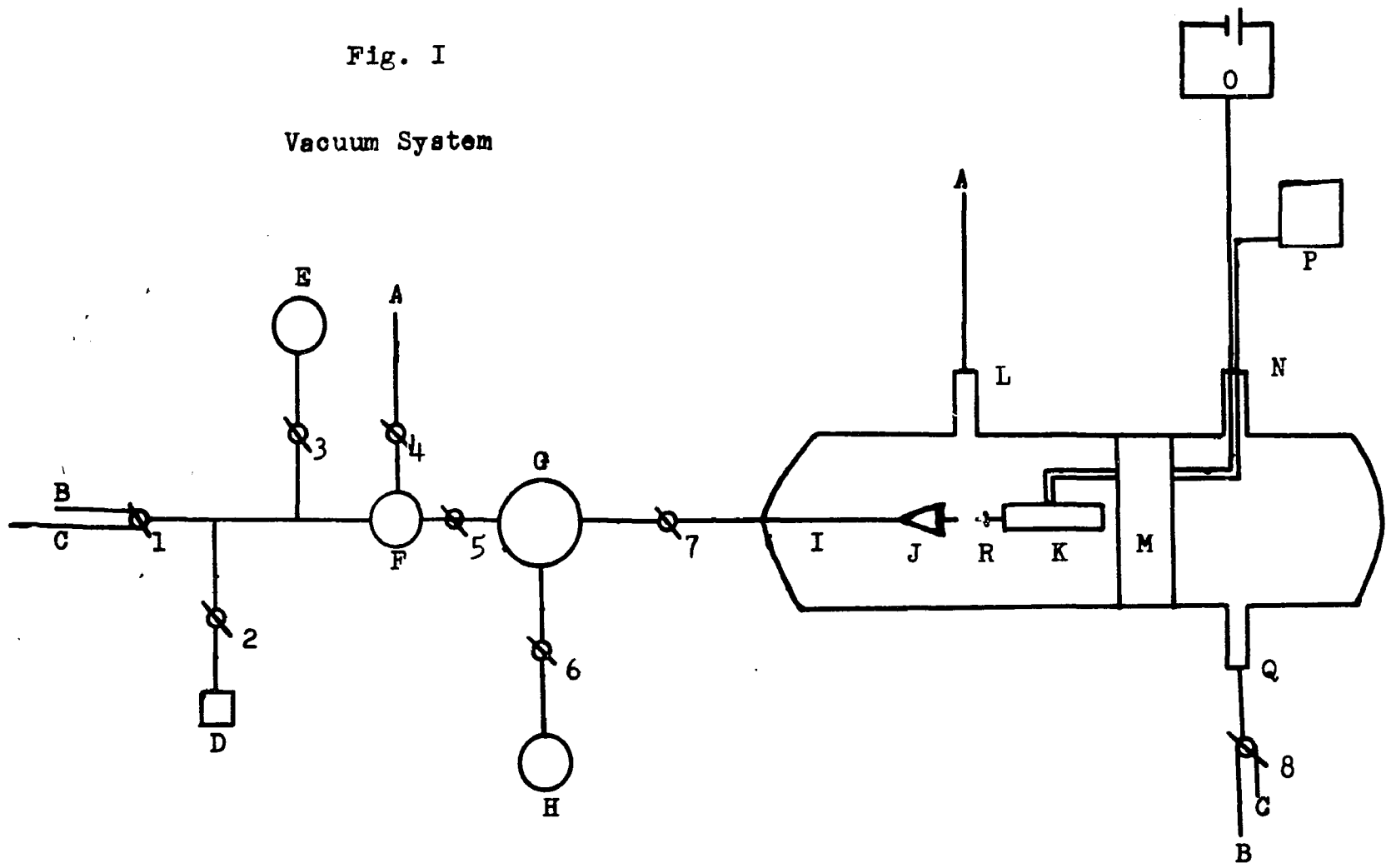
Contact between the glass diaphragm gauge and the lever arm of the wire strain gauge was made through the large nut (R) which could be put in contact with the pointer of the glass membrane by using a long stiff wire and the standard tapered joint (L).

The pressure change during the reaction was followed by employing a wire strain gauge produced by Statham Instruments. The strain sensitive elements of the transducer consist of a resistance wire arranged in the form of a wheatstone bridge.

A change in pressure during the course of the reaction causes an elongation of the wires in the bridge. This

Fig. I

Vacuum System



Legend for Figure I
(all dimensions are given in cm)

- A = to manometer
- B = to pump
- C = to atm
- ∅ = high vac stopcock
- D = Pirani gauge
- E = storage vessel for reducing agent
- F = calibrated pipet, (reducing agent)
- G = reaction vessel
- H = storage vessel, N₂O₅
- I = 10/30 s.t. joint
- J = glass diaphragm gauge
- K = transducer
- L = 19/38 s.t. joint
- M = 71/60 s.t. joint
- N = 24/40 s.t. joint containing four glass to metal seals for circuitry to battery and recorder
- O = battery
- P = recorder

Fig. II

Housing for Transducer

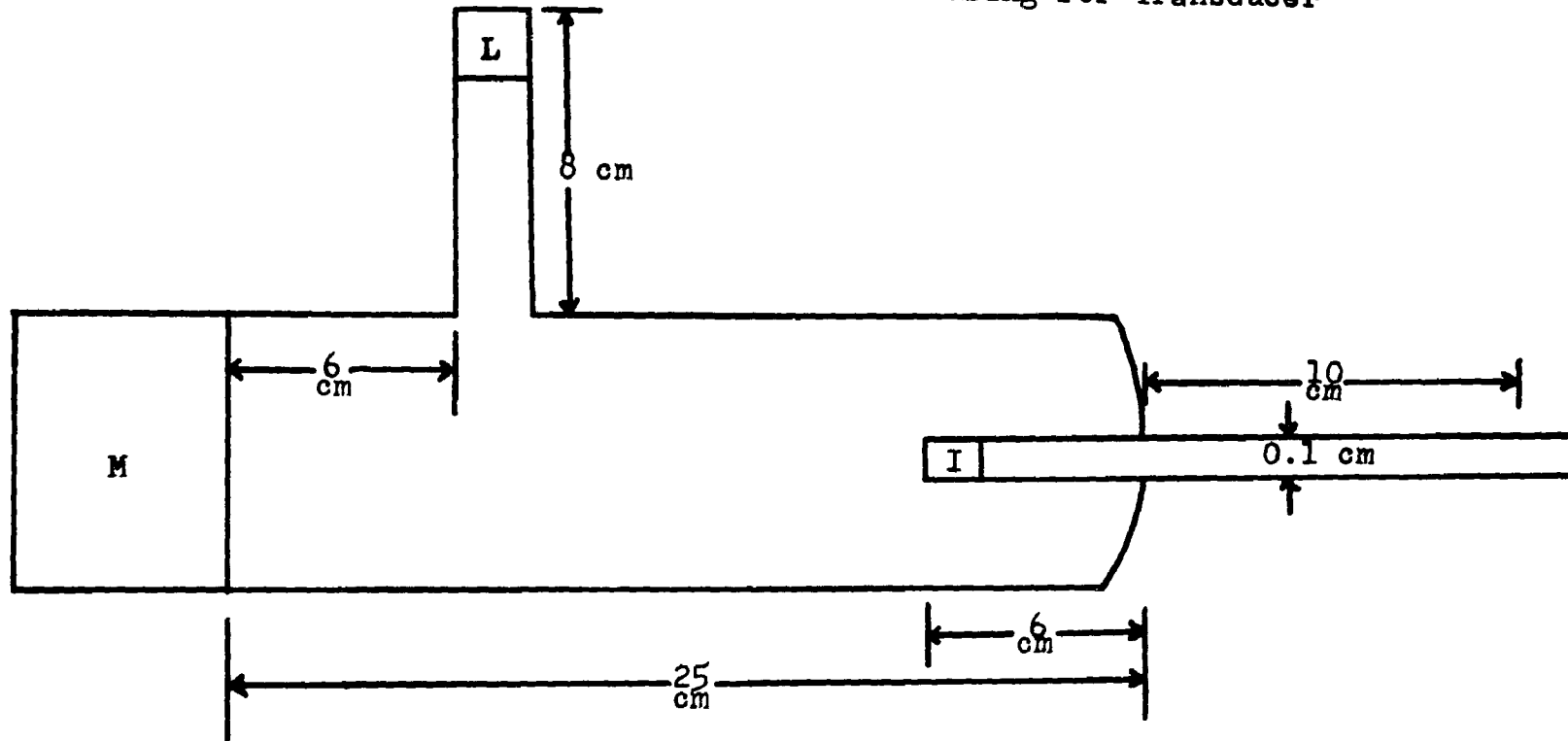


Fig. III
Housing for Transducer

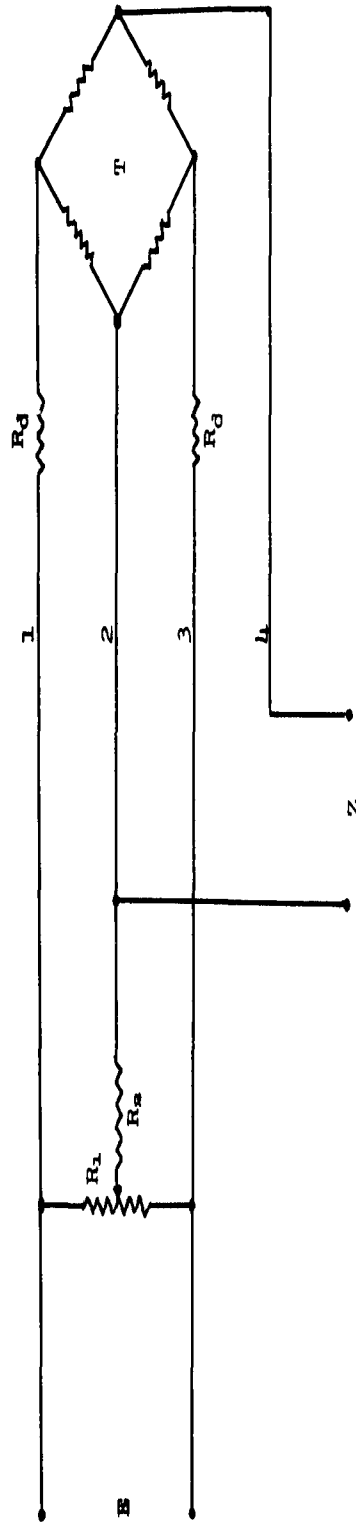
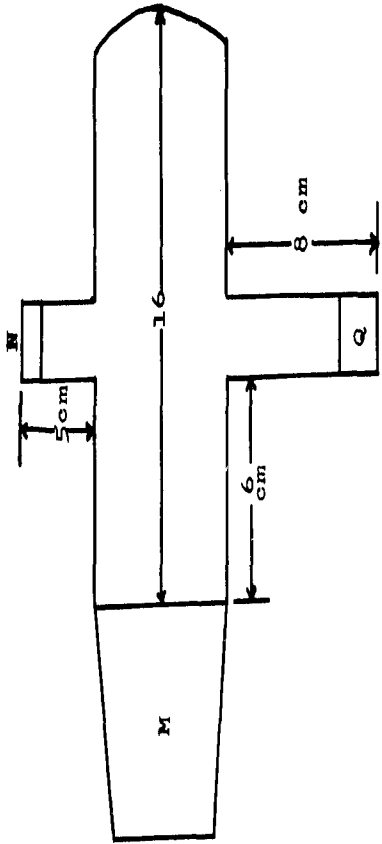


