

Winter 1961

A KINETIC STUDY OF THE GAS PHASE
REACTIONS BETWEEN NITROGEN-
PENTOXIDE AND SOME REDUCING
AGENTS

ROBERT WILLIAM RICCI

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RICCI, Robert William, 1934-
A KINETIC STUDY OF THE GAS PHASE
REACTIONS BETWEEN NITROGEN PENTOXIDE
AND SOME REDUCING AGENTS.

University of New Hampshire, Ph.D., 1961
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

A KINETIC STUDY OF THE GAS PHASE REACTIONS
BETWEEN NITROGEN PENTOXIDE AND SOME REDUCING AGENTS

BY

ROBERT W. RICCI

B. S., Boston College, 1956

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
December 1960

This thesis has been examined and approved.

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December 12, 1960
Date

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to the director of this research project, Dr. A. R. Amell, for his guidance and time given freely. The author would also like to thank Dr. A. F. Daggett for the use of his specially constructed apparatus used in the course of this thesis.

The author is also indebted to the National Science Foundation for the financial assistance in carrying out this work.

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INTRODUCTION

Nitrogen pentoxide thermally decomposes in the gas phase to give nitrogen tetroxide and oxygen according to the equation



The kinetics of this reaction were first studied by Daniels¹ who found the reaction to be first order in N_2O_5 . Subsequent work showed the rate of the reaction to be the same in the gas phase as in a variety of solvents, and the activation energies are about the same. Also the rate is not affected by the surface of the reaction vessel, is uncatalyzed, and is independent of the presence of a great many foreign substances.

As expected in a unimolecular reaction, the first-order rate constant begins to fall off at low pressures and E. F. Hodges and J. H. Linhorst² showed that below 0.004 mm the reaction appears to be second order.

If the reaction is a unimolecular one, the immediate products of the decomposition must react further since the stoichiometry of equation (1) refers to two molecules of the pentoxide. Ogg³ has pointed out that all the facts concerning the nitrogen pentoxide decomposition can be explained by the following mechanism:



Equilibrium steps 2+3 are fast with the equilibrium lying well to the left. The slow step becomes the second-order reaction of step (4). This is followed by the fast reaction (5).

The observed kinetics depend on the relative values of k_1 , k_2 and k_3 and upon the concentration. Applying the steady-state assumption to NO_3 gives

$$\frac{d(\text{NO}_3)}{dt} = k_1(\text{N}_2\text{O}_5) - k_2(\text{NO}_2)(\text{NO}_3) - 2k_3(\text{NO}_2)(\text{NO}_3) = 0$$

$$(\text{NO}_3) = \frac{k_1(\text{N}_2\text{O}_5)}{k_2(\text{NO}_2) + 2k_3(\text{NO}_2)}$$

The rate of decomposition of the pentoxide is

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = 2k_3(\text{NO}_2)(\text{NO}_3) = \frac{2k_3k_1(\text{N}_2\text{O}_5)}{k_2 + 2k_3}$$

$$\text{and } k_{\text{obs}} = \frac{2k_3k_1}{k_2 + 2k_3}$$

The reaction is not a unimolecular one at all on this basis, but involves a prior equilibrium followed by a bimolecular rate determining step. The mechanism also predicts the falling off of the rate constant observed at very low pressures. The dissociation of N_2O_5 into NO_2 and NO_3 is a unimolecular process governed by activation through collision. At very low pressures, the number of collisions can become so low that the equilibrium concentration of activated molecules is not maintained. In the limit the rate of dissociation becomes equal

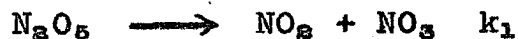
to the rate of activation by collision which is a second-order process.

Attention has been given to the determination of the rate constants of the individual steps of the decomposition and Harold Johnston has compiled a list of the individual rate constants⁴.

There are several approaches to a direct study of k_1 . If Ogg's hypothesis of a rapid equilibrium between N_2O_5 , NO_3 and NO_2 is correct, it should be possible to demonstrate isotopic exchange in a system such as



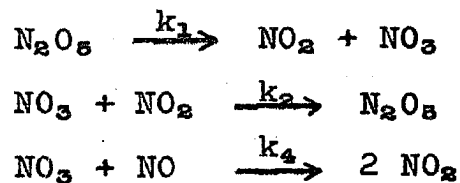
Furthermore, the rate constant of such an exchange should be equal to k_1 , and the reaction should be first-order in nitrogen pentoxide and zero-order in nitrogen dioxide. The rate determining step would be



This behavior has been demonstrated in the gas phase by A. R. Amell and F. Daniels⁵ and by R. A. Ogg in both gas and liquid phases. They found $k_1 = 6 \times 10^{12} e^{-19,000/RT}$ liters/moles sec.

The kinetics of the reaction between nitric oxide and nitrogen pentoxide offers another approach to k_1 . Smith and Daniels⁶ found that nitric oxide reacted with nitrogen pentoxide to form nitrogen dioxide. From the mechanism of the nitrogen pentoxide decomposition, the mechanism of this

reaction should be



with the dissociation the slowest step. The complete rate equation is
$$\frac{-d(\text{NO})}{dt} = \frac{k_1(\text{N}_2\text{O}_5)}{1 + k_2(\text{NO}_2)/k_4(\text{NO})}$$

The reaction has been observed to be first-order in nitrogen pentoxide and zero-order in nitric oxide. At the same total pressure the rate of the reaction with nitric oxide is the same as the rate of isotopic exchange.

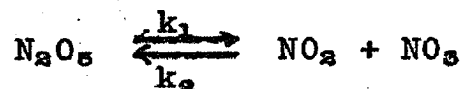
The reaction of nitrogen pentoxide with nitric oxide has been studied more carefully by Mills and Johnston⁷ at high pressure and at low pressure by Johnston and Perrine⁸. The results of Johnston and Perrine were confirmed in general. The dependence of the observed first-order constant on the pressure was used to find the limiting values at zero pressure and infinite pressure. The results give $k_1^0 = 1.3 \times 10^{16} e^{-19,300/RT}$ liter/mole sec. which corresponds to a rate constant of 1.27×10^3 at 27°C., and $k_1^\infty = 0.29 \text{ sec}^{-1}$ at 27°C. with an activation energy of 21 ± 2 kcal.

Nitric oxide should not be unique in increasing the overall rate of decomposition of nitrogen pentoxide and any good gaseous reducing agent should also increase the rate of decomposition. A. R. Amell⁵ has shown in a qualitative manner that this is indeed true. Nitrogen pentoxide was made to react with hydrogen chloride, hydrogen sulfide, sulfur dioxide,

hydrogen bromide, ammonia, formaldehyde, hydrogen iodide and methanol. All the gases except sulfur dioxide and ammonia appeared to increase the rate of decomposition.

STATEMENT OF THE PROBLEM

If the mechanism for the decomposition of nitrogen pentoxide involves the equilibrium



then nitric oxide should not be unique in its ability to react with the strong oxidizing agent, nitrogen trioxide, and thus prevent step 2 from taking place. Any good reducing agent, at least from a thermodynamical point of view, should be capable of reacting with nitrogen trioxide. In order to test this hypothesis we studied the reaction between nitrogen pentoxide and the reducing agent, nitrosyl chloride, in the gas phase.

The problem was one of studying the kinetics of the reaction, and investigating some of those factors which affected the kinetics; i.e., temperature and surface effects. A possible mechanism is proposed and suggestions for further work outlined.

Preliminary studies on the reaction of nitrogen pentoxide with sulfur dioxide and with hydrogen chloride were also carried out.

APPARATUS

Section A - The Optical Bench

The arrangement of the optical bench is shown in Fig. 1. The pieces shown are mounted on an aluminum rod connected rigidly to an aluminum rack which served to mount the rest of the equipment. The light source, lenses and diaphragms are mounted so that three dimensional adjustment is possible.

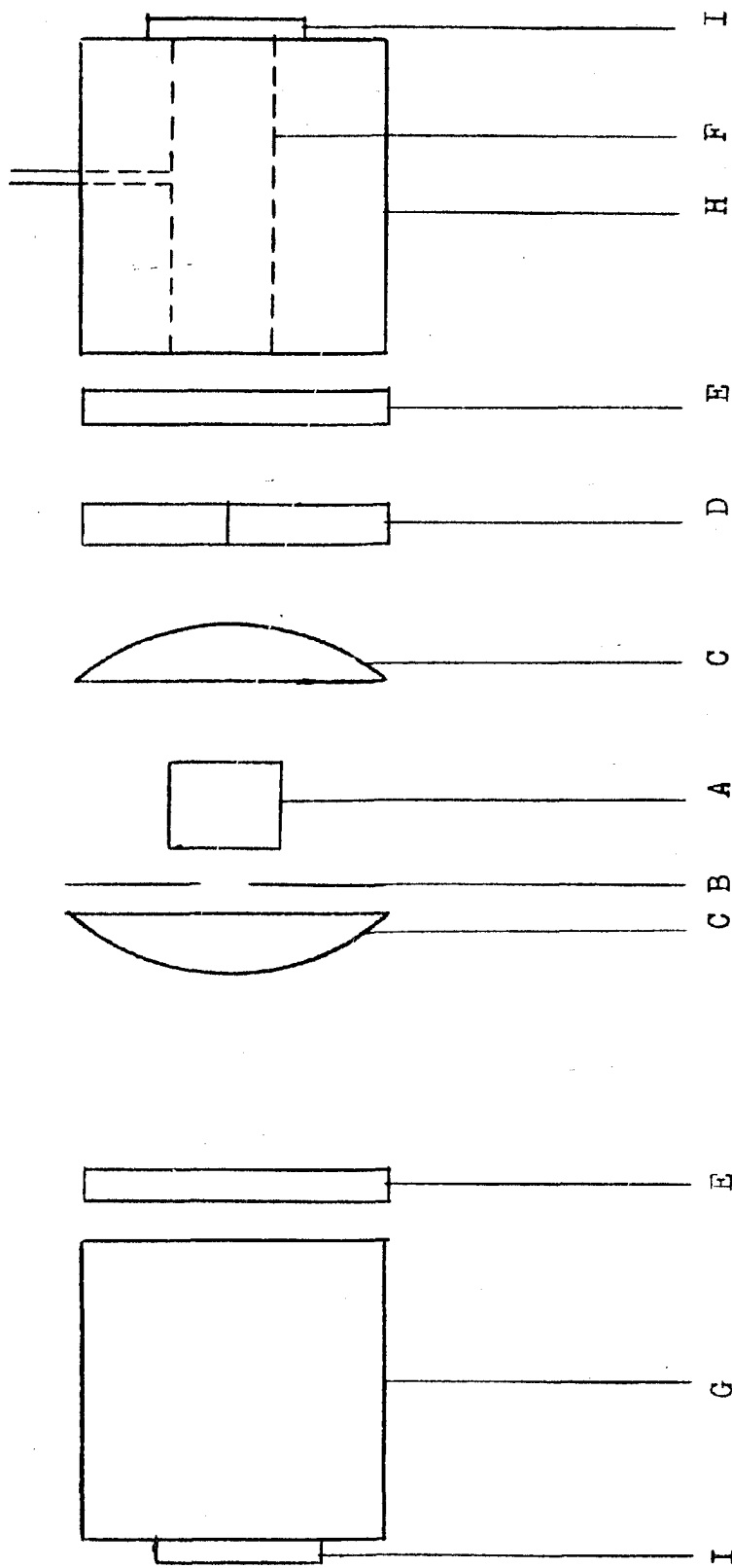
The light source, A, is a 6-8 volt G. E. No. 1000 auto lamp and is connected with both filaments in parallel. The lamp is operated at 6.3 volts supplied by a transformer connected to a stabiline voltage regulator, type IE 5101. The voltage regulator will operate on line voltage from 95 to 135 volts and will maintain a constant 115 volt output to within 0.1 per cent and 0.15 of one per cent for any current change. The leads from the source are soldered to the lamp and a large knife switch is used to make the connection in order to avoid contact differences which would effect the intensity of the lamp. The lamp is housed in a copper cylinder 4 cm. in diameter and 6 cm. in length. The cylinder is closed except for two one-cm. holes on opposite sides of the lamp to supply light to the reaction system and to the optical compensating system. Four copper fins are soldered to the cylinder in order to permit cooling of the lamp and housing to prevent the soldering leads from melting.

The iris diaphragm, B, is used to adjust the amount

FIG. 1

The Optical Bench

- A - Light Source
- B - Iris Diaphragm
- C, C' - Plano-Convex Lenses
- D - Calibration Filter Holder
- E, E' - Filters
- F - Reaction Vessel
- G - Compensating Chamber
- H - Thermostat
- I, I' - Photovoltaic Cells



THE OPTICAL BENCH

FIG. 1

of light going to the compensating system.

The glass plano-convex lenses, C and C', are used to produce parallel light which is collimated to pass through the cylindrical reaction cell. Next to the lens, on the reaction side of the optical system, is placed the holder for the calibration filter used to calibrate the system before each run.

Two copper chloride-calcium chloride filters, E and E, are placed in the optical path to remove light less than 4000 \AA and greater than 4600 \AA which is effective in accelerating the decomposition of nitrogen dioxide.

The reaction cell, F, is constructed of Pyrex with two optically flat Pyrex glass windows attached by Dekhotinsky cement. The inside diameter and length are 2.6 cm. and 14.8 cm. respectively. The reaction cell is connected to the two reactant reservoirs by 2 mm. capillary tubing to minimize the volume of the tubing leading to the reaction vessel. The two reactant reservoirs (not shown in Fig. 1), which are sealed off from the reaction vessel and vacuum system by two-way stopcocks, have a volume of 3.70 ml. (vessel 1) and 3.53 ml. (vessel 2).

The thermostat, H, may be maintained within $\pm .1^\circ\text{C}$. The water in the thermostat is circulated around the reaction vessel by an electrical stirrer; cooled by tap water circulating through a glass coil, and heated by a 20 watt heater which is operated by a relay connected to a mercury Thermo-Regulator (H and B Instrument Co., Phila., Pa., Cat. No. 7540).

The thermostat is a square wooden box with two cylindrical holes bored into two opposite sides into which the reaction cell fits. The reaction cell is held secure by rubber gaskets which also serve to keep the thermostat water tight.

I and I' are General Electric Model No. 8PV1 Photovoltaic cells. They are the barrier-type selenium self-generating photovoltaic cells which are often used in commercial colorimeters.