Fig. IV
Transducer Circuit

Legend for Figure IV
Transducer Circuit

- E. = constant energizing voltage (12 volts DC)
- R_c = calibrating resistor
- R_d = voltage dropping resistor (if required)
- R = transducer bridge resistance in ohms measured between terminals 2 and 3 (369.7Ω)^{**}
- R_m = transducer bridge resistance in ohms measured 1 and 4 (369.7Ω)
- R₁ = wire-wound potentiometer with a value of about 100K (37,000 ohms) for full scale zero adjustment range
- Z = receiving instrument
- T = transducer

^{**}Specifications as given by Statham Instruments Inc.

elongation causes a change in the resistance of the wire in the bridge. The resulting resistance change effects the input voltage which is used to excite the transducer. The change in the output voltage was then recorded on a direct reading General Electric recorder, capable of operating in a variety of ranges and at chart speeds of six inches per hour or six inches per minute.

In order to minimize any heterogeneous reaction, a reaction vessel having a 300 ml. volume was constructed out of Teflon. In order to keep the glass surface to a minimum, all tubing from the storage vessel to the Rx vessel was constructed of capillary tubing. Connection between the reaction vessel and the tubing was afforded by a Mace IOM4 plug constructed by the Mace Corporation of San Gabriel, California.

III. Experimental Procedure

Runs in the temperature range of 0°C to 35°C

A definite amount of nitrogen pentoxide was allowed to enter the evacuated reaction vessel. The amount of nitrogen pentoxide was controlled by keeping the crystalline nitrogen pentoxide at a definite temperature. The initial pressure of nitrogen pentoxide was determined by using the transducer as a null instrument.

After the decomposition had proceeded for a short period of time, the pressure in the rear of the diaphragm was changed so that a new base line was obtained. The recorder was then turned on to fast speed (6" per min.) and a known

amount of the prepurified reducing agent was flashed into the reaction vessel. In some cases the sensitivity was very large and addition of the reducing agent drove the recorder pen off scale. This was adjusted by changing the pressure in the rear of the gauge so that the pen was on scale at the bottom of the chart paper when the reducing agent was added.

Fig. V is a typical trace using nitric oxide and nitrogen pentoxide, made on a multispeed Fisher laboratory recorder at a sensitivity of 1 mv. Several runs were made at zero degrees centigrade. This method was employed in systems where very rapid reactions occurred. The trace BC is due to the pressure change accompanying the reaction. At zero degrees the decomposition of nitrogen pentoxide is very slow, so that after the addition of the nitrogen pentoxide, there was a horizontal portion in the curve before the addition of the reducing agent. Figs. VI and VII show the traces obtained when air and helium are substituted for nitric oxide. Since no reaction is occurring the trace BC is now horizontal.

IV. Calibration of the Vacuum System

The vacuum system was calibrated using air. The pressure was measured with an oil manometer and deflection of the diaphragm was recorded on the recorder. A plot was made of pressure in centimeters of oil versus the millivolt deflection. This procedure was carried out on all the gauges which were used.

In many cases it was desirable to have the pressure change in centimeters of mercury. In order to do this the

Fig. V

Typical Trace Obtained with Nitric Oxide and Nitrogen Pentoxide

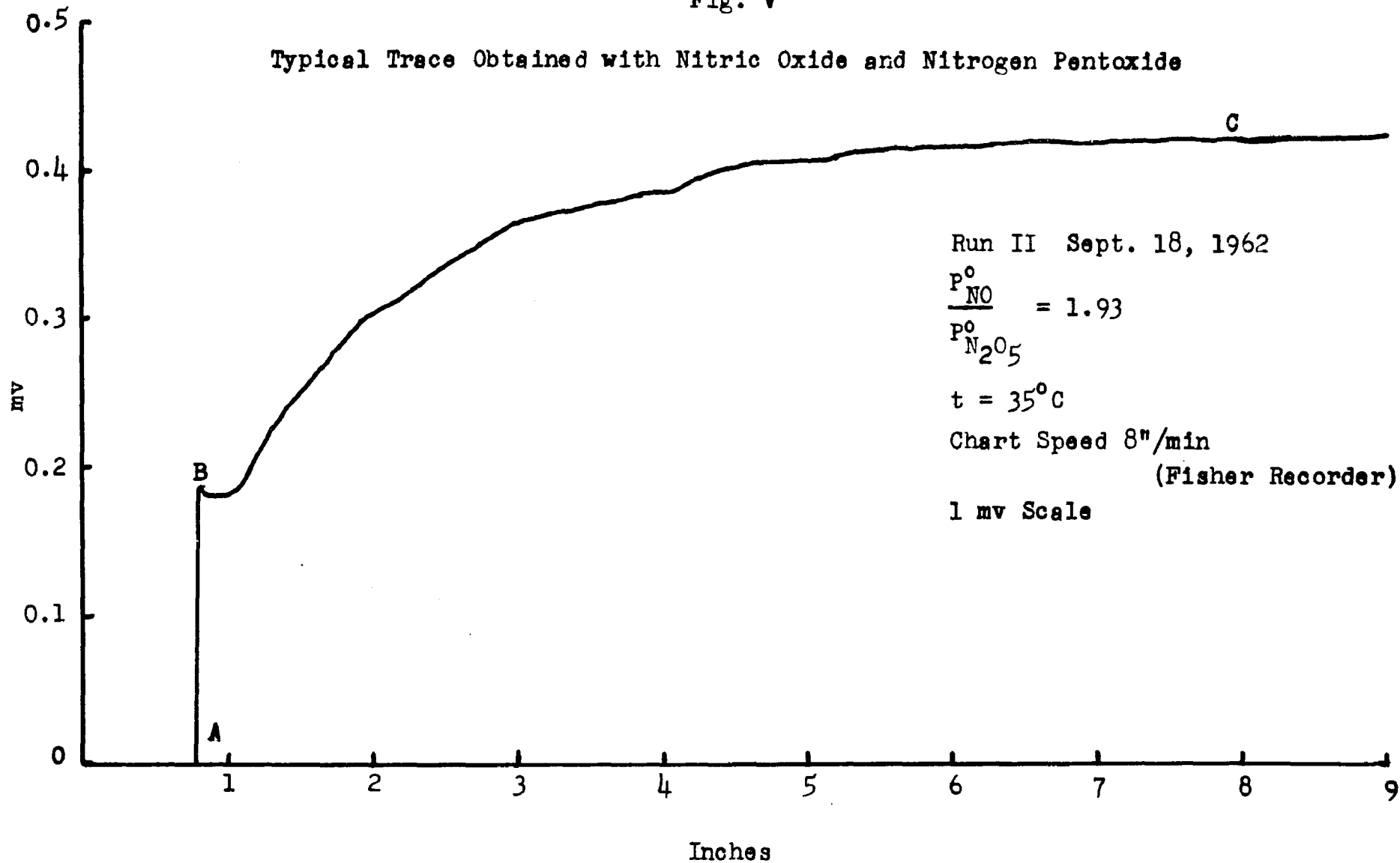


Fig. VI

Typical Trace Obtained Using Air

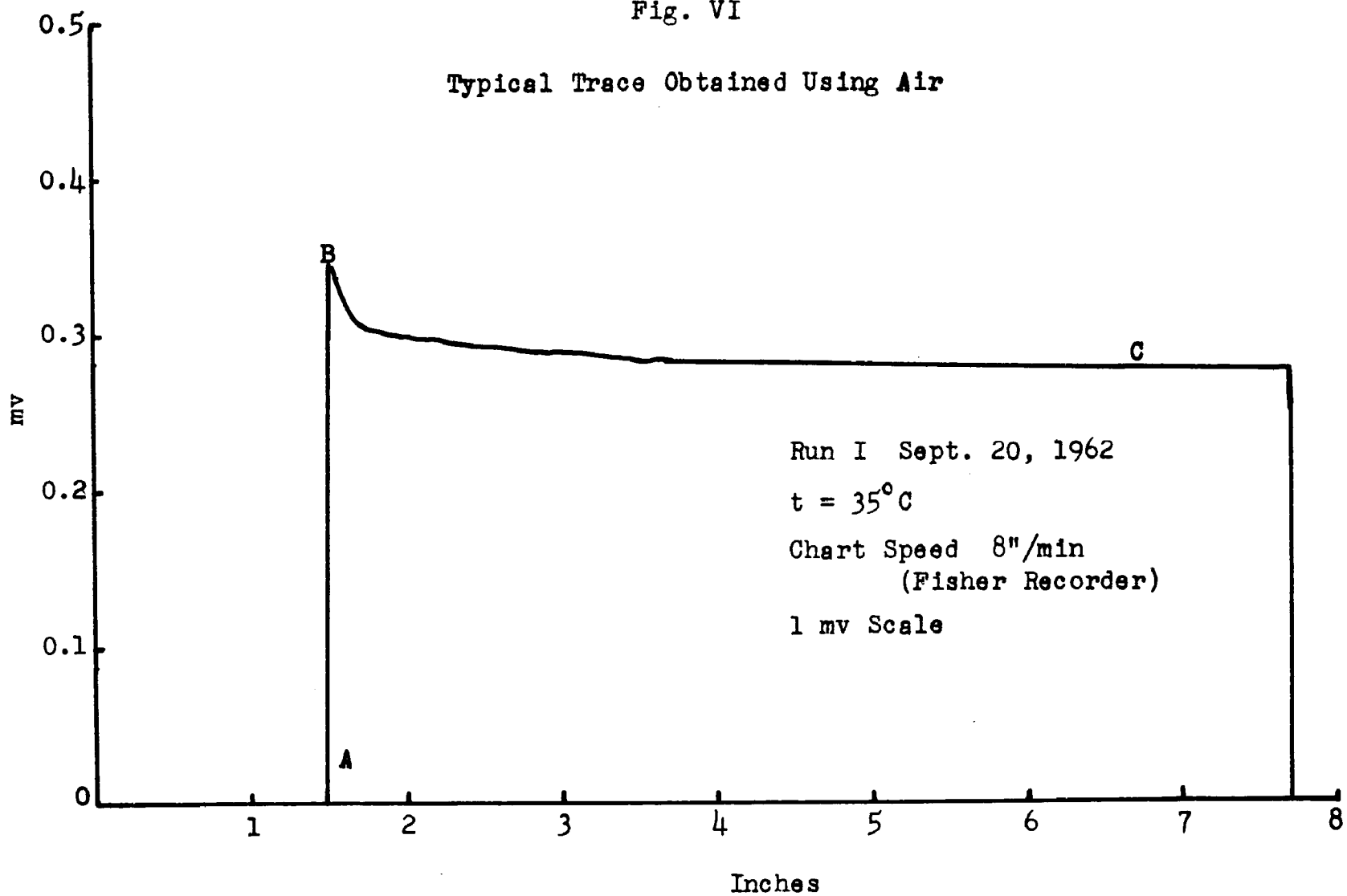


Fig. VII

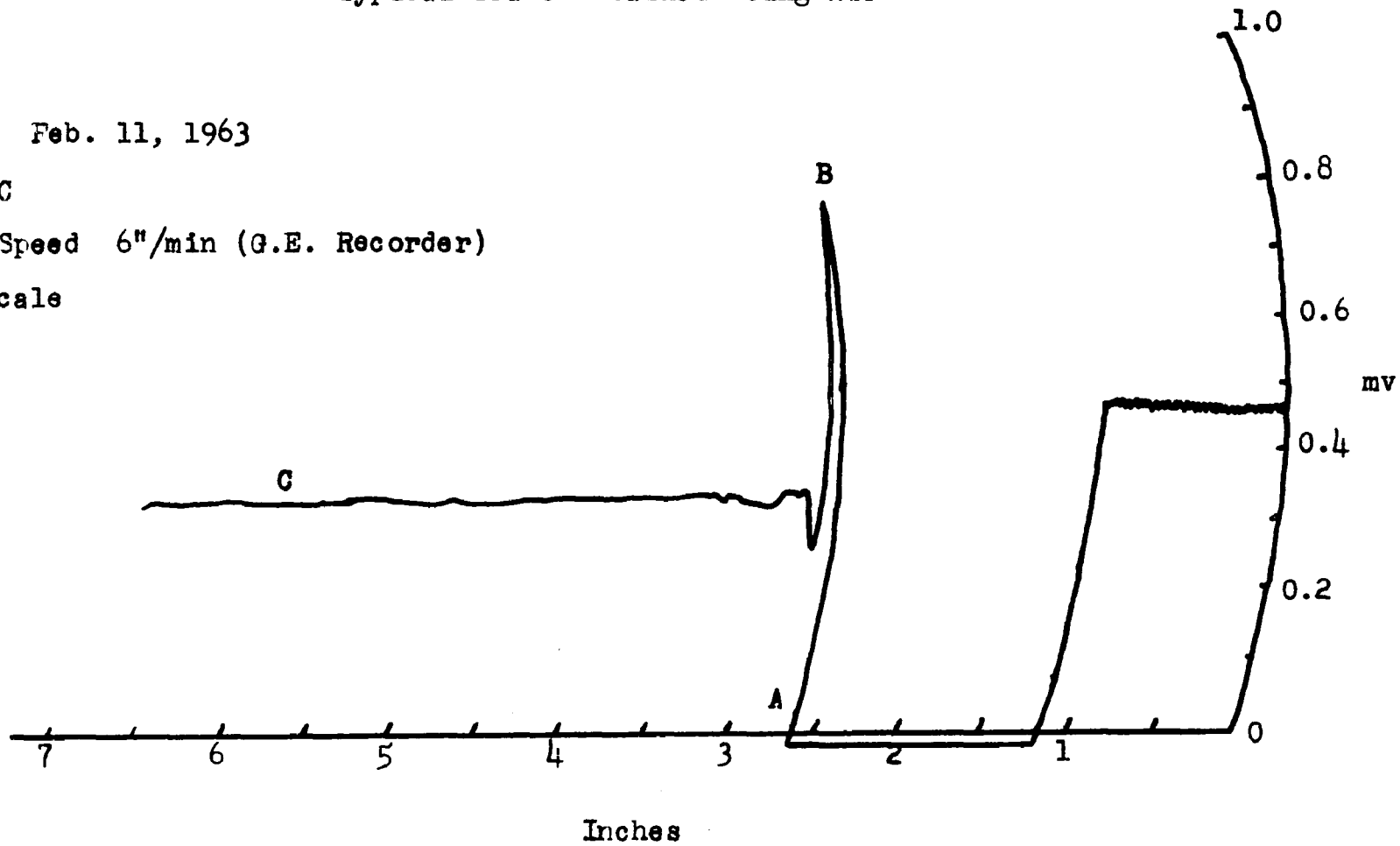
Typical Trace Obtained Using Air

Run II Feb. 11, 1963

$t = 0^{\circ}\text{C}$

Chart Speed 6"/min (G.E. Recorder)

1 mv Scale



density of the Kel-F Polymer oil was determined by use of a specific gravity bottle. The density of the Kel-F oil determined by this method was found to be 7.05 grams/cm.³.

V. Use of the transducer as a null instrument to measure pressure.

With the vacuum system used it was possible to add a quantity of gas to the reaction vessel and, by adding air to the reverse side of the membrane, return the system to its original base line. This method was used to determine the initial amount of N_2O_5 added to the system. To determine the error in this procedure two manometers were employed, one on either side of the membrane and helium was added to the reaction vessel. The system was balanced and the readings on both manometers recorded.

TABLE I

P_A	P_B	Difference	
6.88	6.90	-0.02	P_A = Pressure on the reaction vessel side of the membrane
7.07	6.80	+0.27	
<hr/>			
7.75	7.77	-0.02	P_B = Pressure on the reverse side of the membrane
9.99	9.30	+0.69	
8.66	8.74	-0.08	
7.09	7.60	-0.11	
7.28	7.02	+0.26	
9.10	8.78	+0.32	
12.13	11.85	+0.28	
8.55	8.48	+0.07	
7.44	7.31	+0.13	
		Average	

VI. Comparison with other systems.

After the construction of the various calibration curves the system was checked out by determining the rate constants for known reactions.

One reaction was the decomposition of nitrogen pentoxide at 35°C., which has a half life of eighty minutes. This was done periodically not only to check the system, but also to check the purity of the nitrogen pentoxide. All rate data was compared to the work of Johnston and Daniels.²

To check the system under conditions where a rapid reaction was involved the nitric oxide-nitrogen pentoxide reaction was used and the data compared to the extensive experiments of Mills and Johnston.²⁴ The table below contains the rate constants obtained by the fast pressure measuring apparatus and those of Mills and Johnston at the same temperature and total pressure. As in the case of Mills and Johnston the rate constant was obtained from a plot of $\log P_{N_2O_5}$ vs. time. The method of least squares was applied to each run to obtain the rate constant.

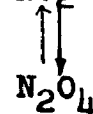
TABLE II

Date	Run No.	$k \text{ sec}^{-1}$ ($\times 10^2$)	P_T^o (cm)	$k_j \text{ sec}^{-1}$ ($\times 10^2$)	$(P_T^o)_j$ (cm)
6/23/63	III	3.27	2.784	3.50	2.85
"	IV	3.96	4.695	4.88	4.66
"	V	5.04	10.69	6.44	10.9
"	VI	3.56	2.845		
"	IX	4.74	4.590		
"	X	6.12	10.73		

P_T^o = total pressure
 k = rate constant

k_j = rate constant
determined by
Mills and Johnston
 $(P_T^o)_j$ = total pressure of
Mills and Johnston

The stoichiometry of the NO-N₂O₅Rx was also checked by measuring the final pressure after reaction had taken place and comparing it to a calculated pressure assuming the stoichiometry for the reaction was $N_2O_5 + NO \longrightarrow 3/2 NO_2$



The results are listed in Table III.

TABLE III

Stoichiometry NO-N₂O₅

Date	Run No.	P° N ₂ O ₅	P° NO	P _f (calc.)	P _f (obs.)
6/23/63	I	0.95	1.889	3.429	3.56
"	II	0.99	1.772	3.232	3.38
"	III	0.91	1.874	3.361	3.07
"	IV	1.09	3.605	5.335	4.98
"	V	0.96	9.729	11.289	11.32
6/24/63	VI	0.98	1.865	3.455	3.28
"	VII	1.73	9.926	12.176	12.10
"	VIII	1.83	9.903	12.533	12.01
"	IX	0.91	3.685	5.195	4.83
"	X	0.99	9.738	11.348	11.04

RESULTS

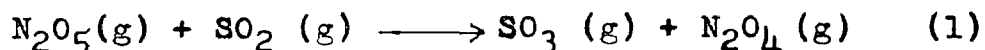
PART I

PRELIMINARY KINETIC RESULTS AND STOICHIOMETRY OF THE REACTIONS
INVOLVING THE VARIOUS REDUCING AGENTS

The reaction between nitrogen pentoxide and several reducing agents were carried out. Only in the case of the nitrosyl chloride and nitrogen pentoxide reaction were extensive runs carried out. In the other case the preliminary runs were carried out mainly to determine whether a given reaction proceeded with an increase in pressure, what the final pressure of the reaction was and to gain some insight as to the products of the reaction.

A. Reactions between N_2O_5 and SO_2

At the beginning of the work we believed that the reaction between nitrogen pentoxide and sulfur dioxide would have the following stoichiometry.



Using recent data reported by Hisatsune³⁷ and the data given in the NBS Tables, the free energy change for the above reaction is found to be -21.25 kcal at $25^\circ C$.

Previous workers have shown that sulfur trioxide is not a product of the reaction.³⁰ Actually, the reaction is very susceptible to certain impurities. The following table

indicates the pressure change due to the reaction. It was assumed that there was no formation of sulfur trioxide and the pressure change was due only to the decomposition of nitrogen pentoxide.