Section B - The Photometer Circuit

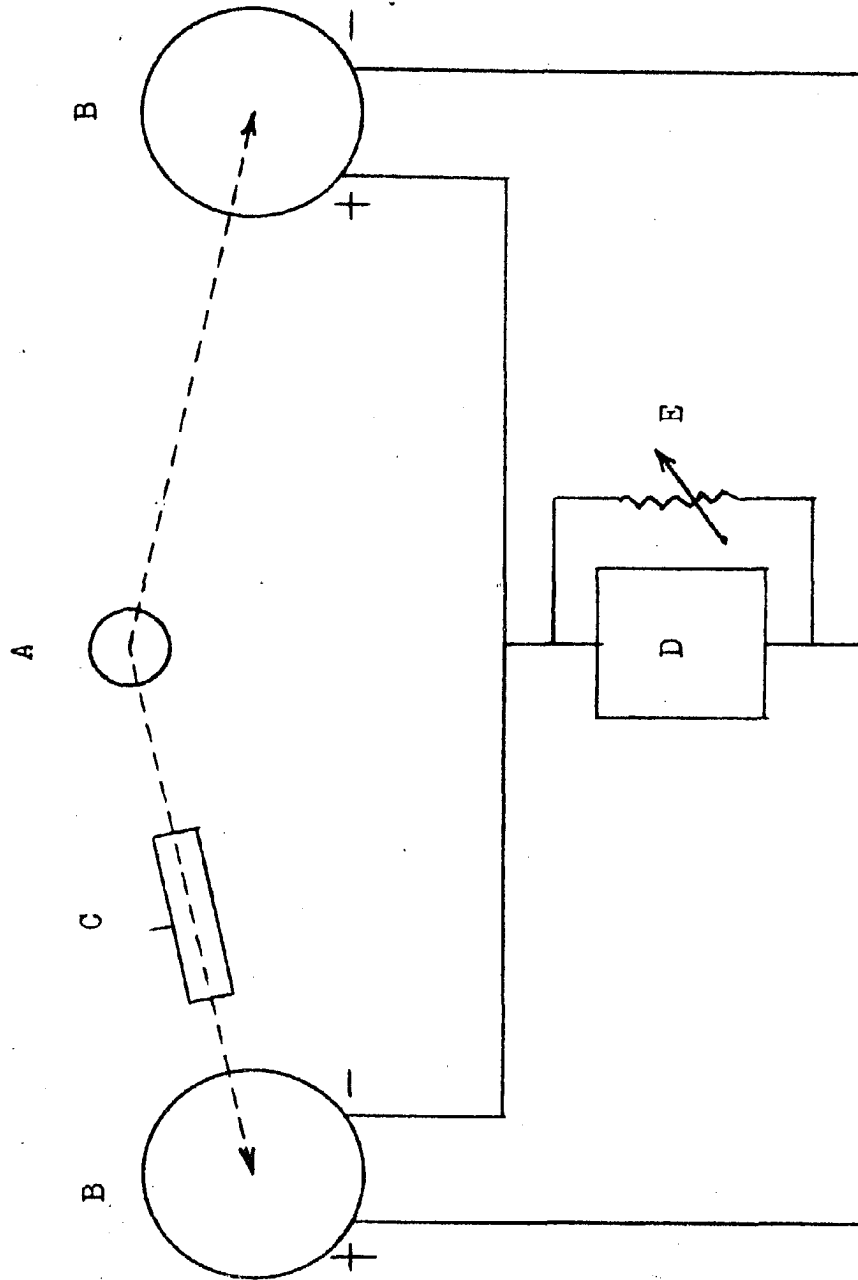
The photometer circuit described below is used to determine the pressure of nitrogen dioxide in the reaction cell at any time during the reaction by measuring the intensity of the light not absorbed by the nitrogen dioxide. By use of the circuit the rate of increase of nitrogen dioxide pressure may be followed and the rate of the reaction determined.

The circuit is shown in Fig. 2. It is constructed so that the barrier cells are in opposition; thus the signal received by the recorder is the net output of the two cells. This serves to compensate for any fluctuation in the light source and also increase the range R obtainable on the recording device. The recorder is a General Electric Direct Reading Multi-Range Recorder with a full scale deflection sensitivity of between .1 mv. and 50 mv. The chart speed can be geared at .1 inch'sec. or .1 inch'min. A variable resistance box of between 1 and 1000 ohms is placed in parallel with the recorder

FIG. 2

The Photometer Circuit

- A - Light Source
- B, B' - Photovoltaic Cells
- C - Reaction Vessel
- D - Direct Reading Recorder
- E - Variable Resistance Box



THE PHOTOMETER CIRCUIT

FIG. 2

so as to be able to adjust the sensitivity of the signal going into the recorder at any desired level. With this set-up the recorder reads the absorption directly. The sensitivity of this circuit was such that with a light path of 14 cm. one could get a full scale deflection of four inches with .1 mm. of nitrogen dioxide with a precision of better than .01 mm. of nitrogen dioxide.

Section C - The Vacuum Train

The Vacuum Train shown in Fig. 3 consists of two main parts, the pumping system and the reaction system.

The pumping system is made up of a Columbia-type mercury diffusion pump backed up by a Cenco Megavac Pump. Both of the pumps are protected by traps cooled with dry ice and trichloroethylene (-78°C).

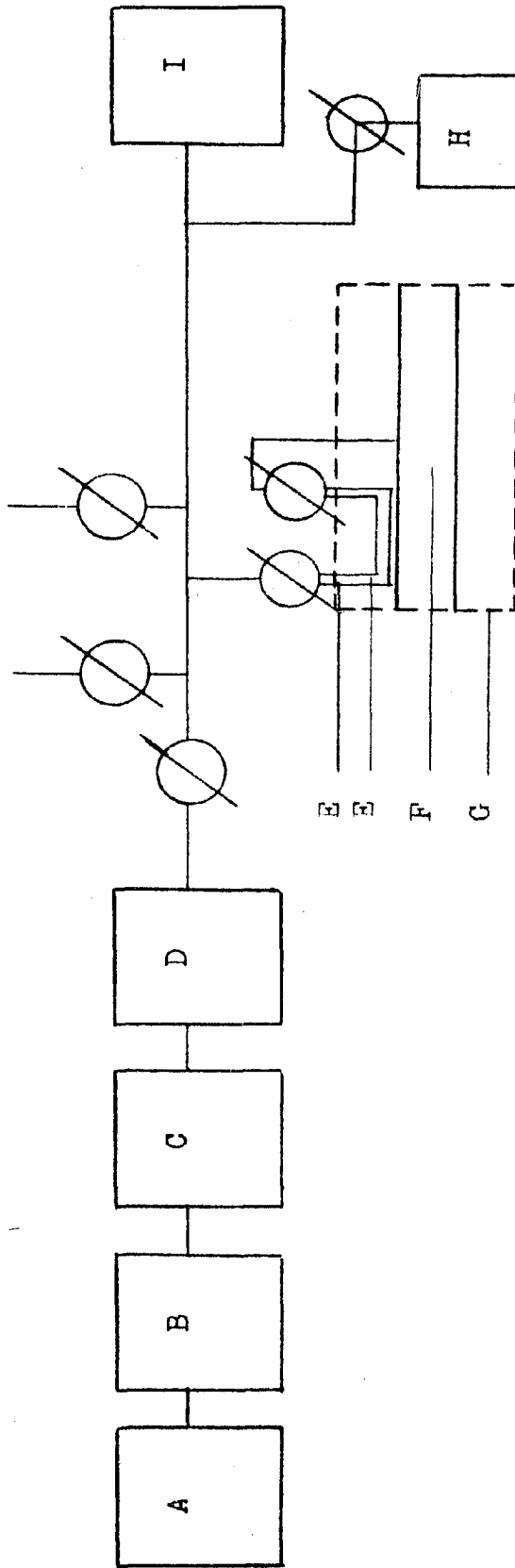
The reaction system consists of the reaction cell and reactant reservoirs (see part B). In addition the system has two outlets which can accommodate the cold traps which hold the reactants. These traps are detachable and are constructed air tight so that they may be pumped down with the rest of the system.

The vacuum train also includes two pressure measuring devices; a Pirani Vacuum Gauge and a U-tube manometer. The Pirani Vacuum Gauge is the Consolidated Electrodynamics Type GP-110. This gauge will measure pressures from 1 micron to 2000 microns. It can be isolated from the rest of the system by a vacuum stopcock. The manometer is a home made device with

FIG. 3

Vacuum Train

- A - Cenco Megavac Pump
- B, D - Dry Ice Cold Traps
- C - Mercury Diffusion Pump
- E, E' - Reactant Reservoirs
- F - Reaction Vessel
- G - Constant Temperature Bath
- H - Pirani Vacuum Gauge
- I - U-Tube Manometer
- ∅ - Vacuum Stopcocks



VACUUM TRAIN

FIG. 3

arms 37 cm. in length and 6 mm. in diameter and are attached to each other through a vacuum stopcock. On one of the arms is 25 cc. bulb which is used to minimize gas contraction errors when the device is used as a differential U-tube manometer. The U-tube was filled half full with Kel-F Fluorocarbon Oil (Product of Kellogg Co.) which is very inert and has a density of 1.916 gr./ml. at 23°C. The oil is ideally suited for measuring pressures of small amounts of corrosive gases. Since 7.07 mm. of the oil = 1 mm. Hg, the manometer was accurate in measuring pressures in the range of .2 mm. to 3 cm. of Hg.

Section D - Procedure for a Typical Run

The procedure used for obtaining the data presented in this thesis is as follows. The freshly prepared reactants nitrogen pentoxide and nitrosyl chloride contained in cold traps frozen with dry ice and trichloroethylene are attached to the vacuum system by ball and socket joints lubricated with fluorocarbon chemically inert stopcock grease. The system is then pumped down with the mechanical pump and flamed. When the pressure has reached 10 microns the mercury diffusion pump is cut in and the pressure brought down to less than one micron. The pumping is continued for at least two hours.

The voltage regulator is turned on and the light source illuminates both photocells which in turn drive the recorder. The system is allowed to come to equilibrium (about 1 hour). Before each run the system must be "zeroed in" and standardized. To do this the recorder is first shunted and the pen set at or near the zero mark on the recorder paper with the mechanical zeroing screw found near the back of the inside of the recorder. In many instances no adjustment is necessary. Next, the recorder is unshunted and the leads of the photo cells are connected to the recorder (Fig. 2). The pen is brought back to the zero mark, if need be, by adjusting the iris diaphragm which permits an increase or decrease of the amount of light falling on the compensating photo cells. The system is now "zeroed in" and if the system is in equilibrium, very little drift of the recorder will be noticed.

A smoke colored filter, 2 cm. x 2 cm. x .22 cm., is used to standardize the system. When the system has reached equilibrium the filter is placed in the filter holder, which is in the path of the light that passes through the reaction vessel. The deflection on the recorder is noted and brought to a predetermined reading, if need be, by adjusting the variable resistor in parallel with the recorder. This predetermined reading was used as a standardization value on all the runs and during the calibration of the system for both nitrogen pentoxide and nitrosyl chloride. In this simple way, uniform sensitivity was assured throughout the project.

The reaction vessel is brought to the desired temperature by turning on the thermostat equipment, circulating tap water through the cooling tubes and turning on the stirrer.

The standardization of the system and the thermostating of the reaction vessel is done while the system is being pumped down.

The system is now ready for making a run. The stopcock leading to the trap containing the frozen nitrogen pentoxide is closed, and the stopcock leading to the nitrosyl chloride is opened and the system pumped down again for a few minutes. The stopcock leading to the pump is closed and the nitrosyl chloride is distilled into the system, allowed to come to equilibrium, and the pressure read on the oil manometer. The stopcocks leading to the reaction vessel and nitrosyl chloride are closed and the stopcock leading to the pump is opened, and the system is flamed and pumped down again.

The trap containing the nitrosyl chloride is removed from the system and in its place is put a liter flask closed off by two stopcocks which contains one atmosphere of extra dry nitrogen. The stopcock leading to the system is then opened and the atmosphere contained in the tubing leading to the nitrogen vessel is evacuated and the glass tubing flamed. When the system has pumped down to one micron, the hollow vacuum stopcock leading to the pumping system is turned 180 degrees, thus closing off the pumping system from the rest of the train and exposes the hollow stem of the stopcock to the vacuum train. The stopcock leading from the nitrogen vessel is opened, allowing the nitrogen to expand into the vacuum train. The stopcock leading from the vacuum system to the nitrogen flask is closed and the stopcock leading to the pumping system is turned another 180 degrees, and the vacuum train is pumped out and flamed again. In this way about one atmosphere of nitrogen is isolated in the hollow stem of the stopcock.

When the system has pumped down to below 1 micron, the stopcock leading to the nitrogen pentoxide trap is opened and a small amount of nitrogen pentoxide is allowed to distill into the system. The stopcock leading to the nitrogen pentoxide trap is closed and the stopcock holding the nitrogen is opened so that the nitrogen flows from the stopcock and mixes with the nitrogen pentoxide. After thirty seconds the stopcock leading from the system to the reactant reservoirs, which are in the thermostat, is closed; thus isolating about 4 cc of the nitrogen-nitrogen pentoxide mixture. When making a run at 0

degrees or 10 degrees, water vapor from the atmosphere would condense on the window of the reaction vessel. In order to eliminate this, dry gas from a tank was blown on the window to keep it dry. At this point, the system is "ready to move". The recorder paper speed is set on high (1 inch/min.) and the stopcock leading from the reactant reservoir, which contains the nitrogen pentoxide and nitrogen mixture, to the reaction vessel, is opened. The nitrogen pentoxide is forced into the reaction vessel by the high pressure of inert nitrogen giving almost instantaneous mixing. The recorder measures the amount of nitrogen dioxide with time.

PREPARATION OF REACTANTS

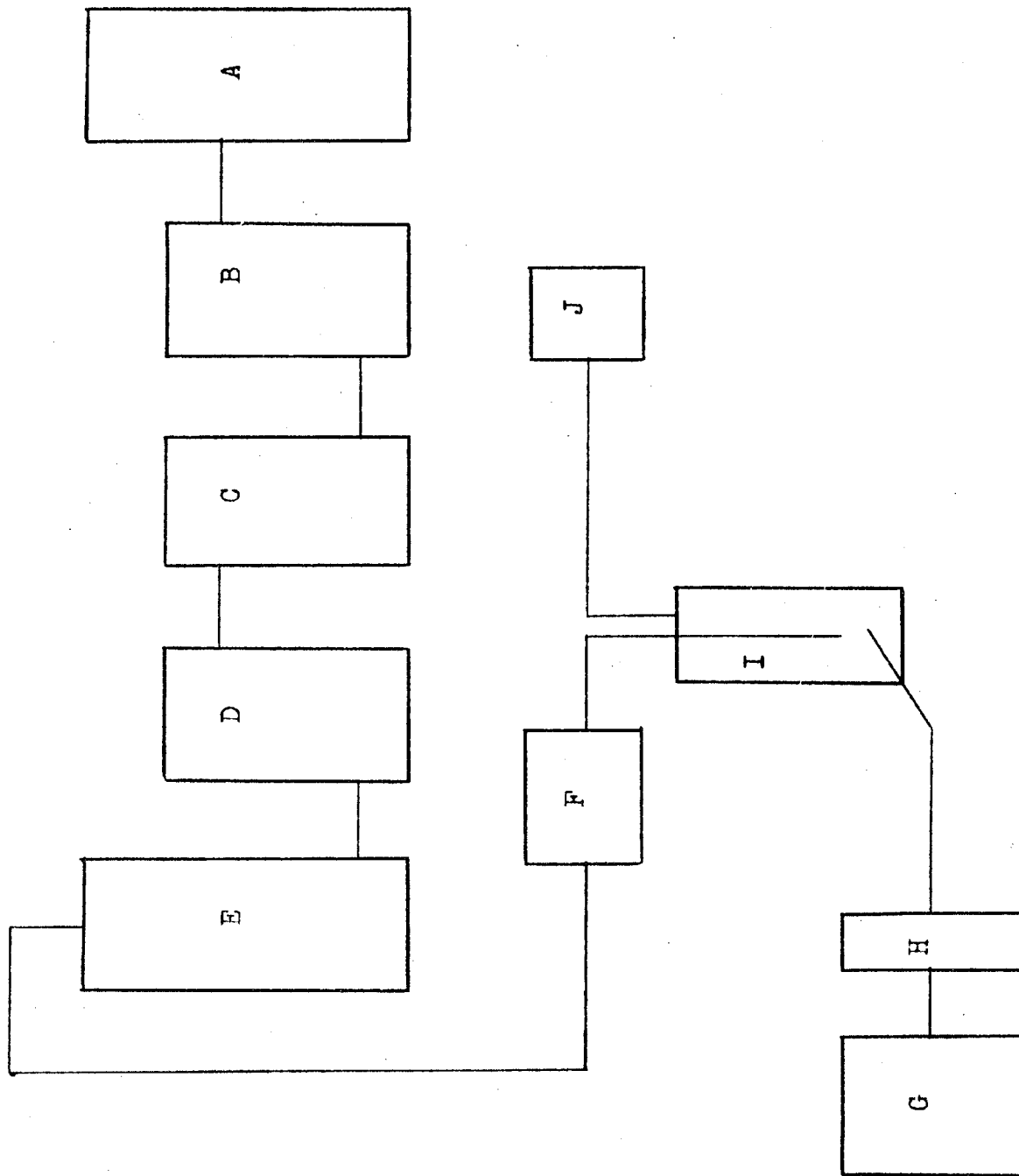
Nitrogen Pentoxide.— Nitrogen pentoxide was prepared by the reaction of ozone with nitrogen tetroxide in the apparatus shown in Fig. 4. Oxygen (Linde) was made to pass through two calcium chloride columns and a column filled with glass wool and phosphorous pentoxide before passing into an ozonizer. The oxygen-ozone mixture issuing from the ozonizer passed into a dry-ice-acetone trap and then fed into the reaction tube where it met the nitrogen tetroxide-nitrogen dioxide stream. The commercially prepared (Matheson) nitrogen dioxide was purified by passing through a phosphorous pentoxide column before reaction with the oxygen-ozone mixture. The flow rates were adjusted so that the stream was colorless after the junction. The ozone-oxygen-nitrogen pentoxide mixture flowed through about two feet of glass tubing, during which time the gas stream could be examined for color, before being collected in a dry ice-acetone trap (-78.0°C).