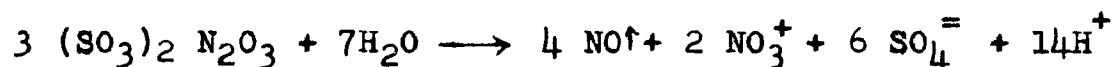
TABLE IV

Run No.	P° N ₂ O ₅	P°SO ₂	Pf(obs.)	NoRx Pf(calc.)	Rx Pf(calc.)
1	1.430	1.366	4.511	4.681	3.966
2	0.643	1.499	3.021	3.051	2.729
3	1.344	3.704	6.950	6.876	6.204
5	0.653	1.428	2.905	3.050	2.723

All pressures are reported in cm (Hg)

There seemed to be no change in the rate constant for the thermal decomposition reaction when the sulfur dioxide was dried over phosphorous V oxide. In some cases when the sulfur dioxide was dried over concentrated sulfuric acid, or when water vapor was added to the reaction mixture, the reaction became erratic.

A white solid was deposited on the walls of the reaction vessel. The solid is believed to be nitrosyl sulfuric anhydride. This compound is described by Wannagat and Hohlstein³⁸ as having the chemical formula, (SO₃)₂ N₂O₃, and that the compound is very hygroscopic. The authors also proposed the following hydrolysis reaction:



It was noticed that the solid instantaneously changed into a liquid on contact with air. In one run the compound formed in the tubing outside the thermostat. An evacuated trap containing water, which was attached to the system, was immersed in liquid nitrogen and the stopcock to the system was opened. A solid of intense blue color was condensed in the trap. After a period of one and a half hours the trap was removed from the system, warmed and shaken vigorously. The solution was tested for sulfate by the addition of barium chloride. The test was negative, but the solution gave a positive test for nitrate ion and a negative test for nitrite ion.

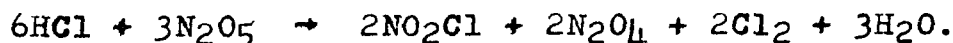
The reaction vessel was removed from the system and flushed with water. This solution was put through the same sequence of tests as the above solution. This solution gave a positive test for sulfate and negative tests for nitrate and nitrite.

As a final possibility one might expect a rapid bimolecular reaction between NO_3 and SO_2 to form a complex which could then decompose. Therefore some runs were carried out with the recorder on a speed of 6 inches per min. In all such runs the traces consisted of horizontal lines which show that there is neither a fast increase or decrease in pressure in the short interval involved.

B. The Reaction between N₂O₅ and HCl

On the basis of various experiments it was found that the reaction between hydrogen chloride and nitrogen pentoxide produced a reddish brown gas almost immediately. This color may be due to nitrogen dioxide or nitrosyl chloride or both.

The following is a possibility for the initial reaction. $\text{N}_2\text{O}_5 + 6\text{HCl} \rightarrow 2\text{NOCl} + 2\text{Cl}_2 + 3\text{H}_2\text{O}$. This reaction would be followed by a rapid consecutive reaction. $\text{N}_2\text{O}_5 + \text{NOCl} \rightarrow \text{N}_2\text{O}_4 + \text{NO}_2\text{Cl}$. Therefore in the presence of excess N₂O₅ the overall stoichiometry would appear to be:



Experiments appear to confirm the presence of NOCl when excess hydrogen chloride was added to N₂O₅. Actually, there is an alternative way in which nitrosyl chloride may be formed, for it has been observed by Talbot and Thomas³⁹ that the reaction between nitrogen dioxide and hydrogen chloride has the following stoichiometry:



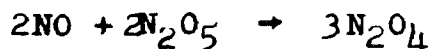
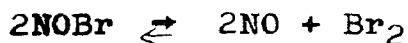
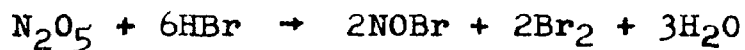
During the reaction the reacting system was opened to a trap immersed in liquid nitrogen. Quantities of a blood red liquid were condensed in the trap. This would seem to confirm the presence of nitrosyl chloride.

Furthermore several runs were made on the fast pressure measuring apparatus under conditions where $P^\circ\text{HCl}/P^\circ\text{N}_2\text{O}_5 = 2$. The runs were carried out on fast and slow recorder speeds. In all of the runs it was shown that there was neither an increase nor a decrease in pressure due to reaction.

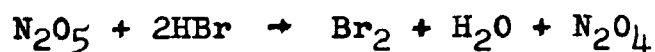
Recently, Heubel⁴⁰ has reported a method for the preparation of nitryl chloride by the action of hydrogen chloride on nitrogen pentoxide and proposes that the reaction take place by the following stoichiometric equation $N_2O_5 + HCl \rightarrow HNO_3 + NO_2Cl$. Heubel also reported that nitryl chloride decomposes in the presence of visible light to nitrogen dioxide and chlorine. In two of our runs made in the dark, the products were allowed to expand into a evacuated trap cooled to liquid nitrogen temperature. The trap was closed off and allowed to come to room temperature in the dark. The gaseous products were then placed in front of an ordinary light source. Immediately one could notice the formation of a reddish brown gas which may be nitrogen dioxide. Initially all the gases in the flask were colorless.

C. Reaction between Hydrogen Bromide and Nitrogen Pentoxide

A few reactions with hydrogen bromide and nitrogen pentoxide were carried out. Again here as in the case of the hydrogen chloride there is a possibility that nitrosyl bromide may be formed. It is interesting to note that in this case the preparation of nitryl bromide has never been reported. So that the reaction sequence might contain the following reactions:



So that the overall stoichiometry might be



In this case one would expect an increase in pressure due to the dissociation of N_2O_4 . Four traces were made, some on rapid recording speed and others on slow speed. In each case there was an increase in pressure. That is, the final pressure of the reaction mixture was greater in this case than $P^\circ\text{N}_2\text{O}_5 + P^\circ\text{HBr}$. This was not true of the reaction between hydrogen chloride and nitrogen pentoxide. In that case the final pressure was equal to $P^\circ\text{N}_2\text{O}_5 + P^\circ\text{HCl}$.

In the table below are listed the final pressures observed and the final pressure calculated based on the above stoichiometric equation.

TABLE V

<u>Run No.</u>	<u>$P^\circ\text{N}_2\text{O}_5$</u>	<u>$P^\circ\text{HBr}$</u>	<u>$P_f(\text{obs})$</u>	<u>$P_f(\text{calc})$</u>
10	0.654	1.403	2.260	2.648
11	0.653	1.338	2.288	2.556
12	0.653	1.293	2.310	2.556
13	0.632	4.267	4.212	5.467

D. The Reaction between Ammonia and Nitrogen Pentoxide.

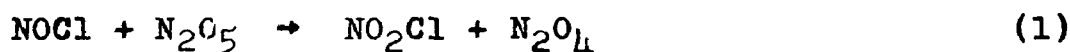
The reaction between nitrogen pentoxide and ammonia proceeded quite readily with a decrease in pressure. As the reaction proceeded the surface of the vessel was covered with a white solid.

There does not appear to be any simple stoichiometric relationship apparent from the pressure measurements. Actually, the reaction might be similar to the reaction between ammonia and nitrogen dioxide.⁴¹ This reaction proceeds with a decrease in pressure and a white solid is formed, which has been identified as ammonium nitrate, the other products being nitrogen and water.

PART II

A. Calculation of the Rate Constants for the System
NOCl-N₂O₅.

The rate constants for the NOCl-N₂O₅ reaction were calculated from a trace of the total pressure vs. time. Nitrogen pentoxide reacts with nitrosyl chloride according to the following equations:



The experimental evidence for equation (1) is given in a later section of this work.

In order to determine the amount of nitrogen pentoxide at any time "t", the following relationship was developed. According to equations (1) and (2), the total pressure at any time "t" is given by

$$P_T = P_{\text{NOCl}} + P_{\text{NO}_2\text{Cl}} + P_{\text{NO}_2} + P_{\text{N}_2\text{O}_5} + P_{\text{N}_2\text{O}_4} \quad (3)$$

where

P_{NOCl} = partial pressure of NOCl at time t

$P_{\text{NO}_2\text{Cl}}$ = " " " NO₂Cl " " t

$P_{\text{N}_2\text{O}_5}$ = " " " N₂O₅ " " t

$P_{\text{N}_2\text{O}_4}$ = " " " N₂O₄ " " t

P_{NO_2} = " " " NO₂ " " t

This assumes that all the nitrogen pentoxide decomposes via reaction with nitrosyl chloride only. The equilibrium expression has been determined by Daniels and is given by $K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$. Equation (3) may then be written as

$$P_T = P_{NOCl} + P_{NO_2Cl} + P_{NO_2} + P_{N_2O_5} + \frac{P_{NO_2}^2}{K_p} \quad (4)$$

Now

$P^{\circ}NOCl$ = initial amount of nitrosyl chloride

$P^{\circ}N_2O_5$ = " " " nitrogen pentoxide

$$\text{then } P^{\circ}NOCl = P_{NOCl} + P_{NO_2Cl} \quad (5)$$

Substituting (5) into (4)

$$P_T = P^{\circ}NOCl + P_{NO_2} + P_{N_2O_5} + \frac{P_{NO_2}^2}{K_p} \quad (6)$$

Also, $P_{NO_2} = 2 \alpha P^{\circ}N_2O_4$ where $P^{\circ}N_2O_4$ is the amount of N_2O_4 if there were no dissociation into NO_2 . Therefore, $P_T = P^{\circ}NOCl + 2 \alpha P^{\circ}N_2O_4 + P_{N_2O_5} + \frac{(2 \alpha P^{\circ}N_2O_4)^2}{K_p}$ (7)

We can also write that $P^{\circ}N_2O_5 = P^{\circ}N_2O_4 + P_{N_2O_5}$. Carrying out this substitution, we may write equation (7) as:

$$P_T = P^{\circ}NOCl + 2 \alpha P^{\circ}N_2O_4 + P_{N_2O_5} - P^{\circ}N_2O_4 + \frac{(2 \alpha P^{\circ}N_2O_4)^2}{K_p} \quad (8)$$

$$P_T^{\circ} = P^{\circ}NOCl + P_{N_2O_5}$$

then

$$P_T - P_T^{\circ} = 2 \alpha P^{\circ}N_2O_4 - P^{\circ}N_2O_4 + \frac{(2 \alpha P^{\circ}N_2O_4)^2}{K_p} = \Delta P \quad (9)$$

ΔP was then calculated for values of $P^{\circ}N_2O_4$ and a plot was made of ΔP vs. $P^{\circ}N_2O_4$. The data for the plot at $27^{\circ}C$ are given in Table IV. By using a graph of this type, pressure-time data could be obtained for the $NOCl-N_2O_5$ reaction traces.