Nitrosyl Chloride.— The nitrosyl chloride was made using a modified version of the apparatus used to make the nitrogen pentoxide. Tank oxygen passed through the various drying tubes of the Ozone apparatus and into the reaction tube where it mixed freely with the nitrogen dioxide dried by passing over phosphorous pentoxide tube. This mixture which contained a large excess of oxygen converted any nitrogen trioxide present to nitrogen tetroxide. The nitrogen tetroxide and oxygen mixture was passed slowly up a 1 1/2 ft. column

FIG. 4

Ozonization Apparatus

- A - Oxygen Tank
- B,C - Calcium Chloride Drying Columns
- D, H - Phosphorous Pentoxide Drying Columns
- E - Silent Electrical Discharge Ozonizer
- F,J - Dry Ice Traps
- G - Nitrogen Dioxide Tank
- I - Reaction Vessel



APPARATUS FOR THE SYNTHESIS OF NITROGEN PENTOXIDE

FIG. 4

containing moist KCl (1% by weight water) where the nitrogen dioxide reacted with the potassium chloride to form nitrosyl chloride and potassium nitrate. The flow rates of the gases were adjusted so that no brown color was observable in the effluent stream. The gas stream which contains oxygen, nitrosyl chloride and water vapor is then passed through two two-foot columns containing phosphorous pentoxide and glass wool. The nitrosyl chloride was collected in a trap immersed in a dry ice-acetone mixture (-78°C). The nitrosyl chloride made in this way is not pure but contains small amounts of nitrogen dioxide and water vapor. Purification of the compound was accomplished by distilling off the nitrosyl chloride which has a much higher vapor pressure than either nitrogen dioxide or water vapor.

Purification of Sulfur Dioxide

Tank sulfur dioxide supplied by Matheson Co. was used as a source. The sulfur dioxide, which contained sulfur trioxide and water vapor as the main impurities, was purified by bubbling the gas through a fritted disk into a 500 ml. gas washing bottle containing concentrated sulfuric acid. This removed the sulfur trioxide and most of the water vapor. The remaining residual water vapor was removed by passing the gas through a drying tube containing phosphorous pentoxide and glass wool. The purified gas was collected in a cold trap cooled with dry ice and trichloroethylene and was used without any further purification.

Purification of Hydrogen Chloride

Tank hydrogen chloride (Matheson Co.) which contains chlorine and water vapor as the principal impurities was purified by passing the gas through a drying tube containing phosphorous pentoxide and glass wool. The effluent gas stream was collected in a cold trap cooled with dry ice and trichloroethylene. Since chlorine has a vapor pressure of 760 mm at this temperature (-80°C), it is effectively separated from the hydrogen chloride. The gas was subsequently distilled into a cold trap containing liquid nitrogen and pumped down for two hours before using.

RESULTS

Calibration Curve

The absorption of the brown nitrogen dioxide in the gas phase, as indicated by the recorder deflections (readings), is a linear function of the concentration of nitrogen dioxide in mm. at both zero and twenty degrees centigrade (see Calibration Curve for nitrogen dioxide). No correction was made in the graph for the extensive dimerization which occurs at zero degrees.

The absorption of the yellow-brown nitrosyl chloride is also a linear function of the concentration of nitrosyl chloride (see Calibration Curve for nitrosyl chloride).

If one assumes no chemical or physical interaction between nitrogen dioxide and nitrosyl chloride, then the total absorption of a mixture of nitrogen dioxide and nitrosyl chloride should be an additive function of the individual absorptions of nitrogen dioxide and nitrosyl chloride. The individual absorptions shown by the curves on the graphs can be analytically represented by the general equation for a straight line which passes through the origin, $y = ax$, where a is the slope of the curve, y is the recorder reading and x , the concentration of a gas. Thus, if we relate the total absorption to the recorder deflection, then

$$R(\text{recorder reading}) = a(\text{NO}_2) + b(\text{NOCl}) \quad \text{I}$$

From the stoichiometry of the reaction,



one can see that two molecules of nitrogen dioxide are produced for every molecule of nitrosyl chloride which reacts with a molecule of nitrogen pentoxide; also one half the final concentration of nitrogen dioxide will be equal to the initial concentration of nitrosyl chloride. If this be the case, then the concentration of nitrosyl chloride at any time "t" will be related to the concentration of nitrogen dioxide in the following manner:

$$(\text{NOCl})_t = 1/2(\text{NO}_2)_{\text{final}} - 1/2(\text{NO}_2)_t. \quad \text{III}$$

Replacing the concentration of nitrosyl chloride in I with its equivalent from III,

$$R = a(\text{NO}_2) + b1/2(\text{NO}_2)_{\text{final}} - b1/2(\text{NO}_2), \quad \text{IV}$$

combining like terms

$$R = (a-b1/2)(\text{NO}_2) + b1/2(\text{NO}_2)_{\text{final}}. \quad \text{V}$$

Calculating the numerical values of the slopes from Graphs 16 and 16A gives

1) at zero degrees centigrade,

$$R = 160(\text{NO}_2) + 5(\text{NO}_2)_{\text{final}} \quad \text{VI}$$

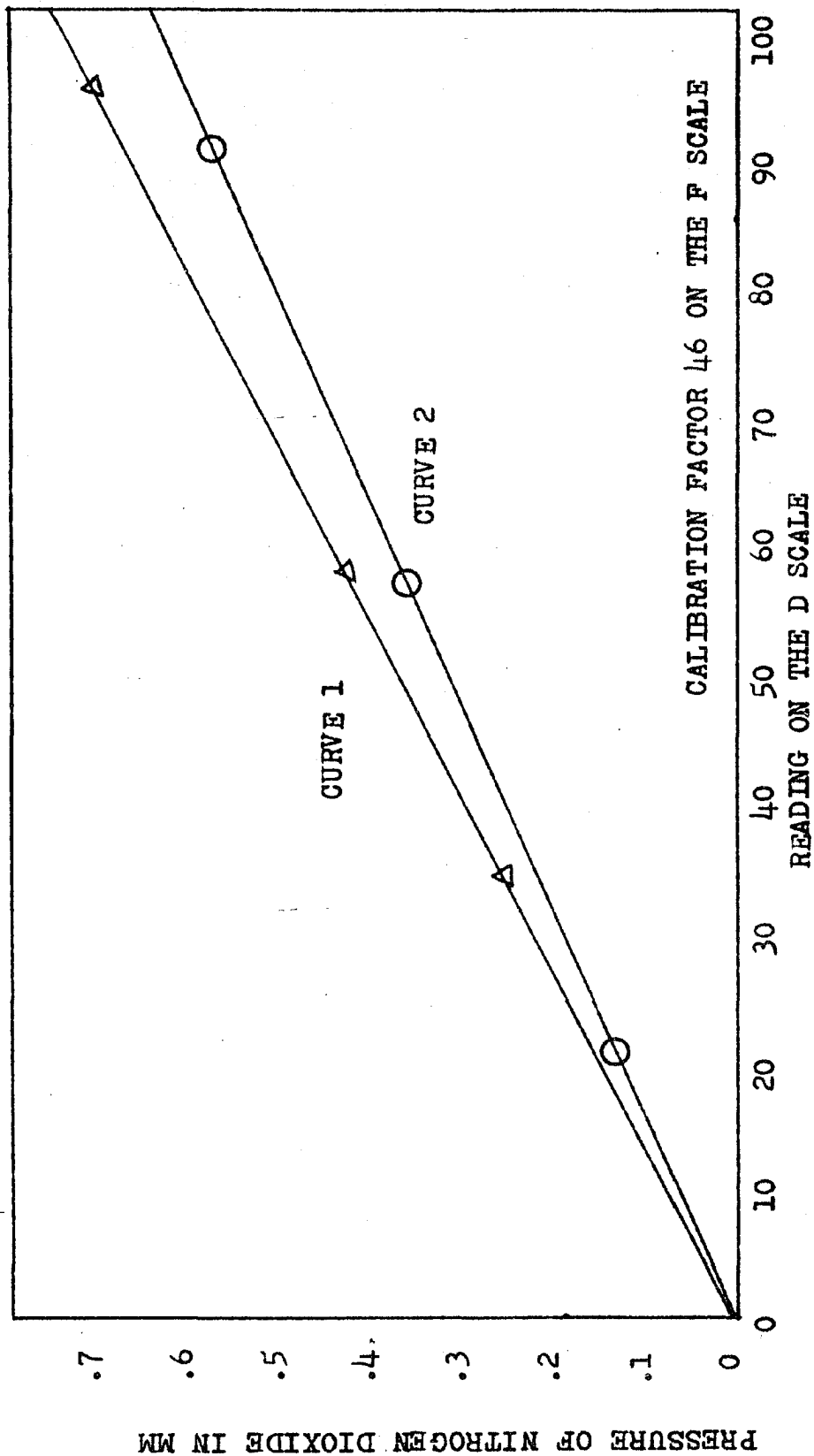
2) at twenty degrees centigrade,

$$R = 145(\text{NO}_2) + 5(\text{NO}_2)_{\text{final}}. \quad \text{VII}$$

Practically speaking, these equations enable one to calculate the concentration of nitrogen dioxide at any time "t" during the reaction and at any temperature between 0°C and 20°C, if one knows the degree of dissociation of nitrogen dioxide as a function of temperature. The calibration curves for nitrogen dioxide were checked by measuring the thermal decomposition of nitrogen pentoxide. The rate constant for this reaction is

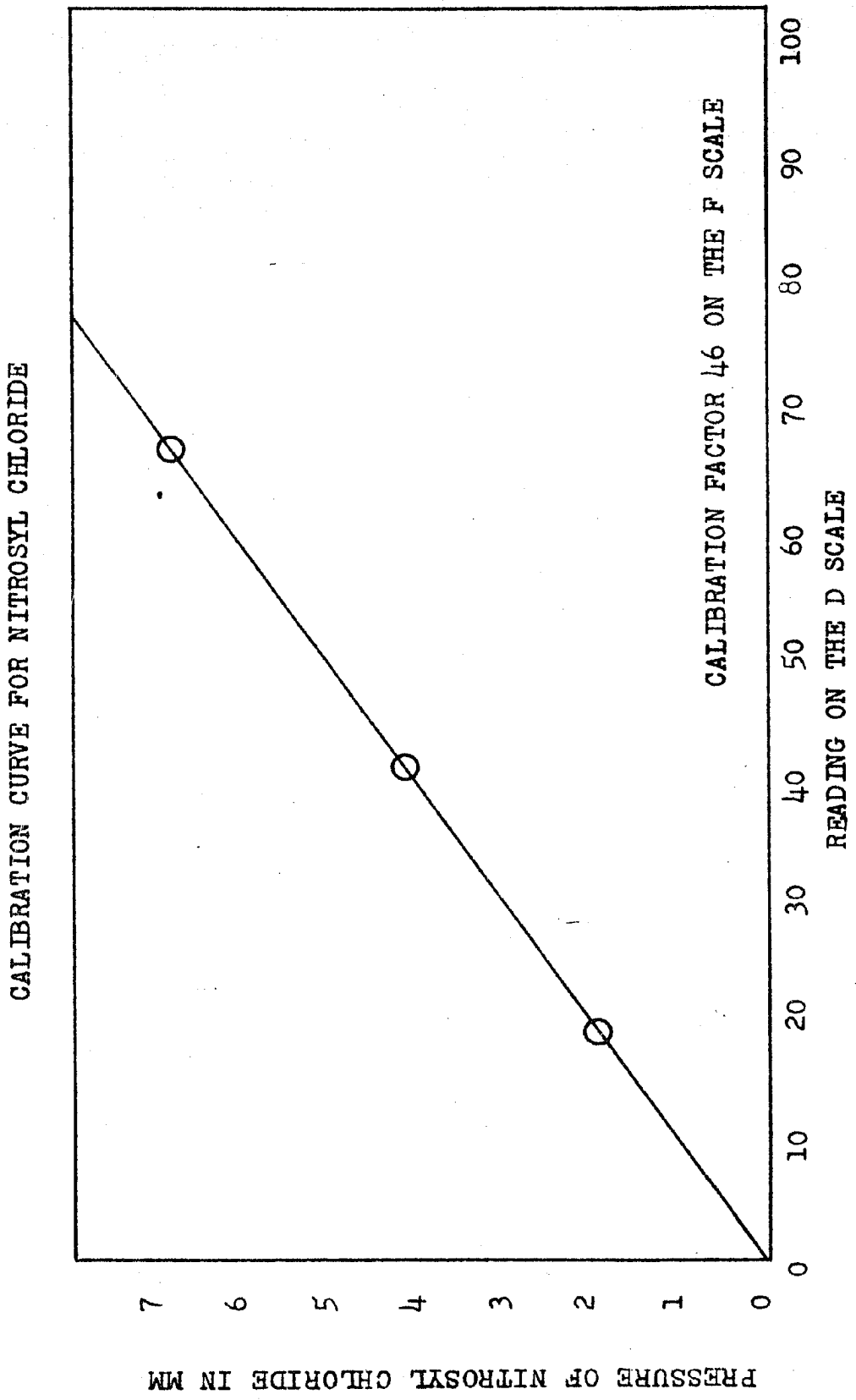
known¹. In Graph 17 the observed rate constant for the first one half an hour of the reaction is $k_{obs} = 3.3 \times 10^{-5} \text{ mm}^{-1}$; the rate constant from the literature is $3.4 \times 10^{-5} \text{ mm}^{-1}$. This close agreement would indicate that the calibration curves were valid.