TABLE VI

$P^{\circ}N_2O_4$	ΔP
0.51	0.49
1.02	1.00
1.53	1.47
2.06	1.92
2.59	2.42
3.13	2.92
4.23	3.92
5.35	4.61
6.49	5.42
7.65	6.32
8.84	6.96
10.00	8.08
11.24	8.74
12.43	9.58
13.71	10.15
14.94	11.15
16.18	11.93
17.44	12.69
20.71	14.44

B. Sample Calculation

This calculation is an example of the method which was used to calculate the rate constants for the particular runs.

Using as an example, Run III, July 15, 1963, $P^{\circ}N_2O_5 = 2.80$ cm, $P^{\circ}NOCl = 10.66$ cm, therefore $P_T^{\circ} = 13.46$ cm. From this data one can calculate the final pressure (P_f) which in this case was 15.18 cm. Therefore, the change in pressure

due to the reaction is equal to $P_f - P^{\circ}T = \Delta P = 15.18 - 13.46$ cm = 1.72 cm. This pressure corresponds to a displacement of 43.0 at the sensitivity used to make the trace. With this information one can calculate the beginning of the trace from the final value.

Once the point of initial reaction was determined, the trace was marked off in 2.5 sec. intervals and the change for every time interval was determined. This change corresponds to the change in pressure due to reaction at that particular time interval. From the various ΔP 's one could obtain $P^{\circ}N_2O_4$ from the plot of ΔP vs. $P^{\circ}N_2O_4$ at that particular temperature. Since $P_{N_2O_5} = P^{\circ}N_2O_5 - P^{\circ}N_2O_4$, the amount of nitrogen pentoxide left at the particular interval could be determined. The data for eight 2.5 sec. interval is given below:

TABLE VII

<u>Time</u>	<u>Trace</u>	<u>Δ mv</u>	<u>ΔP mm</u>	<u>$P^{\circ}N_2O_4$</u>	<u>$P_{N_2O_5}$</u>	<u>$\log P_{N_2O_5}$</u>
2.5	19.3	0.772	7.72	9.70	18.3	1.2625
5.0	21.0	0.840	8.40	10.75	17.25	1.2367
7.5	22.5	0.900	9.00	11.60	16.4	1.2148
10.0	23.8	0.952	9.52	12.40	15.6	1.1931
12.5	24.6	0.984	9.84	12.95	15.05	1.1775
15.0	26.0	1.04	10.4	13.80	14.2	1.1523
17.5	27.0	1.08	10.8	14.4	13.6	1.1335
20.0	28.0	1.12	11.2	15.1	12.9	1.1106

Run made on 1 mv scale; therefore, 1 mv is equal to fifty divisions, Also 1 mv is equal to 1.00 cm (Hg) of pressure. Since the reaction is first order a plot was made of $\log P_{N_2O_5}$ vs. time. The method of least square was used in each case to calculate the slope of this line. Multiplying the

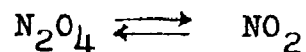
slope of the line by 2.303 gave the rate constant for the particular trace.

All least square calculations were carried out on an IBM 1620 computer. Calculations were randomly checked by the use of a desk calculator.

C. Stoichiometry

Of the reducing agents which were used in the present study, the reaction between NOCl and N₂O₅ seemed to be particularly suited for our purposes. Although the reaction in glass vessels was heterogenous, the work in the waxed vessels seemed promising. Further investigation using beeswax (Fisher White Disc U.S.P.) and Socony paraffin wax, however, dampened this initial hope somewhat, for it was found that there was reaction between the reactants and the various surfaces. This was overcome however by constructing a reaction vessel out of Teflon. Using this reaction vessel the homogenous reaction between NOCl + N₂O₅ was studied.

Weston previously showed that the stoichiometry of the reaction was

$$\text{NOCl} + \text{N}_2\text{O}_5 \longrightarrow \text{NO}_2\text{Cl} + \text{N}_2\text{O}_4$$


This was checked out in the Teflon vessel by mixing known amounts of nitrosyl chloride and nitrogen pentoxide and calculating the final pressure on the basis of the above two equations and comparing it to the observed pressure. The results are given in the table below.

TABLE VIII

Run No.	$P^{\circ}N_2O_5$ (cm)	$P^{\circ}NOCl$ (cm)	P_f (calc) (cm)	P_f (obs) (cm)
45	0.76	1.913	3.30	3.06
45a	0.93	9.997	11.68	11.46
46	0.93	9.983	11.60	11.03
47	0.95	9.931	11.65	11.16
48	0.98	9.912	11.69	11.06
49	0.99	3.591	5.38	5.16
50	0.90	3.736	5.38	5.22
51	0.85	3.713	5.25	5.10
52	2.07	10.011	13.41	12.75
53	2.01	10.053	13.44	12.69
54	2.06	10.129	13.53	13.05

D. Order of the Reaction

The order with respect to each component was determined by calculating the rate of reaction at a definite time under special concentration conditions. The rate equation was assumed to have the following form:

$$R = \text{Rate} = k P_{NOCl}^x P_{N_2O_5}^y$$

which may be written in log form as

$$\log R = \log k + x \log P_{NOCl} + y \log P_{N_2O_5}$$

Under the special conditions:

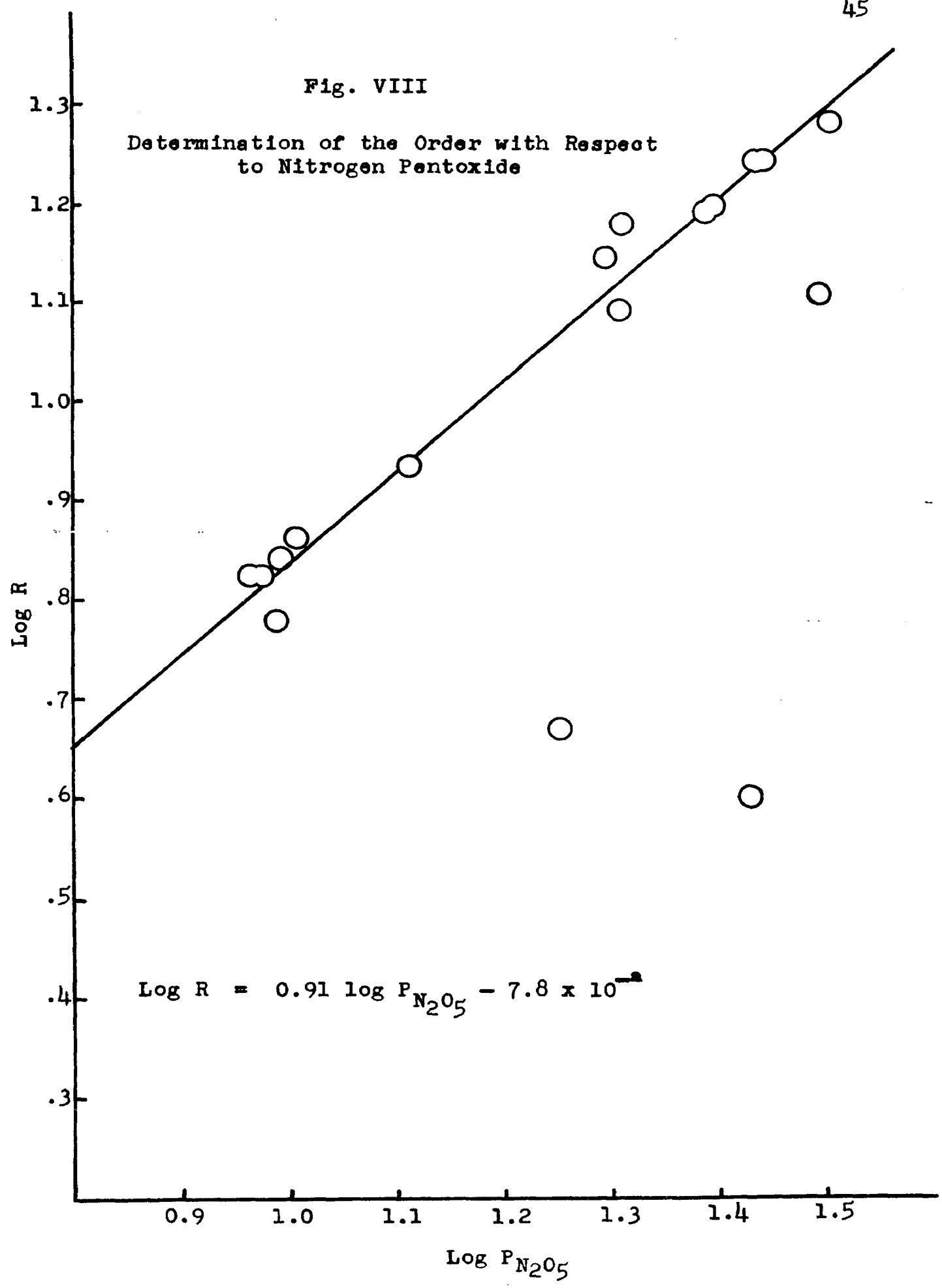
$$a) P_{NOCl} = \text{constant}$$

$$\text{then } \log R = \text{constant} + y \log P_{N_2O_5}$$

This equation under these conditions is one of a straight line and from the slope of a plot of $\log R$ vs. $\log P_{N_2O_5}$ one may obtain y , the order with respect to nitrogen pentoxide. The data and the plot are given below. Using the

Fig. VIII

Determination of the Order with Respect to Nitrogen Pentoxide



method of least squares the relationship is given by the equation

$$\text{Log } R = 0.91 \log P_{\text{N}_2\text{O}_5} - 7.8 \times 10^{-2}$$

TABLE IX

<u>Run No.</u>	<u>Log P_{N₂O₅}</u>	<u>Log R</u>
46	0.9685	0.8248
47	0.9778	0.8248
48	0.9912	0.7832
49	0.9956	0.8432
52	1.3160	1.1786
53	1.03032	1.1453
54	1.3139	1.0927
61	1.4314	0.6010
62	1.4472	1.2442
63	1.3927	1.1881
64	1.4409	1.2442
65	1.5105	1.2821
66	1.4487	1.1062
67	1.0170	0.8639
68	1.2577	0.6702
32	1.1584	0.9365

b) If $P_{\text{N}_2\text{O}_5}^0 = \text{constant}$

the equation may be written as

$$\log R = \text{constant} + x \log P_{\text{NOCl}} \quad (1)$$

where the constant + y log $P_{\text{N}_2\text{O}_5}$. Then for two independent runs one may write

$$\log R_1 = \text{constant} + x \log (P_{\text{NOCl}})_1 \quad (2)$$

$$\log R_2 = \text{constant} + x \log (P_{\text{NOCl}})_2 \quad (3)$$

Dividing equation (2) by equation (3),

$$\log \frac{R_1}{R_2} = x \log \frac{(P_{\text{NOCl}})_1}{(P_{\text{NOCl}})_2}$$

or x the order with respect to nitrosyl chloride is given by

$$x = \frac{\log \frac{R_1}{R_2}}{\log \frac{(P_{\text{NOCl}})_1}{(P_{\text{NOCl}})_2}}$$

Values of x are given in the table below.