CALIBRATION CURVE FOR NITROGEN DIOXIDE AT 0° C & 20° C



CURVE 1 TOTAL PRESSURE UNCORRECTED FOR DIMERIZATION OF NITROGEN DIOXIDE
CURVE 2 TOTAL PRESSURE OF NITROGEN DIOXIDE CORRECTED FOR DIMERIZATION

GRAPH 16



GRAPH 16-A

NITROGEN PENTOXIDE AND NITROSYL CHLORIDE

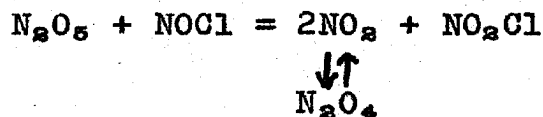
Section A - Stoichiometry and Products of the Reaction

The stoichiometry and products of the reaction between nitrosyl chloride and nitrogen pentoxide were determined by Weston.²⁸ He found that upon admission of nitrosyl chloride to a reaction vessel containing nitrogen pentoxide at 0°C, brown fumes were immediately observable. The products were completely condensable at -195°C, but a fraction volatilized at -78°C. This volatile fraction was colorless and condensed at some temperature between -78°C and -195°C to a colorless liquid and then to a white solid. In one experiment he used an excess of nitrogen pentoxide so that only this colorless product volatilized at -78°C. This was condensed into a small Faraday tube which was sealed off from the system. He then heated it for a few hours at a hundred degrees and found the brown color of nitrogen dioxide produced. He then condensed this gas into one leg of the tube at -78°C. The other leg was sealed off and opened to the atmosphere. Water was immediately added and the resultant solution gave a positive test for chlorine with silver nitrate. It is fairly evident that the colorless product is a nitrogen chloride compound and in all probability is nitryl chloride. It is also known¹⁰ that nitrosyl chloride

²⁸Dr. Ralph Weston, in a private communication, kindly allowed us access to his work on the nitrosyl chloride and nitrogen pentoxide reaction. The author wishes to acknowledge his debt to Dr. Weston.

will undergo thermal decomposition to form principally nitrogen dioxide and chlorine.

From the above it would seem that the reaction is



If one used an excess of nitrosyl chloride then, from the stoichiometry of the above reaction

$$\frac{P_{\text{NO}_2}^0}{P_{\text{N}_2\text{O}_5}^i} = 2$$

and if one uses an excess of nitrogen pentoxide, one should find

$$\frac{P_{\text{NO}_2}^0}{P_{\text{NOCl}}^i} = 2$$

where $P_{\text{NO}_2}^0 = P_{\text{NO}_2} + P_{\text{N}_2\text{O}_4}$

and $\frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = K$

Values of the equilibrium constant K used were those obtained by Verhoek and Daniels¹¹.

Weston tested these theoretical ratios by using both optical measurements and pressure measurements. He found the ratios agree with the theoretical ones within a standard deviation of 5% over a twenty-fold variation in the ratio of reactant concentrations.

Section B - Kinetics

In order to determine the role the various reactants play in the mechanism of the reaction it is helpful to know the effect, if any, the reactants have on the rate of the reaction. Generally speaking the rate of a simple reaction, R , has the following dependency.

$$R = k(Ca)^a (Cb)^b \dots (Cx)^x, \quad \text{I}$$

k represents the rate constant, Ca , Cb , \dots , Cx are the concentrations of the various reactants, and the exponents a , b , \dots , x represent the order with respect to the given reactant. These exponents may be positive or negative, whole or fractional numbers.

For the reaction under investigation we assume the following form

$$R = k(N_2O_5)^x (NOCl)^y \quad \text{II}$$

The Order with Respect to Nitrogen Pentoxide

By carrying out the reaction under conditions where the concentration of nitrosyl chloride is in large excess, when compared to the concentration of nitrogen pentoxide, we can introduce the following simplification

$$k(NOCl)^y = k' \quad \text{III}$$

equation two becomes

$$R = k'(N_2O_5)^x \quad \text{IV}$$

The rate of the oxidation is followed by determining the change in concentration of nitrogen dioxide with time.

From the stoichiometry of the reaction this change is equal to twice the change in nitrogen pentoxide concentration with time.

$$\frac{-d(N_2O_5)}{dt} = k' (N_2O_5)^x \quad V$$

if x is equal to one we have a simple first-order reaction and integrating equation five yields

$$\log(N_2O_5) = \frac{k't}{2.3} + C \quad VI$$

Thus if this reaction is first-order with respect to nitrogen pentoxide, a plot of $\log(N_2O_5)$ vs. time should yield a straight line with a slope equal to k' .

Runs #1,2,3,4,5,6 and 10 on Graphs 1,2,3,4,5,6 and 10 show the results of plotting the $\log(N_2O_5)$ vs. time in sec. Under these conditions of concentration and temperature, i.e., $NOCl = 5.45$ mm, N_2O_5 varied from .0448 mm to .204 mm, temp. = .5°C., the reaction is first-order with respect to nitrogen pentoxide over at least two half-lives of the reaction.

The Order with Respect to NOCl

The order with respect to nitrosyl chloride was determined from runs #9, 10, 11, 23, 23A, 25A.

In runs #9, 10 and 11, (Graphs 7,8 and 9), a large excess of nitrogen pentoxide was made to react with a known amount of nitrosyl chloride. The contraction of nitrogen pentoxide was determined at various time intervals and a plot of $\log(N_2O_5)$ vs. time yielded reasonably straight lines over at least two half-lives of the reaction. Due to the short half-life of these reactions (about 2 sec.) the accuracy of

these runs is not as good as the accuracy obtained when determining the order with respect to nitrogen pentoxide. Because of the method used to transfer the N_2O_5 from the reactant reservoir to the reaction cell, and because of the thermal decomposition which took place during transfer, the amount of nitrogen pentoxide present during these runs was unknown. In brief, these results needed to be confirmed by further work.

In runs #23, 23A and 25A (Graph #11), a known excess of NOCl was varied over a two fold range and made to react with a known amount of N_2O_5 . The pseudo first-order rate constants obtained from these runs are listed in column 4 of Table I.

TABLE I

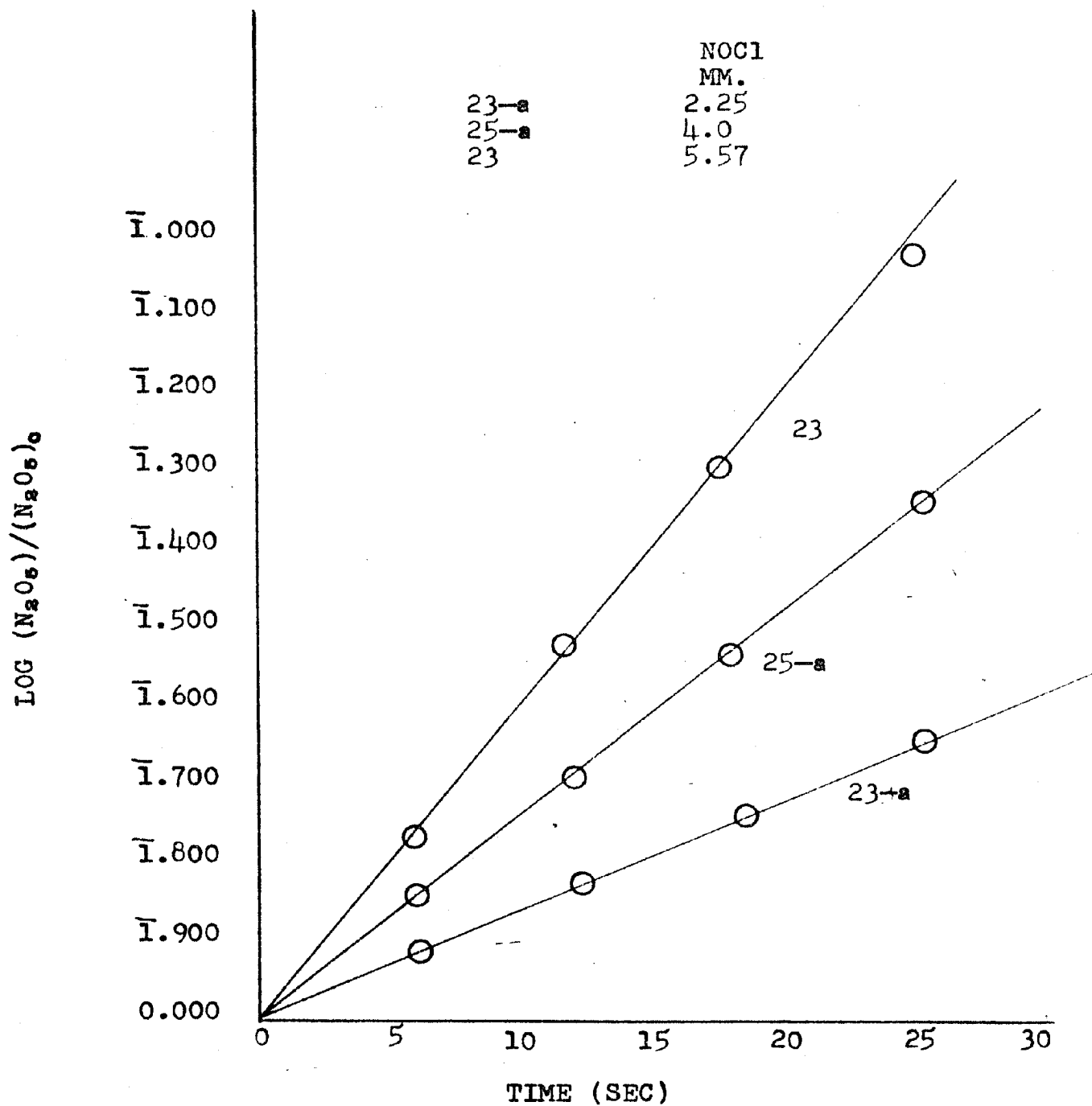
Determination of the Order
with Respect to Nitrosyl Chloride I

Run	Con. NOCl mm	Con. N_2O_5 mm	$k' \times 10^2$ sec ⁻¹	$\frac{-k'}{(NOCl)} \times 10^2$ m ⁻¹ sec ⁻¹
23	5.57	.170	11.7	2.1
23A	2.25	.135	4.4	2.0
25A	4.0	.160	7.7	1.9

Dividing the pseudo first-order rate constant by the concentration of nitrosyl chloride raised to the first power gives a reasonably constant value for the rate constant (col. 5). No other order with respect to nitrosyl chloride gives consistent rate constants. This is further proof of the first-

GRAPH # 11

3 CURVES SHOWING THE EFFECT OF THE NOCl CONCENTRATION ON THE RATE OF THE REACTION



order nature of the reaction with respect to nitrosyl chloride.

Activation Energy

An activation energy was determined for the reaction over a temperature range from 0° to 20°C. Graph 12 is an Arrhenius plot of the data. This data yielded the following equation:

$$k = 2.7 \times 10^2 e^{-\frac{3680}{RT}} \text{ mm}^{-1} \text{ sec}^{-1}$$

TABLE II

Data used to Determine Activation Energy

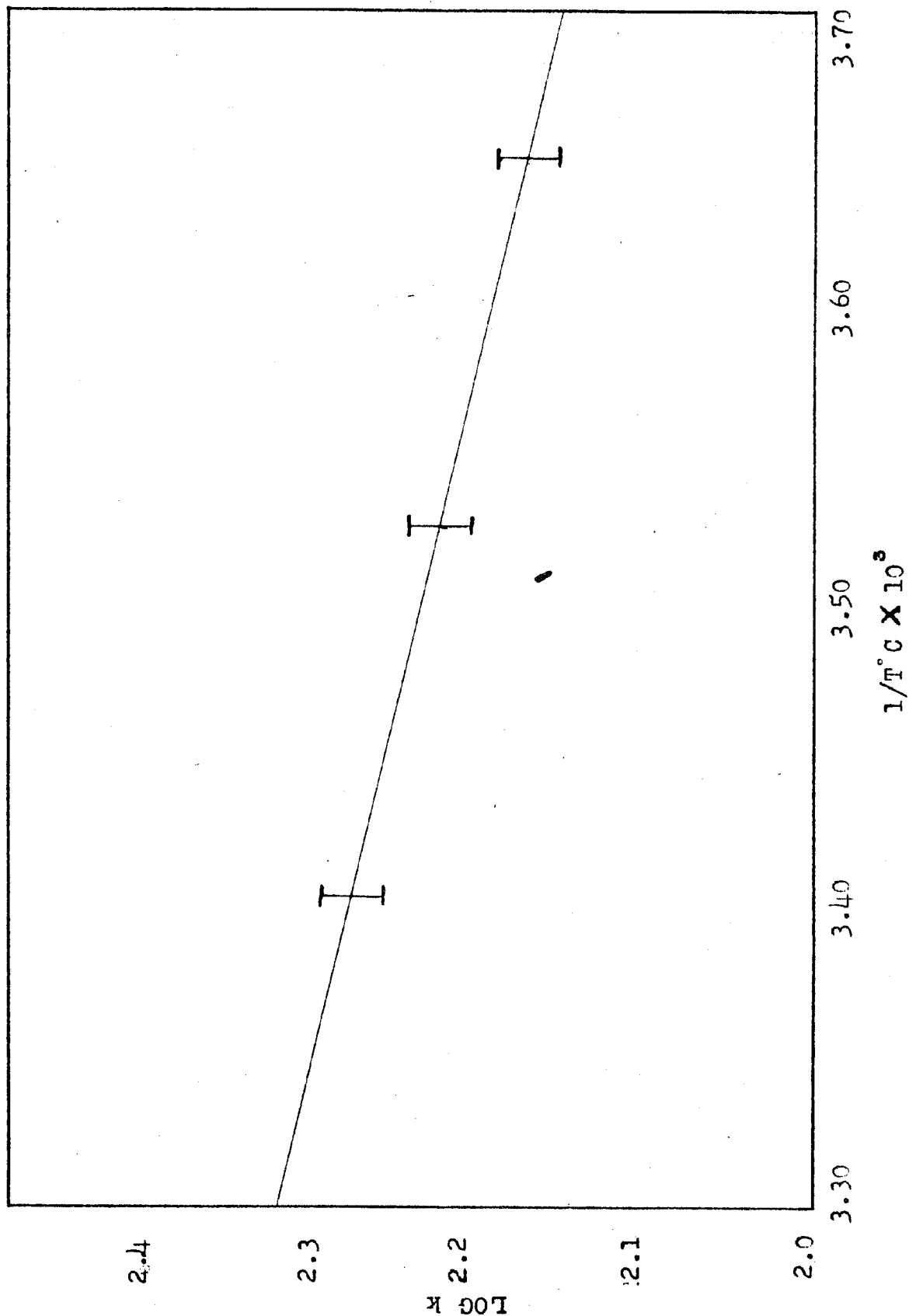
Run	Con. NOCl	Con. N ₂ O ₅	Temp. °C	k x 10 ² (mm ⁻¹ sec ⁻¹)
1	5.45	.165	.5	1.6
3	5.45	.087	.5	1.6
5	5.45	.193	.5	1.6
6	5.45	.100	.5	1.2
7	5.45	.0448	.5	1.1
8	5.45	.128	.5	1.5
13	5.45	.197	.5	2.1
20 ¹	5.55	.320	10.6	1.7
21 ²	5.70	.170	10.0	1.8
22 ³	5.70	.115	10.0	1.8
23 ⁴	5.57	.170	20.0	2.1
24 ⁵	5.57	.220	20.0	2.0
25 ⁶	5.71	.380	20.0	2.2

1,2,3 Graph 13

4,5,6 Graph 14

GRAPH # 12

ARRHENIUS PLOT FOR THE REACTION BETWEEN NITROGEN PENTOXIDE AND NITROSYL CHLORIDE



Section C - Surface Reaction

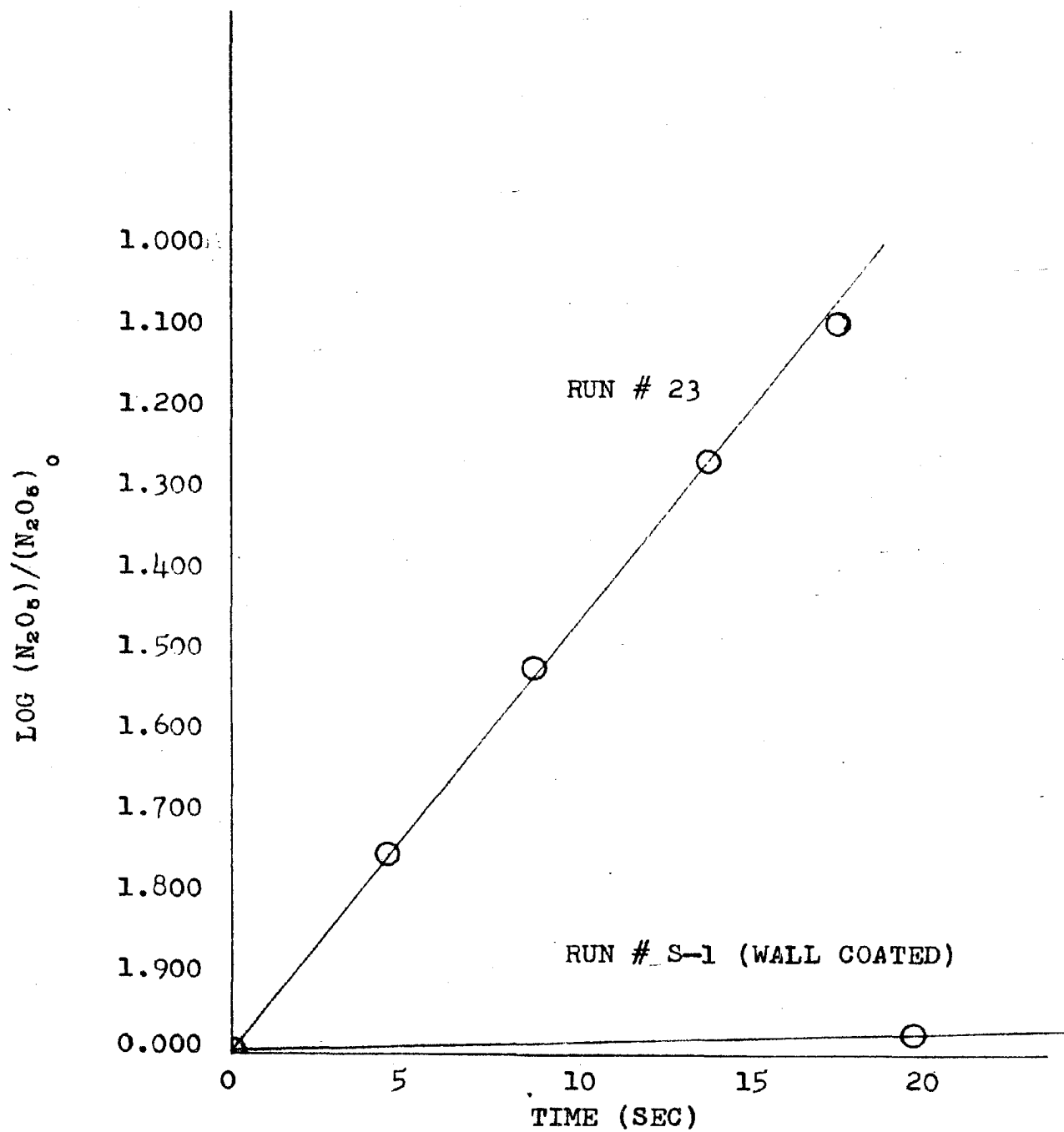
The walls of the reaction vessel were coated with Gulf "Tavern Paraseal Wax", a mixture of non-polar hydrocarbons, in order to determine whether the glass surface of the reaction vessel was catalyzing or inhibiting the rate of the reaction. Because the windows of the reaction vessel had to be optically clear, they could not be waxed. If one considers the surface of the microbore tubing leading to the reaction vessel to be negligible, compared to the surface area of the reaction vessel, then the ratio of the glass surface area exposed before coating the vessel with wax and after coating with wax is about 12 to 1 (124.7 sq. cm. before waxing to 10.8 sq. cm. after waxing).

The effect of coating the walls with wax on the reaction between nitrogen pentoxide and nitrosyl chloride is drastic. The effect is shown in Graph 15. The approximate concentrations of the reactants are the same and the temperature was 20°C in both cases. The surface of the reaction vessel during run #1-S was coated with wax; with run #23, however, the glass surface of the reaction vessel was entirely exposed. The difference in the slopes would seem to indicate that the surface of the reaction vessel has a catalytic effect on the reaction. Comparison of the rate constants (below) indicates that there is almost a twenty-fold decrease in the rate of the reaction when the surface of the reaction vessel is coated with wax.

The reaction in the waxed vessel seems to be first-

GRAPH # 15

ILLUSTRATING THE EFFECT WHICH COATING THE WALLS OF THE REACTION VESSEL WITH A NON-POLAR SUBSTANCE HAS ON THE SPEED OF THE REACTION



order with respect to nitrogen pentoxide. This was determined by running the reaction with a large excess of nitrosyl chloride.

Sample results are shown in Table I-A. Column 3 contains the rate constants obtained by using the first-order rate equation on the data in columns 1 and 2. The relative consistency of the k values during any given run would seem to indicate that the reaction is first-order in nitrogen pentoxide. The rate constant is not consistent from one run to another because the concentration of nitrosyl chloride varied from run to run.

TABLE I-A

Order with Respect to N_2O_5
Surface Reaction

RUN #3-S			RUN #1-S		
Time (min)	(N_2O_5) (mm)	$k \times 10^4$ (sec^{-1})	Time (min)	(N_2O_5) (mm)	$k \times 10^4$ (sec^{-1})
0	.120 [†]		0	.145	
2	.100	15.4	5	.090	16.3
5	.067	19.5	10	.056	15.9
10	.046	15.8	15	.037	15.2
15	.029	15.6	20	.022	16.3

[†] Extrapolated Value

RUN #6-S

Time (min)	(N_2O_5) (mm)	$k \times 10^4$ (sec^{-1})
0	.262	
2.5	.224	10.4
5	.181	12.3
10	.131	11.5
15	.080	13.2
20	.046	14.5

The order with respect to nitrosyl chloride was a little more difficult to achieve. Table III shows that the rate of the reaction is only slightly dependent on the concentration of nitrosyl chloride. There is a small but consistent increase in the value of the pseudo first-order rate constant when we increase the concentration of nitrosyl chloride by seven fold. If the reaction were first-order in nitrosyl chloride we would expect the pseudo first-order rate constant to change from 12.5×10^{-4} at $\text{NOCl} = 2.94$ mm to about 95×10^{-4} at $\text{NOCl} = 21.8$ mm.

TABLE III

Order with Respect to NOCl

Run	(NOCl) (mm)	$k_{\text{obs}} \times 10^4$ (sec^{-1})	$\frac{k_{\text{obs}} \times 10^4}{(\text{NOCl})^{.1}}$
S-6	2.94	12.5	11.2
S-5	3.12	13.1	11.7
S-1	4.95	13.6	11.6
S-2	5.45	15.5	13.0
S-3	21.8	15.9	11.7
S-4	21.8	17	12.5

The rate constants in column 3 of Table II are the pseudo first-order rate constants for the reaction. These are obtained from the slope of the line when the log of the nitrogen pentoxide concentration is plotted against time. It should be noted that the rate of the reaction in the waxed vessel approaches that of the thermal decomposition rate of

nitrogen pentoxide which is $.2 \times 10^{-4} \text{ sec}^{-1}$ at 20°C . Consequently in order to determine the rate constant for the reaction of nitrogen pentoxide with nitrosyl chloride we assume the rate of loss of nitrogen pentoxide is due to both reactions,

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1(\text{NOCl})^x(\text{N}_2\text{O}_5)^y + k_2(\text{N}_2\text{O}_5) \quad (1)$$

since we have seen that the reaction is first-order in N_2O_5 ,

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = (k_1(\text{NOCl})^x + k_2)(\text{N}_2\text{O}_5). \quad (2)$$

If we use a large excess of nitrosyl chloride, then

$$k_1^1 = k_1(\text{NOCl})^x \quad (3)$$

and equation (2) becomes,

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = (k_1^1 + k_2)(\text{N}_2\text{O}_5) \quad (4)$$

integrating

$$\log(\text{N}_2\text{O}_5) = \frac{(k_1^1 + k_2)t}{2.3} + c; \quad (5)$$

thus the slope of the line obtained by plotting $\log \text{N}_2\text{O}_5$ against time is equal to

$$\frac{k_1^1 + k_2}{2.3} \quad (6)$$

The k_{obs} in Table III is obtained by multiplying the slope by 2.3 and subtracting k_2 . Consequently k_{obs} is equal to $k_1(\text{NOCl})^x$.

Column 4 of Table III shows the results of dividing k_{obs} by the concentration of nitrosyl chloride raised to the one-tenth power. The consistency of the k values would seem to indicate the order with respect to nitrosyl chloride is one-tenth.

Nitrogen Pentoxide and Sulfur Dioxide

A study was undertaken of the reaction between nitrogen pentoxide and sulfur dioxide. Sulfur dioxide, like nitric oxide, is a good reducing agent and might be expected to act like nitric oxide in its reaction with nitrogen pentoxide; i.e.,



A. R. Amell⁵ has made a qualitative study of this reaction and found that there was no increase in the rate of the decomposition of nitrogen pentoxide (estimated visually from the rate of appearance of nitrogen dioxide), but it was decided that the apparent simplicity of the proposed reaction and the fact that water, a suspected catalyst in many nitrogen pentoxide reactions, is not one of the reaction products warranted a more thorough investigation of the reaction. The final results were inconclusive.

In a preliminary study nitrogen pentoxide was mixed with sulfur dioxide in an evacuated liter flask. Initially, no reaction occurred on the basis that no change in the brown color of nitrogen dioxide occurred. After approximately one minute, a mist began to appear which condensed onto the bottom of the reaction flask as a white powder. The addition of water caused a decrease in the total pressure. Since the sulfur dioxide used in this experiment was only partially dried by bubbling through concentrated sulfuric acid, a small amount of water vapor was present when the reactants were mixed. Essentially, we have present the conditions for the Lead Chamber process for making sulfuric acid, and it is quite prob-

able that the white powder formed on the walls of the reaction flask is solid nitrosulfuric acid.

At any rate it was decided that an analysis of the reaction products should be made. To this end a gas chromatographic analysis was attempted for sulfur trioxide. From the work done by C. Kyrocas¹² on the separation of permanent gases by gas phase chromatography, it appeared that we might be able to use Molecular Sieve (Linde 5-A) 20-60 mesh for the column packing. Samples containing 10^{-6} moles of sulfur trioxide and an excess of air were run under a variety of conditions using a Perkin-Elmer Model 154-B Vapor Fractometer. The flow rate, using helium as a carrier gas, was varied from 20 to 50 cc/min. and the temperature was varied from room temperature to 200°C. In all cases the sulfur trioxide seemed to be permanently adsorbed on the column; i.e., no sulfur trioxide peak was detected after one hour and fifty minutes of running time. The air was easily separated into nitrogen and oxygen. The data for a typical run was as follows:

Column packing	-	Molecular Sieve 5-A, 20-60 mesh
Carrier gas	-	Helium
Flow rate	-	44 cc/min.
Column temp.	-	20 degrees cent.
Retention times	-	oxygen 3.2 nitrogen 4.5

Other columns such as silica gel (activated and non-activated) were employed with similar results. Since sulfur trioxide is known to be adsorbed on glass, samples were run in aluminum tubing with molecular sieve as the packing. Neg-

ative results were obtained.

Rate studies were also inconclusive. Kinetic runs in a new reaction vessel were erratic and settled down only after repeated aging of the walls of the reaction vessel by flushing with sulfur dioxide, sulfur trioxide, nitrogen pentoxide and nitrogen dioxide. As the aging process continued the rate of the reaction between nitrogen pentoxide and sulfur dioxide, which was slight even in the unaged reaction vessel, decreased. Graph 17 shows the final result obtained. The mixing of equal amounts of sulfur dioxide and nitrogen pentoxide at 30°C does not seem to bring about any reaction as is seen by the fact that the rate of thermal decomposition is unaffected by the addition of sulfur dioxide. It is tentatively concluded that under the conditions of temperature and pressure used in this experiment and under very dry conditions the rate of the reaction of nitrogen pentoxide with sulfur dioxide is several times slower than the actual decomposition of nitrogen pentoxide, if indeed the reaction takes place at all under these experimental conditions.