TABLE X

<u>Run No.</u>	$P_{\text{N}_2\text{O}_5}^{\circ}$ (cm)	P_{NOCl}° (cm)	$R \frac{\text{mv}}{\text{cm}}$
113	1.28	1.701	0.7600
114	1.24	3.417	0.7696
115	1.27	9.865	0.8537
	<u>Combination of Runs</u>	x <u>order w.r.t. NOCl</u>	
	113 and 114	0.01	
	113 and 115	0.07	
	114 and 115	0.09	
		avg. 0.06	

Then the complete rate equation may be written as being $R = kP_{\text{N}_2\text{O}_5}$ for the decomposition of nitrogen pentoxide in the presence of nitrosyl chloride.

E. Determination of the Rate Constant

Once the order of the reaction was determined it was possible to determine the value of the rate constant from the slope of a plot of $\log P_{\text{N}_2\text{O}_5}$ vs. time.

The rate constants at 20.05, 27.0 and 35°C are listed

in the tables below.

TABLE XI

<u>Run No.</u>	P° <u>N_2O_5 (cm)</u>	P° <u>$NOCl$ (cm)</u>	P° <u>T (cm)</u>	$k_{obs.}$ <u>sec^{-1} $\times 10^6$</u>
24	1.216	1.763	2.979	7.18
25	1.206	1.701	2.907	5.39
29	1.206	3.487	3.487	8.48
30	1.211	1.833	3.044	10.11
32	1.440	9.602	11.042	20.68
34	1.404	1.786	3.180	6.84
35	1.373	1.734	3.107	8.38
36	1.348	1.795	3.143	6.93
45	0.76	1.913	2.613	9.90
46	0.93	9.997	10.827	3.59
47	0.93	9.983	10.913	21.21
48	0.98	9.91	10.89	22.91
49	0.99	3.59	4.58	10.16
50	0.90	3.74	4.64	15.66
51	0.85	3.71	4.56	12.62
52	2.07	10.01	12.08	16.26
53	2.01	10.05	12.06	20.19
54	2.06	10.13	12.19	19.64
62	2.80	10.66	13.46	21.30
63	3.24	10.61	13.85	22.87
64	2.76	10.58	13.34	21.30
65	2.47	10.72	13.85	7.34
66	2.81	10.33	13.14	18.22
67	0.94	10.07	10.71	17.43
68	1.81	11.06	12.87	19.99
106	1.41	1.687	3.10	7.97
107	1.03	1.898	2.93	6.63
108	0.87	1.988	2.86	9.12
109	0.95	3.830	4.78	11.45
110	0.90	3.807	4.71	14.74
111	0.90	3.925	4.83	12.42
112	1.18	3,878	5.06	14.14

TABLE XII

<u>Run No.</u>	<u>P^o_{N₂O₅}</u>	<u>P^o_{NOCl}</u>	<u>P^o_T</u>	<u>k_{obs.}</u>
76	1.00	1.89	2.89	20.78
77	0.81	2.05	2.86	23.20
78	0.81	1.86	2.67	21.18
79	1.00	1.94	2.94	18.24
80	0.80	3.89	4.69	18.28
81	0.80	4.39	5.19	24.08
82	0.98	4.39	5.33	23.96
83	0.93	4.54	5.47	30.54
84	1.16	4.46	5.62	27.64
85	0.94	4.45	5.39	26.83
86	0.78	9.69	10.48	47.26
87	1.20	9.76	10.96	42.28
88	0.88	9.87	10.75	48.78
89	0.86	9.49	10.35	54.90
90	1.72	9.74	11.46	40.58
91	0.96	12.41	13.37	56.56
92	2.30	4.49	6.79	-
93	2.70	1.88	4.58	21.83

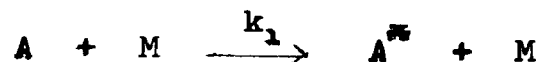
TABLE XIII

<u>Run No.</u>	<u>P^o_{N₂O₅}</u>	<u>P^o_{NOCl}</u>	<u>P^o_T</u>	<u>k_{obs.}</u>
94	1.60	2.218	3.82	18.01
95	1.81	2.148	3.96	19.55
96	1.75	4.949	6.70	8.52
97	1.94	4.677	6.62	19.32
98	1.62	4.827	6.45	20.35
99	2.55	9.771	12.32	15.98
100	1.55	9.861	11.41	22.40
101	2.29	9.748	12.04	16.40
102	1.80	11.62	11.62	23.03
103	2.04	4.559	6.54	17.75
104	2.10	2.190	4.29	13.19
105	1.40	2.312	2.77	14.79

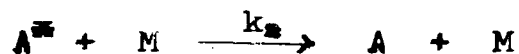
F. Pressure Effect

Any true unimolecular process may be described by the Lindemann Hypothesis which, in general, consists of three elementary reactions:

1. Activation



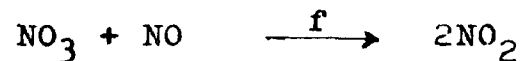
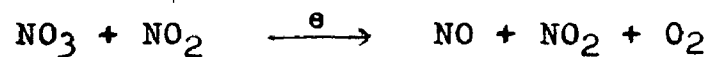
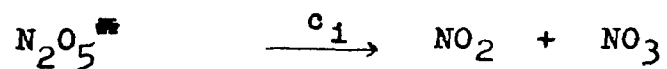
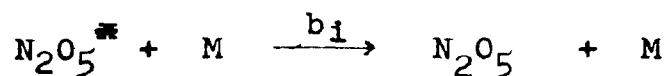
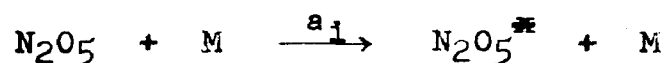
2. Deactivation



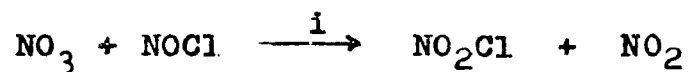
3. Spontaneous Reaction



In the case of nitrogen pentoxide we will use the notation of H. S. Johnston. The decomposition of N_2O_5 and several related reactions may be described by the following elementary reactions.



The following reaction must be included for the present work.



If we assume for the present that $\text{NOCl} + \text{N}_2\text{O}_5$ and $\text{NO} + \text{N}_2\text{O}_5$ reactions are similar in mechanism, then in the case of $\text{NOCl} + \text{N}_2\text{O}_5$ reaction, the mechanism would include steps a, b, c, d, and i.

Applying the Bodenstein approximation to N_2O_5^* and NO_3 :

$$\frac{d(\text{N}_2\text{O}_5^*)}{dt} = 0 = a_1(\text{N}_2\text{O}_5)(\text{M}) - b_1(\text{N}_2\text{O}_5^*)(\text{M}) - c_1(\text{N}_2\text{O}_5^*) + d_1(\text{NO}_2)(\text{NO}_3)$$

$$\frac{d(\text{NO}_3)}{dt} = 0 = c_1(\text{N}_2\text{O}_5^*) - d_1(\text{NO}_2)(\text{NO}_3) - i(\text{NO}_3)(\text{NOCl})$$

$$R = \frac{-d(\text{N}_2\text{O}_5)}{dt} = \frac{(\text{M})(\text{N}_2\text{O}_5) \frac{c_1 a_1}{b_1(\text{M}) + c_1}}{1 + \frac{(\text{M})(\text{NO}_2)}{i(\text{NOCl})} \frac{d_1 b_1}{b_1(\text{M}) + c_1}}$$

Under initial reaction conditions $(\text{NO}_2) \approx 0$, then

$$R = \frac{-d(\text{N}_2\text{O}_5)}{dt} = (\text{M})(\text{N}_2\text{O}_5) \frac{c_1 a_1}{b_1(\text{M}) + c_1}$$

Since the macroscopic rate of reaction is defined as

$R = k_{\text{obs}}(\text{N}_2\text{O}_5)$ where k_{obs} is the experimentally observed rate constant we may write

$$\frac{k_{\text{obs}}}{(\text{N}_2\text{O}_5)} = (\text{M})(\text{N}_2\text{O}_5) \frac{c_1 a_1}{b_1(\text{M}) + c_1}$$

$$k_{\text{obs}} = \frac{c_1 a_1 (\text{M})}{b_1(\text{M}) + c_1}$$

$$\frac{1}{k_{\text{obs}}} = \frac{b_1}{c_1 a_1} + \frac{1}{a_1 (\text{M})}$$

There are two important effects that one should notice in the above equation. First, that the observed rate constant is a function of the total pressure of the gases present in the reaction vessel, and secondly, that any molecule M should be effective in activating a reactant molecule A. For a true unimolecular process, both of these conditions have to be satisfied.

In the preceding tables the total pressure is listed with each corresponding rate constant. In these systems only reactant gases were present. Plots of $\frac{1}{k_{\text{obs}}}$ vs. $\left(\frac{1000}{P_T^0}\right)$ are shown in the following graphs. The straight lines shown were obtained by the method of least squares. Evaluation of the slope and the y intercept gave values of $\frac{b_1}{c_1 a_1}$ and $\frac{1}{a_1}$. These are listed below in Table XIV.

TABLE XIV

Temp.	$\frac{b_1}{c_1 a_1}$	$\frac{1}{a_1}$
27°C	30.7	2360.7
35°C	15.5	1062.5

The runs which contained inert gases are listed in Table XV. In each case nitrosyl chloride was mixed with the inert gas so that the final pressure was one atmosphere. In all of the mixtures the ratio of P_{NOCl}^0 to $P_{\text{N}_2\text{O}_5}^0$ was approximately equal to three.

Fig. IX

Dependence of the Observed Rate Constant
on Total Pressure

$$\frac{1}{k} = 2.36 \left(\frac{1000}{P_T^0} \right) + 30.7 \quad \text{at } 27^\circ\text{C}$$

$$\frac{1}{k} = 15.5 \left(\frac{1000}{P_T^0} \right) + 1.06 \quad \text{at } 35^\circ\text{C}$$

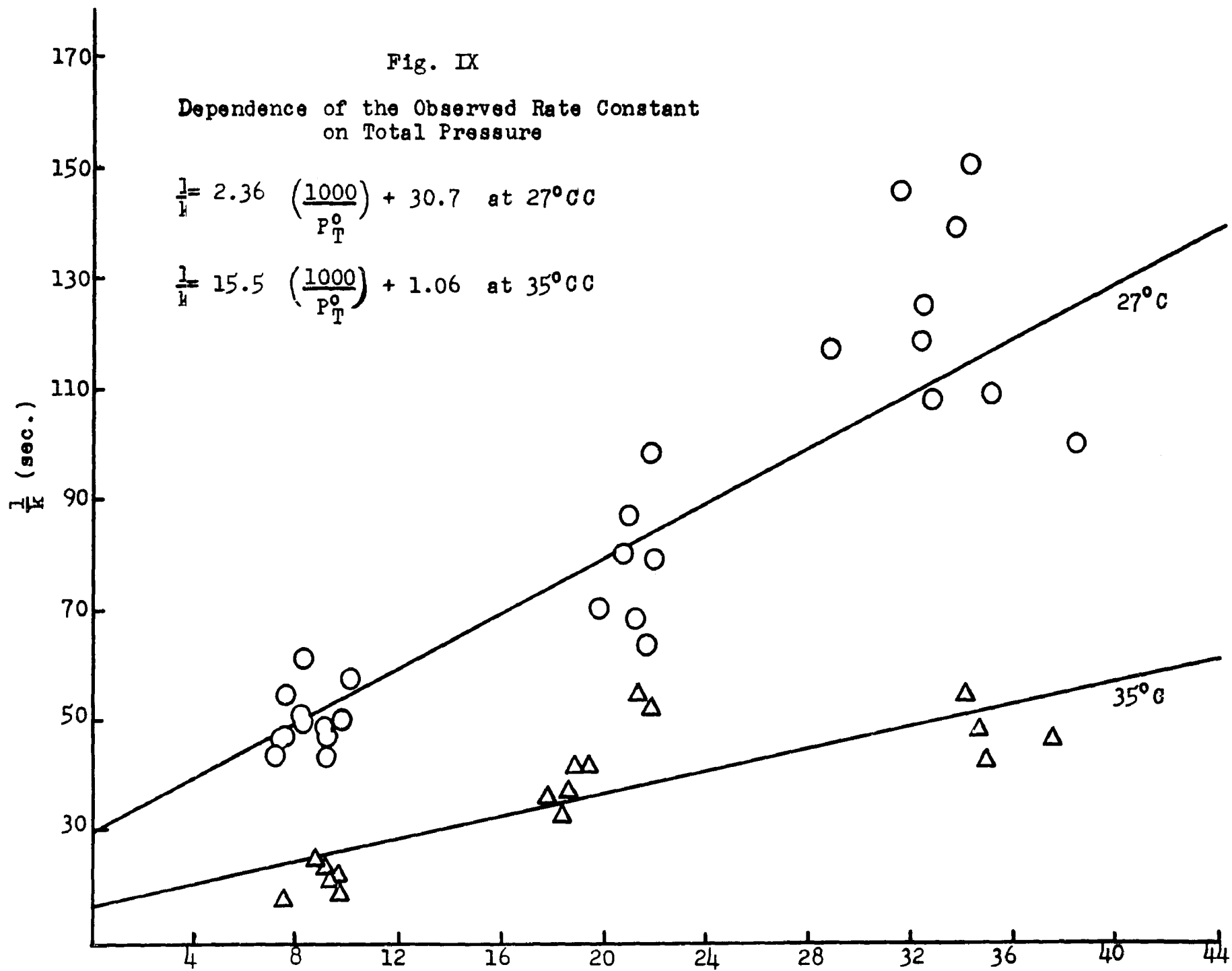


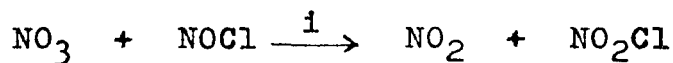
TABLE XV

<u>Gas</u>	<u>Run No.</u>	<u>P_{N₂O₅}^o (cm)</u>	<u>P_T^o (cm)</u>	<u>k_{obs.} x 10⁻⁴</u>
CO ₂	55	1.02	10.81	14.03
	56	0.98	10.86	6.45
	57	0.98	17.62	17.66
	58	0.90	16.17	15.75
	59	1.01	10.65	9.95
	60	0.92	10.70	16.58
Ar	69	1.20	11.16	5.68
	70	1.20	11.25	6.86
N ₂	71	0.95	10.93	6.63
	72	1.07	11.27	3.80
	73	0.84	11.21	3.04
	74	1.10	11.46	6.22
	75	0.86	11.24	4.88

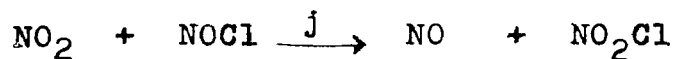
DISCUSSION

The reaction between nitrosyl chloride and nitrogen pentoxide in a Teflon vessel appears to be a homogenous first-order reaction in the temperature and pressure region in which it was studied.

The previous assumption that the reaction proceeds via a modified $\text{NO-N}_2\text{O}_5$ mechanism appears to be justified. Since the order of the reaction is essentially first-order with respect to nitrogen pentoxide and zero-order with respect to nitrosyl chloride, only nitrogen pentoxide or its decomposition products may be involved in the rate determining step. Therefore any reaction involving nitrosyl chloride cannot be the rate determining step; namely



and



There is other experimental evidence to justify this conclusion, for reactions i and j have appeared in other kinetic studies. The magnitude of i has been determined previously by Leighton and Johnston⁴³ in the nitrogen pentoxide catalyzed reaction between ozone and nitrosyl chloride. They assigned a value of $0.7 \times 10^8 \text{ cc mole}^{-1} \text{ sec}^{-1}$ to i at 40°C . Schott and Davidson¹⁶ have recently revised the value of i to $2.3 \times 10^7 \text{ cc mole}^{-1} \text{ sec}^{-1}$ at 40°C . In either case the reaction is too rapid to be the rate determining step in

our kinetic scheme.

An idea of the rate of reaction j may be obtained from the work of Freiling, Johnston and Ogg⁴⁴ who studied the rapid bimolecular reaction $\text{NO}_2\text{Cl} + \text{NO} \xrightarrow{1} \text{NOCl} + \text{NO}_2$ from 1 to 71°C. In order to determine the extent of reaction, mixtures of nitrogen dioxide and nitrosyl chloride were made up and observed for a period of 48 minutes. No reaction was observed and the authors concluded that reaction j was about 99% complete.

The idea that nitrosyl chloride reacts with nitrogen pentoxide in a manner kinetically similar to nitric oxide is consistent with above experimental facts. Therefore, the elementary rate constants should be compared to the data obtained by Johnston in the $\text{NO}-\text{N}_2\text{O}_5$ system.

From the slopes of the plots of $\frac{1}{k}$ sec. vs. $\frac{1000}{P_T^0}$ mm⁻¹ the elementary rate constant a_1 for the rate of activation of nitrogen pentoxide may be determined. From the y intercept of the same plots the ratio $\frac{b_1}{a_1 c_1}$ may be determined. In order to evaluate c_1 an assumption must be made on the magnitude of b_1 . H. S. Johnston has assigned a value of 1×10^{14} cc mole⁻¹ sec⁻¹ to this constant. This is the kinetic theory collision constant for simple gas molecules. This assumption is consistent with the collisional theories of unimolecular gas reactions⁴⁵ which state that essentially every collision of an excited molecule results in energy redistribution and the loss of the excited molecule. The results at 27° are compared to the values obtained by Johnston

in Table XVI.

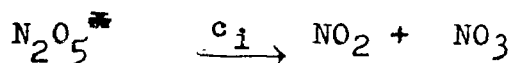
An attempt was made to study the reaction at three temperatures but the results at 20°C were very scattered, so that plot of $\frac{1}{k}$ vs. $\frac{1000}{P_T^0}$ could not be made. Therefore, the activation energies had to be evaluated from the data at 27°C and 35°C. The high pressure rate constant (k_{∞}) and the rate constant for the activation of nitrogen pentoxide molecules, expressed in the form of the Arrhenius equations, are

$$k_{\infty} = 10^{10} e^{-15,800/RT} \text{ sec}^{-1}$$

$$a_1 = 6.99 \times 10^{14} e^{-18,100/RT} \text{ l mole}^{-1} \text{ sec}^{-1}$$

The value of a_1 obtained by Johnston is approximately three times the value of a_1 obtained in our work. Therefore assuming a similar value of b_1 our value of c_1 should be less than the value of c_1 reported by Johnston by a factor of three.

An alternative way of proceeding on this problem is to assume that our value of c_1 is equal to the value of c_1 calculated by Johnston. This is equivalent to saying that an excited nitrogen pentoxide will undergo the following reaction



at the same rate in the nitrosyl chloride system as in the nitric oxide system if both systems are at the same temperature. This would then make the value of $b_1 = 2.81 \times 10^{14} \text{ cc mole}^{-1} \text{ sec}^{-1}$. The value for the collision diameter used by

TABLE XVI

<u>Constant</u>	<u>This Work</u>	<u>Johnston's Value</u>
a_i	$45.6 \times 10^8 \text{ cc mole}^{-1} \text{ sec}^{-1}$	$127 \times 10^8 \text{ cc mole}^{-1} \text{ sec}^{-1}$
b_i	$1 \times 10^{14} \text{ cc mole}^{-1} \text{ sec}^{-1}$	$1 \times 10^{14} \text{ cc mole}^{-1} \text{ sec}^{-1}$
c_i	$7.14 \times 10^7 \text{ sec}^{-1}$	$2 \times 10^8 \text{ sec}^{-1}$
$\frac{a_i c_i}{b_i} = k_{\infty}$	0.0325 sec^{-1}	0.29 sec^{-1}

Johnston in the calculation of b_1 $3 \pm 5 \text{ \AA}$. This value of b_1 does not seem to be unreasonable since there is great uncertainty in any value which is used as the collision diameter.

In some of the runs an inert gas was added to the $\text{NOCl-N}_2\text{O}_5$ mixtures in order to gain some insight as to the efficiency that the various molecules have in maintaining the observed rate constant. The gases used were carbon dioxide, nitrogen and argon. Column two contains the observed rate constant ($k_{\text{obs.}}$), column three contains the total pressure, column four, the sum of the partial pressures of nitrogen pentoxide and nitrosyl chloride, while the fifth column contains the rate constant if only nitrogen pentoxide and nitrosyl chloride ($k_{\text{calc.}}$) were present at the total pressure given in column three (Table XVII).

Of the three gases which were used carbon dioxide was the most efficient while nitrogen and argon gave results which were inconsistent with the usual results obtained from inert gas studies. It is a general rule that usually the more vibrational modes a molecule has the more efficient it is in its ability to transfer vibrational energy. On this basis it would be expected that carbon dioxide would have a greater efficiency than nitrogen, while nitrogen in turn would have a greater efficiency than argon.