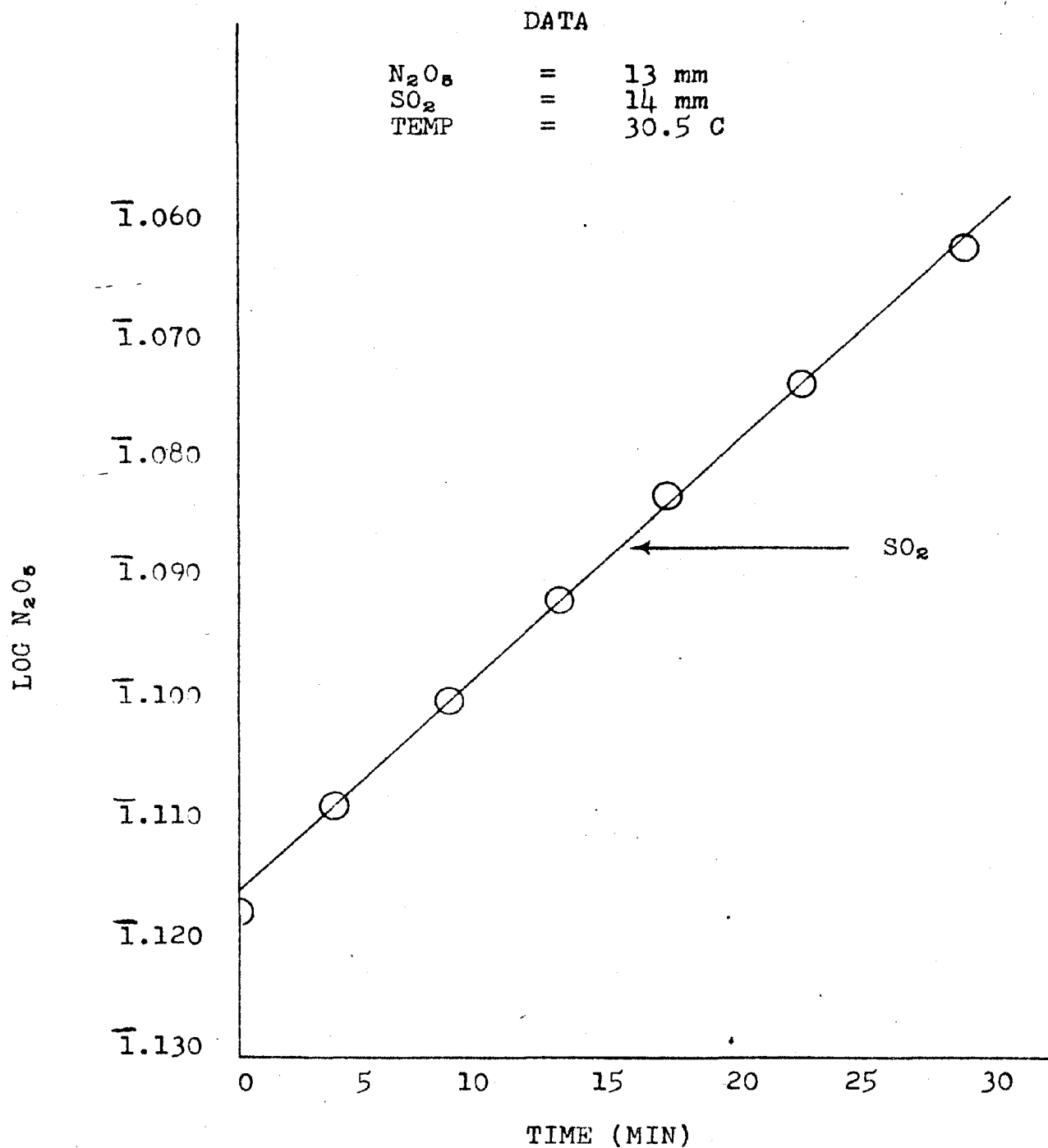
Hydrogen Chloride and Nitrogen Pentoxide

A third reaction studied during the course of this problem was the fast reaction between hydrogen chloride and nitrogen pentoxide.

Tank hydrogen chloride (Linde) was purified by passing the gas through a phosphorous pentoxide column to remove water vapor then trapped out in a liquid nitrogen trap. The nitrogen pentoxide was prepared as mentioned in the section on Prepar-

GRAPH # 17

ILLUSTRATING THE NEGLIGIBLE EFFECT OF SULFUR DIOXIDE ON
THE RATE OF DECOMPOSITION OF NITROGEN PENTOXIDE



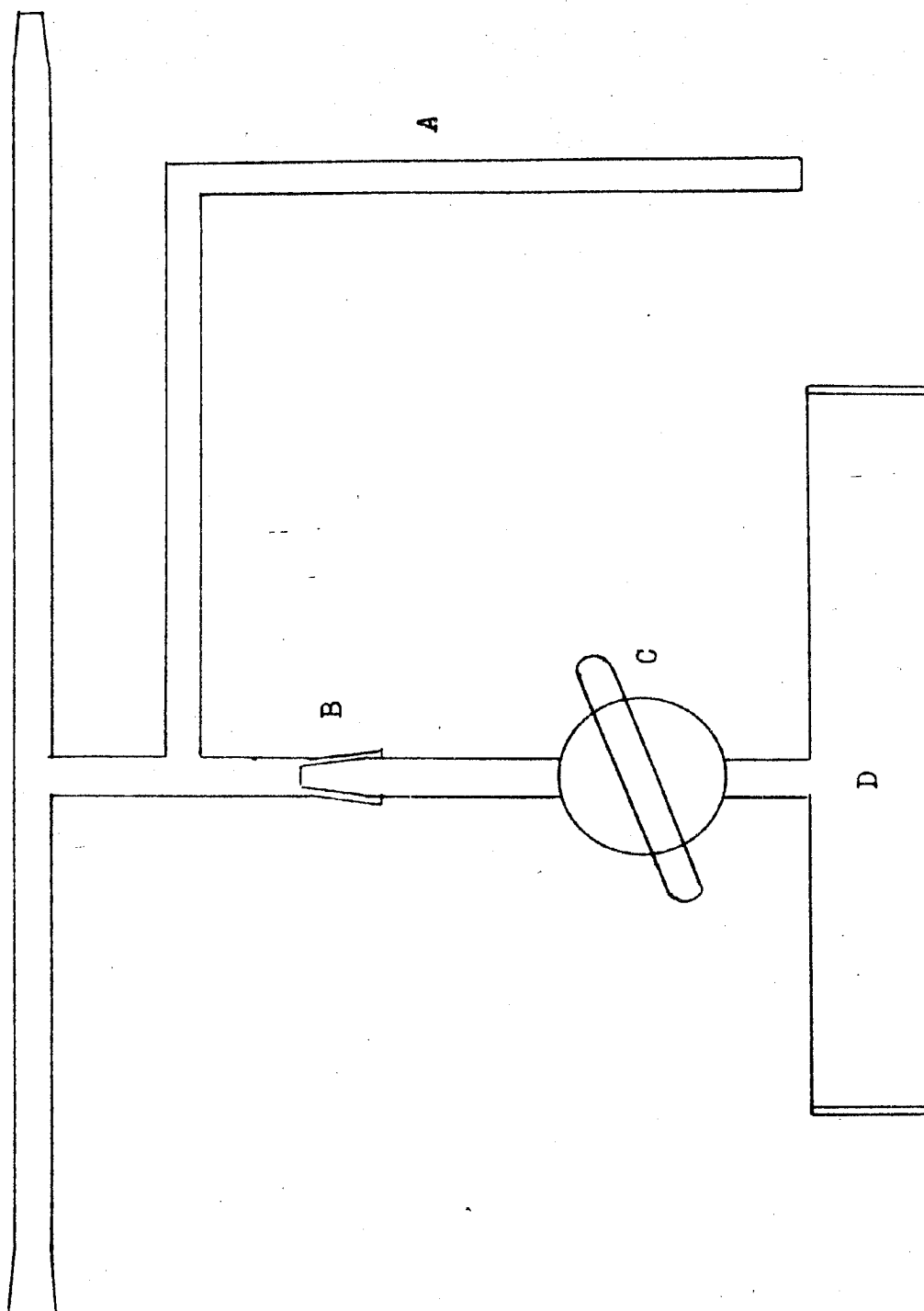
ations of Reactants.

When twenty mm of nitrogen pentoxide was expanded into a liter reservoir flask containing an equal amount of hydrogen chloride, an intense brown color could be noticed almost instantaneously. The reaction mixture was allowed to react for about a half-hour. The apparatus shown in Fig. 5 was then attached by way of gas-tight ground glass joints to the reaction flask which was separated from the apparatus in Fig. 5 by a closed stopcock. The system was evacuated with an oil pump and then closed off from the pump by a stopcock. The stopcock to the reaction vessel was opened and the reaction product mixture expanded into the system. Arm A in Fig. 5 was immersed in liquid nitrogen and the reaction mixture trapped out. When a sufficient amount of reaction mixture had been frozen in the side arm, the stopcock leading to the reaction vessel was closed, the liquid nitrogen removed, and the gas allowed to expand into the gas cell. When arm A reached room temperature, the stopcock leading to the gas cell was closed and the gas cell removed from the system by way of the ground glass joints. The cell was suitable for taking visible and near ultraviolet spectra of the gaseous mixtures. The cell has a path length of 12 cm. and optically flat pyrex glass windows sealed on with Dekhotinsky cement. Spectra of the reaction mixture were recorded on a Perkin-Elmer Model 4000 Ultraviolet Spectrophotometer. By comparing the spectra obtained from the reaction mixture with the spectra of known compounds, it was determined that chlorine, nitrogen dioxide and nitrosyl chloride were among the reaction products. Nitrosyl chloride was also de-

FIG. 5

Gas Cell

- A - Side Arm for Trapping
Gaseous Mixtures
- B - Ground Glass Connecting Joint
- C - Stopcock
- D - Gas Cell



GAS CELL ATTACHED TO A SIMPLE DEVICE FOR TRAPPING GASEOUS MIXTURES

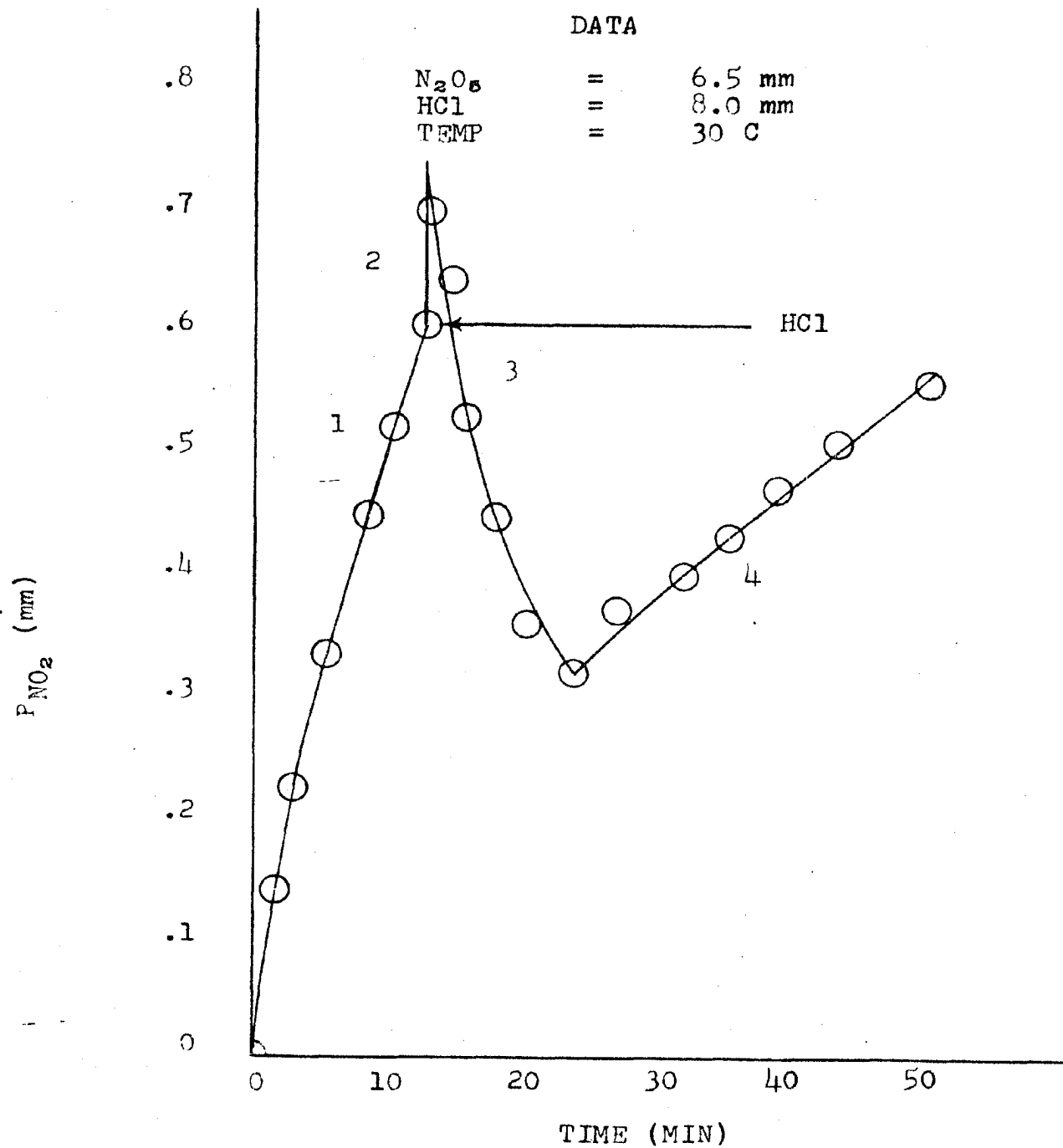
FIG. 5

tected by its characteristic yellow-red color when frozen to its crystalline form. A mist which condensed out on the walls of the reaction vessel seemed to indicate the presence of water.

Kinetic studies were undertaken in the same manner as with the nitrosyl chloride, nitrogen pentoxide reaction. The photometer circuit used to record the absorption of nitrogen dioxide was not, however, the barrier cells and G. E. Recorder used for the work on the nitrosyl chloride and nitrogen pentoxide. In place of the barrier cells were two R.C.A. 926 vacuum photoelectric cells which were sensitive in the visible region with a maximum at about 4500 Angstroms. The photoelectric cells were mounted in ground-glass sealed tubes which contained a desiccant, dehydrite with cobaltous chloride. The desiccant prevented water from being adsorbed on the surface of the photoelectric cells which would result in leakage of electricity. The ground-glass tubes were mounted in a brass cylinder and the tubes and brass cylinder were covered with aluminum foil which was held by friction tape and grounded to act as a shield and prevent electrical pick-up by the photoelectrical circuit. The output of these photocells was fed into an amplifier designed by H. R. Anderson¹³ and built by A. F. Daggett (E. F. Worden Master's Thesis, Nt W924p). The amplifier is insensitive to line voltage fluctuations due to symmetry. When used with a sensitive galvanometer with a short period, the circuit is capable of high precision and rapid response. The galvanometer used (in place of the G. E.

GRAPH # 18

ILLUSTRATING THE EFFECT OF ADDING HYDROGEN CHLORIDE
TO NITROGEN PENTOXIDE



Recorder used in conjunction with the barrier cells) was a Leeds and Northrup wall mounted galvanometer, type P, No. 2500a, fitted with a lens of one meter focal length. The optical system for the galvanometer consisted of a 6-8 volt single filament lamp as a light source with a hair line placed in such a position that its image reflected from the galvanometer mirror was focused on a translucent scale, 50 cm. in length, and one meter from the galvanometer. The scale could be read to 1 mm. and the galvanometer had a sensitivity of .5 microvolts/mm. Directions for operating this circuit can be found in E. F. Worden's Master Thesis (above), page 17.

Graph 18 is a plot of nitrogen dioxide concentration as a function of time. Curve 1 represents the thermal decomposition of nitrogen pentoxide. The addition of hydrogen chloride resulted initially in a rapid reaction indicated by Curve #2. This reaction proceeded until an apparent maximum of .75 mm of nitrogen dioxide were produced. Curve #3 represents a slower reaction resulting in a decrease in the concentration of nitrogen dioxide. The rate of this reaction decreased and reached a minimum at twenty-four minutes, when a fourth reaction represented by Curve #4 dominated and resulted in an increase in the concentration of nitrogen dioxide for as long as the reaction was followed -- about fifty minutes.

Curve #1 represents the thermal decomposition of nitrogen pentoxide. The addition of hydrogen chloride results in a rapid reaction (Curve #2) which could not be followed accurately with the experimental apparatus used in this thesis.

Curve #3 may represent the loss of nitrogen dioxide by reaction with hydrogen chloride. This reaction is known to take place under the conditions of this experiment with the production of nitrosyl chloride and water vapor. Curve #4 would seem to be due to a simple thermal decomposition of the remaining nitrogen pentoxide.

The investigation into the nature of this reaction was terminated at this point because of the complexity of the reactions involved.

DISCUSSION

The experimental data indicates that the rate of oxidation of nitrosyl chloride follows a simple second-order dependence (first-order in each reactant) when the reaction is carried out in a glass vessel (surface/volume ratio = 1.6). The reaction is very rapid with an experimental rate constant at 20°C of $2.1 \times 10^{-3} \text{ mm}^{-1} \text{ sec}^{-1}$ and has an activation energy of only 4 Kcal.

Coating the glass walls of the reaction vessel (but not the windows of the vessel which had to be kept clear to allow the light beam to pass through) with a non-polar wax effected the kinetics drastically. The rate of oxidation was then found to be only slightly dependent on the concentration of nitrosyl chloride, though it remained first-order in nitrogen pentoxide. The rate of the reaction decreased greatly, the rate constant now being $1.2 \times 10^{-3} \text{ mm}^{-1} \text{ sec}^{-1}$ at 20°C.

The low activation energy and the pronounced effect which changing the nature of the reaction wall has on the rate of the reaction points to a complex mechanism. In general, the reaction seems to take place both heterogeneously and homogeneously and thus we can write the total rate of the reaction as the sum of the two contributions:

$$R (\text{overall}) = R (\text{hetero.}) + R (\text{homo.})$$

For reasons which will be made clear later it seems reasonable to assume the overall rate can be expressed in the following

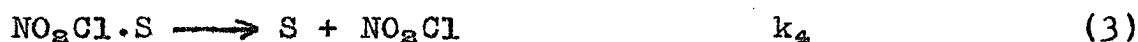
complex rate equation:

$$R(\text{overall}) = k_{\text{obs.}}(\text{N}_2\text{O}_5)(\text{NOCl}) + k_{\text{obs.}}^{\text{I}}(\text{N}_2\text{O}_5)$$

The first term represents the heterogeneous contribution to the rate and the second term represents the homogeneous contribution to the rate. We shall first look at the heterogeneous reaction and attempt to devise a mechanism and then we shall turn our attention to the homogeneous reaction.

The twenty-fold decrease in rate of the reaction which resulted from coating the walls of the reaction vessel with wax would seem to imply that the reaction in the glass-walled vessel was almost entirely heterogeneous. If this be so, then the heterogeneous reaction is first-order in both nitrogen pentoxide and nitrosyl chloride. Heterogeneous catalysis theory indicates there are two possible mechanisms which will fit the data. The first, known as the Rideal mechanism, postulates that the reaction takes place between an adsorbed species and one in the gas phase. The second mechanism, known as the Langmuir-Hinshelwood mechanism, is based on the theory that both reacting species are adsorbed on the surface of the reaction vessel.

The steps of the Rideal mechanism are



Where S represents the active sites on the surface of the reaction vessel.

$$\text{now} \quad \frac{-d(\text{N}_2\text{O}_5)}{dt} = k_3(\text{N}_2\text{O}_5)(\text{NOCl}\cdot\text{S}) \quad (4)$$

$\frac{k_1}{k_2}$ represents the equilibrium constant K for the adsorption process involving nitrosyl chloride.

$$K = \frac{(\text{NOCl} \cdot \text{S})}{(\text{NOCl})(\text{S})} \quad (5)$$

or

$$(\text{NOCl} \cdot \text{S}) = K(\text{NOCl})(\text{S}) \quad (6)$$

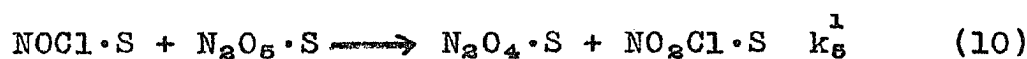
inserting the righthand side of equation (6) for its equivalent in equation (4)

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_3 K (\text{N}_2\text{O}_5)(\text{NOCl})(\text{S}) \quad (7)$$

which fits the experimentally observed rate expression.

The assumption made in the above derivation is that step 2 in the mechanism is the rate-determining step and the equilibrium between the gas phase nitrosyl chloride and the adsorbed species is rapid and complete. We will examine these assumptions later.

The second mechanism involves two adsorbed species:



now

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_5 (\text{NOCl} \cdot \text{S})(\text{N}_2\text{O}_5 \cdot \text{S}) \quad (11)$$

Representing the adsorption equilibrium for both nitrosyl chloride and nitrogen pentoxide

$$K^1 = \frac{(\text{NOCl} \cdot \text{S})}{(\text{NOCl})(\text{S})} \quad (12)$$

$$K_1^1 = \frac{(\text{N}_2\text{O}_5 \cdot \text{S})}{(\text{N}_2\text{O}_5)(\text{S})} \quad (13)$$

inserting these in the rate equation, we arrive at

$$\frac{d(N_2O_5)}{dt} = k_5^1 K_1^{-1} (N_2O_5)(NOCl) \quad (14)$$

A more vigorous derivation of this equation would show that it is valid only when K_1^{-1} and K^1 represent rapid and complete equilibrium and when the walls of the reaction vessel are sparsely covered with reactants.

There are five possibilities for the rate-determining step in the mechanisms listed above.

1. Transport of gaseous reactants to the surface.
2. Adsorption of the gases on the walls of the reaction vessel.
3. Reaction on the surface of the reaction vessel.
4. Desorption of the products.
5. Transport of the products away from the wall of the vessel.

Stages 1 and 5 are ordinary diffusion processes and if either of them were the rate-determining step the temperature coefficient of the rate would be the same order as for gaseous diffusion. The rate of diffusion of a gas does not vary exponentially with the temperature, however, as the rates of heterogeneous chemical reactions, but increases in proportion to the square root of the temperature. This is not the case.

In general the process of adsorption and desorption may be expected to be the slow step in a heterogeneous reaction if the activation energy of adsorption is high or if the surface reaction is rapid because of a low activation energy. A

clear-cut answer at this point is not possible because of the uncertain knowledge of the sorption isotherms of all the species involved. It seems fair to say, however, that both nitrosyl chloride and nitrogen pentoxide would be adsorbed on the glass by weak Van der Waal forces rather than being chemically adsorbed (chemisorption). This is true of the products, nitryl chloride and nitrogen dioxide (nitrogen tetroxide) also. Now physical adsorption is characterized by a rapid and reversible attainment of equilibrium with the gas phase, and the measured heats of adsorption are found to be in the order of magnitude of the heats of liquefaction of the adsorbate. On this basis the rate-determining step should be the reaction occurring on the surface. The heats of evaporation of the compounds in question are as follows:

$$\text{NOCl} = 5350 \text{ cal/mole}^{(15)}$$

$$\text{N}_2\text{O}_4 = 5600 \text{ cal/mole}^{(16)}$$

If the second mechanism is the correct one then we should find

$$E_{\text{exp}} = E_{k_3} + E_k + E_{k_1}.$$

Now assuming the heats of adsorption are similar to their heats of liquefaction

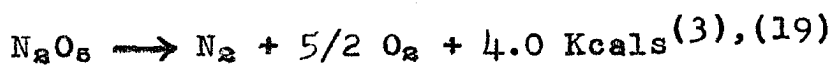
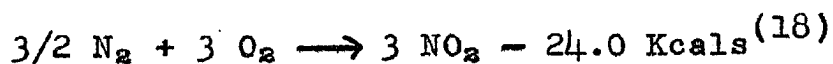
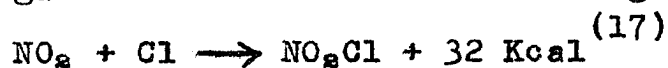
$$4 \text{ Kcals} = E_{k_3} + (-5 \text{ Kcals}) + (-5 \text{ Kcals})$$

$$E_{k_3} = 14 \text{ Kcals}.$$

This value, as we shall see when we examine the reaction taking place on the surface, is a reasonable one.

The experimental activation energy, 4 Kcals, also

correlates with the expected heat of the reaction under investigation. Consider the following process:

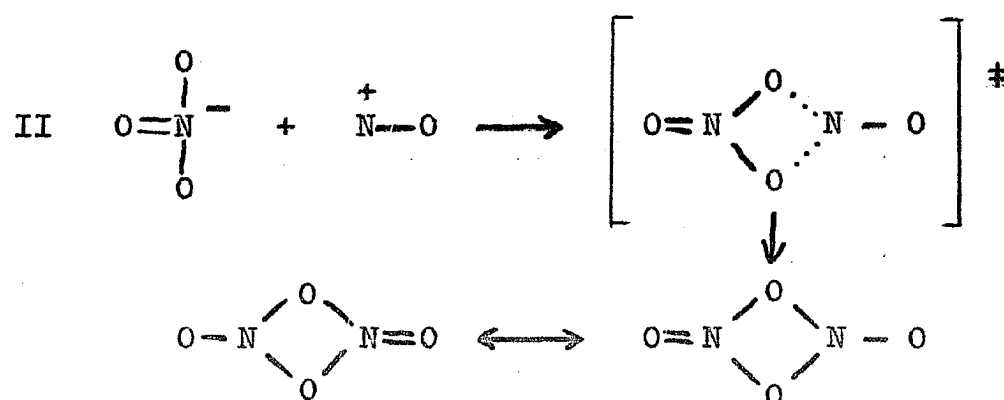
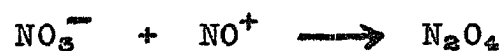
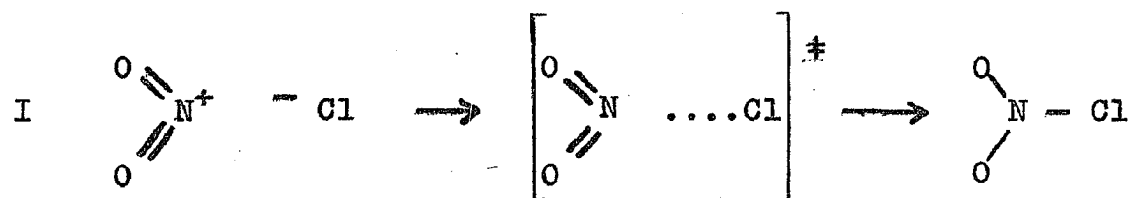
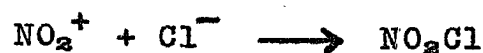


The sum of these steps is the reaction observed and the energy obtained by applying Hess' Law is -3 Kcals. Hence the activation energy is $E \cong 3$ Kcals. If one assume that the product of the reaction is N_2O_4 , rather than 2NO_2 , the energy of the reaction is increased by an amount corresponding to the dissociation energy of nitrogen tetroxide (14.6 Kcals), so that the reaction becomes exothermic by 12 Kcals. Thus, the activation energy may be 4 Kcals.

On the whole the second mechanism seems the most reasonable, especially in view of the simple but effective picture which can be postulated for the surface reaction step, which would take place according to the second mechanism. The mechanism of the reaction taking place on the surface of the vessel (Step 10) seems to be most readily explained if we look upon the glass surface as a two- or three-dimensional network containing chemically unsaturated centers, which produce localized sites of high dielectric intensity. At these sites, the nitrosyl chloride and nitrogen pentoxide are physically adsorbed and ionization reactions are facilitated; i.e.,



Now the reactants in their ionic form can readily undergo reaction if they are on adjacent sites. The transition from reactants to products might be pictured in the following way:



In support of this mechanism, both nitrogen pentoxide and nitrosyl chloride have been shown to exist in the ionic form in the solid state. J. A. Ketelaar²⁰ has shown by electron diffraction data that nitrosyl chloride exists as a resonance hybrid between the homopolar form and the ionic form



Grison et al²¹, and Eriks²² have shown by X-ray diffraction data that nitrogen pentoxide exists in the ionic form having

NO_2^+ anions and NO_3^- cations. This tendency to revert to an ionic form when under the influence of high electrical charges would imply that they might revert to the ionic form when adsorbed on sites of high electrical unsaturation.

It is also interesting to note that this reaction was actually used to prepare nitryl chloride in quantitative yields at -80°C (9). Both nitrosyl chloride and nitrogen pentoxide are solids at this temperature and, as we have seen above, exist as ions. Thus at this temperature it would seem that the reaction can take place only by an ionic mechanism.

This mechanism is interesting from another point of view also. Once the ions have lined themselves up on the surface so that the chloride ion is in the vicinity of the nitrogen dioxide radical and the nitrate ion is under the influence of the nitrosonium ion (both processes aided by the charge affinities) then a rearrangement of electrons is all that is needed to form the products. Nitrogen tetroxide is formed when two oxygens from the nitrate ion bond to the nitrogen of the nitrosonium ion. This ring closure gives the Longuet-Higgins molecule²³ for nitrogen tetroxide. The transition state complex for this reaction is symmetrical and favored by the fact that the product in the configuration suggested is stabilized by resonance. Nitryl chloride is formed when the electrons from the chloride ion are shared with the positive nitrogen on the nitrogen dioxide radical.

The reason the reaction proceeds so much more slowly on the walls of the waxed vessel is now clear. The non-polar

wax cannot provide the sites for a reaction which requires such high electronic densities. Thus the reaction which now predominates is the gas phase reaction.

In addition to slowing the rate of oxidation considerably, waxing the walls of the reaction vessel also decreased the dependency of the rate of oxidation on the nitrosyl chloride concentration. In fact, reducing the amount of glass surface exposed to the reactants to 10% of its former area, reduced the order with respect to the nitrosyl chloride from one to one tenth (.1). It is not apparent that there is a direct relationship here, but it would seem to imply that a new reaction path is now predominating which is much less dependent on the nitrosyl chloride concentration, if at all.

Several factors which will be discussed below indicate that this "new" reaction path is the homogeneous oxidation of nitrosyl chloride by nitrogen pentoxide.

Assuming the homogeneous reaction rate is zero-order in nitrosyl chloride and first-order in nitrogen pentoxide, we write the following mechanism:



We derive the rate equation in the following way:

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1(\text{N}_2\text{O}_5) - k_2(\text{NO}_2)(\text{NO}_3) \quad (18)$$

$$\frac{d(\text{NO}_3)}{dt} = k_1(\text{N}_2\text{O}_5) - k_2(\text{NO}_2)(\text{NO}_3) - k_3(\text{NO}_3)(\text{NOCl}) \quad (19)$$

Applying the steady state assumption to nitrogen trioxide,

$$(\text{NO}_3) = \frac{k_1(\text{N}_2\text{O}_5)}{k_2(\text{NO}_2) + k_3(\text{NOCl})} \quad (20)$$

thus,

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1(\text{N}_2\text{O}_5) - \frac{k_2(\text{NO}_2) k_1(\text{N}_2\text{O}_5)}{k_2(\text{NO}_2) + k_3(\text{NOCl})} \quad (21)$$

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1(\text{N}_2\text{O}_5) \left(1 - \frac{k_2(\text{NO}_2)}{k_2(\text{NO}_2) + k_3(\text{NOCl})}\right) \quad (22)$$

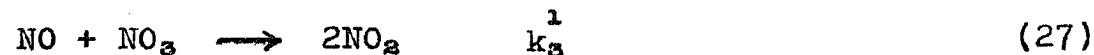
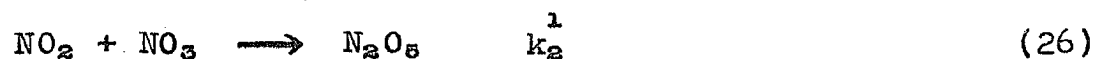
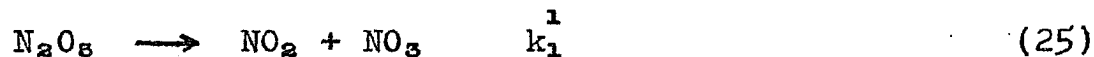
$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1(\text{N}_2\text{O}_5) \frac{k_3(\text{NOCl})}{k_2(\text{NO}_2) + k_3(\text{NOCl})} \quad (23)$$

Now if $k_3(\text{NOCl}) \gg k_2(\text{NO}_2)$, which is certainly true at the beginning of the reaction when the concentration of nitrogen dioxide is very small, and always true if the concentration of nitrosyl chloride is in large enough excess, then the rate equation reduces to

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1(\text{N}_2\text{O}_5) \quad (24)$$

which is equal to the experimental rate equation.