According to the table referred to above, carbon dioxide did show this ability to maintain the observed rate constant. The results with argon and nitrogen are difficult to explain because the rate constants for the mixtures are

TABLE XVII

<u>Run No.</u>	<u>$k_{\text{obs.}}$ $\times 10^6$ sec^{-1}</u>	<u>P_T° (cm)</u>	<u>$P_{\text{N}_2\text{O}_5}^{\circ}$ and P_{NOCl}° (cm)</u>	<u>$k_{\text{calc.}}$ $\times 10^6$ sec^{-1}</u>
CO₂				
55	14.03	10.81	3.67	10.5
56	6.45	10.86	3.66	10.5
57	17.66	17.62	6.20	14.5
58	15.75	16.17	5.70	13.8
59	9.95	10.65	4.04	11.2
60	16.58	10.70	3.99	11.1
Ar				
69	5.68	11.16	4.27	11.1
70	6.86	11.25	4.22	11.6
N₂				
71	6.63	10.93	4.38	11.8
72	3.80	11.27	4.58	12.1
73	3.04	11.21	4.85	12.6
74	6.22	11.46	5.11	13.0
75	4.88	11.24	4.88	12.6

lower than the rate constants where only the pure components are present. About the only explanation that can be offered in this case is that some impurity in the argon and the nitrogen is inhibiting the rate of reaction. The inert gases were not purified in any manner before they were used to make up the mixtures.

The rate constant for the activation of nitrogen pentoxide molecules has been determined in other systems. Linhorst and Hodges²³ have reported that a_1 has a value of 320 liter mole⁻¹sec⁻¹ from the decomposition of pure nitrogen

pentoxide at low pressures. Mills and Johnston²⁴ have assigned a value of 230 liter mole⁻¹sec⁻¹ to a_1 in the low pressure decomposition of nitrogen pentoxide in the presence of nitric oxide. Perrine and Johnston²⁵ restudied this reaction in a 22-liter reaction vessel and determined a_1 to have a value of 127 liter mole⁻¹sec⁻¹. The difference between the value reported by Linhorst and Hodges and Perrine and Johnston is due to the different efficiencies that a gas has in transferring energy. The reacting molecule has an efficiency of 1.00, while nitric oxide has a relative efficiency of 0.30.^{27,28} Therefore the low pressure rate constant in the decomposition of pure nitrogen pentoxide would be expected to have a greater value.

The value of a_1 in this work has been determined to be 45.6 liter mole⁻¹sec⁻¹. From this it would appear that the nitrosyl chloride molecule is not as efficient as the nitric oxide molecule in activating a nitrogen pentoxide molecule. This is surprising because nitrosyl chloride is a non-linear molecule and it would contain $(3n - 6)$ or three vibrational modes, while nitric oxide, since it is diatomic, would only contain one mode of vibration. But nitric oxide contains some interesting properties because of its unpaired electron. This unpaired electron gives rise to two electronic states and introduces a factor of two in the Boltzman distributions. This degeneracy would increase the population of the vibrational energy states; therefore the transfer of vibrational energy would become more probable.

The results obtained from this work seem to be in general agreement with the work that has been done on the nitrogen pentoxide decomposition mechanism. More detailed kinetic studies should be made, especially in the pressure regions where it was impossible to carry out studies with our fast pressure measuring apparatus. It should be possible to develop an absorptiometric technique similar to the one used by Mills and Johnston in the nitric oxide-nitrogen pentoxide system. Three regions of interest could then be studied:

- 1) high pressure region consisting of reaction mixtures with total pressures greater than one atmosphere;
- 2) the low pressure region where a_1 could be determined directly;
- 3) a more detailed study in the low pressure region in the presence of inert foreign gases.

With these studies a better comparison could be made with the nitric oxide-nitrogen pentoxide system.

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APPENDIX

Below is a list of the kinetic runs which make up the bulk of the experimental support for this thesis. The list does not contain all of the runs which the author carried out.

Runs were omitted for various reasons. In many cases runs had to be made to check on experimental procedure, to check the purity of one of the reagents, to season a reaction vessel, or simply to gain experience in using a vacuum system. In some cases experimental difficulties, such as adding too much reducing agent, discovering an air leak, and the numerous other harassments which accompany any gas kinetic problem, were present. These, along with the reactions between nitrosyl chloride and nitrogen pentoxide which were carried out in glass vessels, were omitted from the list.

The list will also serve as a bridge between the two numbering systems used by the author, the one used in this thesis (column 3) and the other used in his research notebooks (column 4). For example, Run 3/5/63-I refers to Run I made on March 5, 1963.

Runs from #16 on were carried out in a Teflon reaction vessel. Previous runs were carried out in glass or wax-coated vessels.

LIST OF RUNS

<u>Components</u>	<u>Temp. degrees C</u>	<u>Run No.</u>	<u>Book No.</u>
SO ₂ -N ₂ O ₅	35° C	1	3/5/63-I
	"	2	3/5/63-II
	"	3	3/6/63-III
	"	4	3/7/63-V
HCl-N ₂ O ₅	0	5	2/28/63-I
	0	6	3/1/63-II
	35° C	7	3/1/63-III
	"	8	3/4/63-IV
	"	9	3/9/63-I
HBr-N ₂ O ₅	"	10	3/8/63-I
	"	11	3/9/63-II
	"	12	3/10/63-III
	"	13	3/10/63-IV
NH ₃ -N ₂ O ₅	"	14	3/11/63-I
	"	15	3/11/63-II
NO-N ₂ O ₅	27° C	16	4/12/63-II
	"	17	4/12/63-III
	"	18	4/28/63-I
	"	19	4/28/63-II
	"	20	4/28/63-III
NOCl-N ₂ O ₅	"	21	4/28/63-I
	"	22	4/28/63-II
	"	23	4/28/63-III
	"	24	5/4/63-I
	"	25	5/4/63-II
	"	26	5/6/63-I
	"	27	5/6/63-II
	"	28	5/8/63-I
	"	29	5/8/63-II
	"	30	5/8/63-III
	"	31	5/10/63-III
	"	32	5/13/63-I
	"	33	5/21/63-I

<u>Components</u>	<u>Temp. degrees C</u>	<u>Run No.</u>	<u>Book No.</u>
NOCl-N ₂ O ₅	27° C	34	5/21/63-II
	"	35	5/25/63-III
	"	36	5/25/63-IV
	"	37	5/25/63-V
	"	38	6/24/63-III
NO-N ₂ O ₅	"	39	6/24/63-IV
	"	40	6/24/63-V
	"	41	6/24/63-VI
	"	42	6/24/63-VIII
	"	43	6/24/63-IX
	"	44	6/24/63-X
NOCl-N ₂ O ₅	"	45	6/28/63-I
	"	45 ^a	6/28/63-II
	"	46	6/29/63-III
	"	47	6/29/63-IV
	"	48	6/29/63-V
	"	49	6/29/63-VI
	"	50	6/29/63-VII
	"	51	6/29/63-VIII
	"	52	6/29/63-IX
	"	53	6/29/63-X
	"	54	6/29/63-XI
NOCl-N ₂ O ₅ -CO ₂	"	55	7/8/63-I
	"	56	7/8/63-II
	"	57	7/9/63-I
	"	58	7/9/63-II
	"	59	7/9/63-IV
	"	60	7/12/63-III
NOCl-N ₂ O ₅	"	61	7/15/63-II
	"	62	7/15/63-III
	"	63	7/15/63-IV
	"	64	7/15/63-V
	"	65	7/17/63-VI
	"	66	7/17/63-VII
	"	67	7/17/63-VIII
NOCl-N ₂ O ₅ -Ar	"	68	7/17/63-IX
	"	69	7/18/63-I
	"	70	7/19/63-II

<u>Componernts</u>	<u>Temp. degrees C</u>	<u>Run No.</u>	<u>Book No.</u>
NOCl-N ₂ O ₅ -N ₂	27° C	71	7/19/63-V
	"	72	7/19/63-VI
	"	73	8/1/63-V
	"	74	8/1/63-VI
	"	75	8/1/63-VII
NOCl-N ₂ O ₅	35° C	76	8/10/63-I
	"	77	8/10/63-II
	"	78	8/10/63-III
	"	79	8/11/63-IV
	"	80	8/11/63-V
	"	81	8/11/63-VI
	"	82	8/11/63-VII
	"	83	8/11/63-VIII
	"	84	8/11/63-IX
	"	85	8/11/63-X
	"	86	8/11/63-XII
	"	87	8/11/63-XIIIa
	"	88	8/11/63-XIV
	"	89	8/11/63-XV
	"	90	8/11/63-XVI
	"	91	8/11/63-XVIIa
	"	92	8/11/63-XVIII
	NOCl-N ₂ O ₅	20.05° C	93
"		94	8/13/63-I
"		95	8/13/63-II
"		96	8/16/63-III
"		97	8/16/63-IV
"		98	8/16/63-V
"		99	8/16/63-VI
"		100	8/16/63-VII
"		101	8/16/63-VIII
"		102	8/17/63-IXa
"		103	8/18/63-X
"		104	8/17/63-XIa
"		105	8/17/63-XII

<u>Components</u>	<u>Temp.</u> <u>degrees C</u>	<u>Run</u> <u>No.</u>	<u>Book</u> <u>No.</u>
NOCl-N ₂ O ₅	27° C	106	9/10/63-I
	"	107	9/10/63-III
	"	108	9/10/63-IV
	"	109	9/10/63-V
	"	110	9/10/63-VI
	"	111	9/10/63-VII
	"	112	9/10/63-VIII
	"	113	9/10/63-IX
	"	114	9/10/63-X
	"	115	9/10/63-XI
NOCl-NO ₂ -N ₂ O ₅	"	116	9/6/63-I
	"	117	9/7/63-II
	"	118	9/7/63-III
	"	119	9/7/63-IVa

<u>Components</u>	<u>Temp. degrees C</u>	<u>Run No.</u>	<u>Book No.</u>
$\text{NOCl-N}_2\text{O}_5$	27° C	106	9/10/63-I
	"	107	9/10/63-III
	"	108	9/10/63-IV
	"	109	9/10/63-V
	"	110	9/10/63-VI
	"	111	9/10/63-VII
	"	112	9/10/63-VIII
	"	113	9/10/63-IX
	"	114	9/10/63-X
	"	115	9/10/63-XI
$\text{NOCl-NO}_2\text{-N}_2\text{O}_5$	"	116	9/6/63-I
	"	117	9/7/63-II
	"	118	9/7/63-III
	"	119	9/7/63-IVa