The mechanism proposed above is analogous to the mechanism proposed for the nitrogen pentoxide gas phase oxidation of nitric oxide. Nitric oxide is in many ways similar to nitrosyl chloride and might be expected to act like nitrosyl chloride. Smith and Daniels⁶, who were the first to study this reaction, proposed the following mechanism:



applying the same reasoning as above we find

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1^1(\text{N}_2\text{O}_5) \frac{k_3^1(\text{NO})}{k_2^1(\text{NO}_2) + k_3^1(\text{NO})} \quad (28)$$

which reduces to

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = k_1^1(\text{N}_2\text{O}_5) \quad (29)$$

when $k_2^1(\text{NO}_2) \ll k_3^1(\text{NO})$.

Johnston and Perrine⁸ have studied this reaction over a wide range of concentration of nitrogen pentoxide and nitric oxide and carried out the reaction in a twenty-two liter flask so as to eliminate the heterogeneous reaction. The reaction was followed manometrically. The rate of Step 27 is known²⁴ and is extremely rapid compared to both Step 25 and Step 26. Thus the presence of nitric oxide should prevent Step 26 from taking place and the rate should be determined by Step 25. Now k_1^1 is the rate constant for a unimolecular decomposition and, as explained by the Lindemann²⁵ mechanism, is dependent on the total pressure. Johnston and Perrine found that at 27°C and at a total pressure of ten millimeters, k_1^1 was equal to $1.5 \times 10^{-3} \text{mm}^{-1} \text{sec}^{-1}$. They found an activation energy of nineteen kilocalories. Applying the Arrhenius equation k_1^1 is found to be equal to $5.0 \times 10^{-4} \text{mm}^{-1} \text{sec}^{-1}$ at twenty degrees. In this study under comparable conditions, a rate constant of $1.2 \times 10^{-3} \text{mm}^{-1} \text{sec}^{-1}$ at twenty degrees was obtained. This is about the same order of magnitude one would expect if the reaction proceeded by the same mechanism. K_3 of the proposed mechanism was determined by Johnston and Leighton²⁶ in their

work on the nitrogen pentoxide catalyzed oxidation of nitrosyl chloride by ozone. They found k_3 to be equal to 1.4×10^{10} mm^{-1}sec . This is obviously very rapid, and cannot be the rate-determining step.

In determining the order with respect to nitrosyl chloride in the waxed vessel the assumption was made that we could express the rate law as follows:

$$R = k_{\text{exp}}(\text{N}_2\text{O}_5)^x(\text{NOCl})^y \quad (30)$$

For theoretical interpretations, however, it is more useful to employ the more complex mechanism describing both homogeneous and the heterogeneous reaction

$$R = k_{\text{exp}}(\text{N}_2\text{O}_5) + k_{\text{exp}}^1(\text{N}_2\text{O}_5)(\text{NOCl}) \quad (31)$$

now k_{exp}^1 , the heterogeneous rate constant, contains a surface dependence term and can be written,

$$k_{\text{exp}}^1 = k_s^1(s) \quad (32)$$

so that,

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = R = k_{\text{exp}}(\text{N}_2\text{O}_5) + k_s^1(s)(\text{N}_2\text{O}_5)(\text{NOCl}) \quad (33)$$

$$\frac{-d(\text{N}_2\text{O}_5)}{dt} = [k_{\text{exp}} + k_s^1(s)(\text{NOCl})](\text{N}_2\text{O}_5) \quad (34)$$

integrating without limits,

$$\ln(\text{N}_2\text{O}_5) = [k_{\text{exp}} + k_s^1(s)(\text{NOCl})] t + c \quad (35)$$

Thus the slope of the curve obtained by plotting $\ln(\text{N}_2\text{O}_5)$ vs. t should be equal to

$$\text{slope} = k_{\text{exp}} + k_s^1(s)(\text{NOCl}) \quad (36)$$

If the total surface area — glass walls and windows — of the reaction vessel have the same surface characteristics,

it might be possible to argue that the overall heterogeneous rate constant k_{exp}^1 is simply a function of the fraction of the surface exposed. After waxing the walls of the reaction vessel (but not the windows) it was calculated that 1/12 the original glass area was left exposed. Thus, in the waxed vessel, the heterogeneous contribution has 1/12 its former value and we can replace $k_s^1(s)$ in equation (36) with $(k_{\text{exp}}^1 \frac{1}{12})$. The assumption that the glass walls and the glass windows have the same surface characteristics is invalid, however, because their history is different. The glass windows were subjected to a thorough grinding and polishing treatment to make them optically flat. This will change their surface characteristics profoundly. Also, the glass walls of the reaction vessel were treated with a chromic acid cleaning solution, but the windows were not. Chromic acid is known to have a leeching effect on glass and will alter the surface characteristics. It is commonly known that catalytical activity is highly specific with regard to the nature of the surface and its past history. Consequently we might expect the catalytical behavior of the glass walls might differ in some respects from that of the glass windows. If this be true, then equation (36) cannot be applied until further experimental evidence on the nature of the surface is forthcoming.

TABLE IV

Data

RUN #1			RUN #3		
Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)	Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)
0	0	.165	0	0	.087
5	43	.101	5	22	.055
10	60	.073	10	34	.035
15	70	.057	15	41	.024
∞	104		20	46	.016
			∞	54	
Calibration Factor		$\frac{46}{46}$	Calibration Factor		$\frac{46}{46}$

RUN #5			RUN #6		
Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)	Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)
0	0	.193	0	0	.100
5	38	.137	5	18	.075
10	64	.096	10	30	.056
15	79	.070	15	40	.039
20	90	.051	20	49	.024
25	100	.035	25	55	.014
30	108	.021	30	59	.008
∞	120		∞	64	
Calibration Factor		$\frac{46}{46}$	Calibration Factor		$\frac{46}{46}$

TABLE IV (cont.)

RUN #7			RUN #8		
Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)	Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)
0	0	.045	0	0	.128
5	8	.033	5	36	.081
10	13	.026	10	54	.054
15	17	.019	15	66	.038
20	21	.013	20	74	.026
25	24	.0061	25	79	.019
30	26	.0049	30	84	.011
∞	29		∞	92	
Calibration Factor $\frac{46}{46}$			Calibration Factor $\frac{46}{52}$		

RUN #9			RUN #10		
Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)	Time (sec)	Reading Scale C	(N ₂ O ₅) (mm)
0	0	.083	0	0	.083
.5	20	.055	1	19	.057
1	30	.040	2	29	.041
1.5	38	.027	3	36	.034
2.0	42	.021	4	40	.024
2.5	44	.017	5	43	.019
3.0	47	.013	∞	54	
4.0	49	.010			
5.0	51	.006			
∞	54				
Calibration Factor $\frac{46}{46}$			Calibration Factor $\frac{46}{46}$		

TABLE IV (cont.)

RUN #13			RUN #20		
Time (sec)	Reading Scale D	(N_2O_5) (mm)	Time (sec)	Reading Scale D	(N_2O_5) (mm)
0	0	.197	0	0	.309
5	32	.096	5	31	.212
10	44	.053	10	57	.123
15	50	.031	15	69	.082
20	54	.017	20	79	.049
25	56	.010	25	86.5	.021
∞	58		∞	93.0	0
Calibration Factor $\frac{46}{44}$			Calibration Factor $\frac{46}{42}$		

RUN #21			RUN #22		
Time (sec)	Reading Scale D	(N_2O_5) (mm)	Time (sec)	Reading Scale C	(N_2O_5) (mm)
0	0	.169	0	0	.113
5	23	.095	5	28	.068
10	34	.061	10	44	.040
15	41	.034	15	56	.020
20	46	.016	20	62	.010
25	49	.007	∞	68	
∞	52				
Calibration Factor $\frac{46}{42}$			Calibration Factor $\frac{46}{42}$		

TABLE IV (cont.)

RUN #23			RUN #23A		
Time (sec)	Reading Scale C	(N_2O_5) (mm)	Time (sec)	Reading Scale C	(N_2O_5) (mm)
0	0	.172	0	0	.127
5	49	.093	5	15	.105
10	74	.050	10	27	.085
15	86	.029	15	36	.069
20	92	.019	20	44	.055
∞	100	0	25	50	.045
			30	53	.040
			∞	76	
Calibration Factor $\frac{46}{46}$			Calibration Factor $\frac{46}{46}$		

RUN #24			RUN #25		
Time (sec)	Reading Scale D	(N_2O_5) (mm)	Time (sec)	Reading Scale D	(N_2O_5) (mm)
0	0	.234	0	0	.417
5	34	.125	5	66	.187
10	49	.073	10	86	.116
15	58	.042	15	100	.059
20	62	.029	20	109	.028
∞	70		∞	117	
Calibration Factor $\frac{46}{46}$			Calibration Factor $\frac{46}{43}$		

TABLE IV (cont.)

RUN #25A			RUN #11		
Time (sec)	Reading Scale C	(N_2O_5) (mm)	Time (sec)	Reading Scale E	(N_2O_5) (mm)
0	0	.160	0	0	.314
5	34	.107	5	22	.141
10	53	.074	10	30	.070
15	66	.051	15	34	.036
20	76	.034	20	36	.018
25	83	.022	∞	38	
∞	96				
Calibration Factor		$\frac{46}{46}$	Calibration Factor		$\frac{46}{46}$

RUN #1-S			RUN #2-S		
Time (min)	Reading Scale D	(N_2O_5) (mm)	Time (min)	Reading Scale D	(N_2O_5) (mm)
0	0	.171	0	0	.470
5	24	.090	5	33	.342
10	32	.056	10	57	.235
15	37	.037	15	77	.147
20	41	.22	20	93	.076
25	44		25	100	.045
∞	47		∞	111	
Calibration Factor		$\frac{46}{42}$	Calibration Factor		$\frac{46}{36}$

TABLE IV (cont.)

RUN #3-S			RUN #4-S		
Time (min)	Reading Scale D	(N ₂ O ₅) (mm)	Time (min)	Reading Scale D	(N ₂ O ₅) (mm)
0	0	.182	0	0	.225
2	21	.100	2.5	17	.161
5	29	.067	5	27	.120
10	34	.046	10	36	.082
15	38	.029	15	44	.045
20	42	.013	20	48	.032
∞	45		∞	56	
Calibration Factor $\frac{46}{38}$			Calibration Factor $\frac{46}{38}$		

RUN #5-S			RUN #6-S		
Time (min)	Reading Scale C	(N ₂ O ₅) (mm)	Time (min)	Reading Scale C	(N ₂ O ₅) (mm)
0	0	.240	0	0	.262
2.5	27	.201	2.5	27	.224
5	43	.173	5	48	.181
10	80	.108	10	80	.133
15	102	.072	15	111	.080
20	124	.034	20	130	.046
∞	144		∞	157	
Calibration Factor $\frac{46}{46}$			Calibration Factor $\frac{46}{46}$		

SAMPLE CALCULATION

In this section the method used to obtain meaningful concentration - time values from the raw data will be outlined and an illustrative example will be given, using the recorder curve taken during run #3.

1) The zero point on the recorder graph for the run is corrected for any nitrogen dioxide initially present, due to thermal decomposition of the nitrogen pentoxide. This is done by a simple inspection of the curve obtained during the run. The nitrogen pentoxide is stored in a reservoir under pressure prior to its reaction with the nitrosyl chloride. Opening the stopcock between the reservoir and the reactant vessel containing the nitrosyl chloride allows the nitrogen pentoxide to flow into the reactant vessel almost instantaneously. The recorder pen, activated by the small amount of nitrogen dioxide present because of the decomposition of the nitrogen pentoxide, traces a curve almost parallel with the x-axis of the recorder graph paper from between one quarter to one and one-half inches in length. The nitrogen dioxide from the reaction is produced relatively slowly, as is shown by the deviation of the recorder tracing from the base line; the point at which the deviation starts is taken as the zero point of the reaction. At five-second intervals readings are taken assuming a reading of zero at the zero point.

Time sec.	Scale C on Recorder
0	0
5	22
10	34
15	41
20	46
∞	54

2) The readings are recalculated to a common scale, the D Scale on the recorder, if need be. The recorder has the following full-scale deflection voltage values: H (Scale) - 50 mv.; G - 20 mv.; F - 10 mv.; E - 5 mv.; D - 2 mv.; C - 1 mv.; B - .5 mv.. Thus to correct the readings from the C Scale to the D Scale, multiply by .5.

Time sec.	Corrected to Scale D on Recorder
0	0
5	11
10	17
15	20.5
20	23
∞	27

3) The D Scale readings are corrected by a calibration factor. This calibration factor is obtained at the time the run is being made by placing a square of smoked glass in the path of the light beam and noting the deflection reading of the recorder. This deflection is compared to the de-

flection obtained by the same square of glass when the calibration for the nitrogen dioxide and nitrosyl chloride were determined. If the deflection reading taken immediately prior to a run differs from the deflection reading taken during the calibration (46 units on the D Scale), then the readings for the run are multiplied by the fraction

$$\frac{\text{forty-six}}{\text{deflection reading at time of the run.}}$$

In the case of run #3, no correction had to be applied.

4) The concentration of nitrogen dioxide at any time "t" is determined using equation (6) (Calibration section) for the runs at 0°C and equation (7) for the runs at 20°C. The final concentration of nitrogen dioxide is determined by using the concentration of nitrogen dioxide corresponding to the reading of the run at infinite time. A small error is thus introduced, but it is negligible.

Time sec.	(NO ₂) mm pressure
0	0
5	.063
10	.101
15	.123
20	.139
	.168

5) For the runs made at zero and ten degrees the concentration of nitrogen dioxide must be corrected for the dimerization of nitrogen dioxide. At 20°C this correction is taken care of in the calibration curve. The correction for

dimerization is accomplished by multiplying the concentration of nitrogen dioxide by the degree of dissociation at that pressure and temperature and adding the product obtained to the concentration of nitrogen dioxide. The degree of dissociation of nitrogen tetroxide was obtained from F. H. Verhock and F. Daniels⁶.

Time sec.	(NO ₂) mm pressure
0	0
5	.064
10	.103
15	.125
20	.142
∞	.173

6) The concentration of nitrogen pentoxide is calculated from the assumption that all the nitrogen dioxide originated in the nitrogen pentoxide:

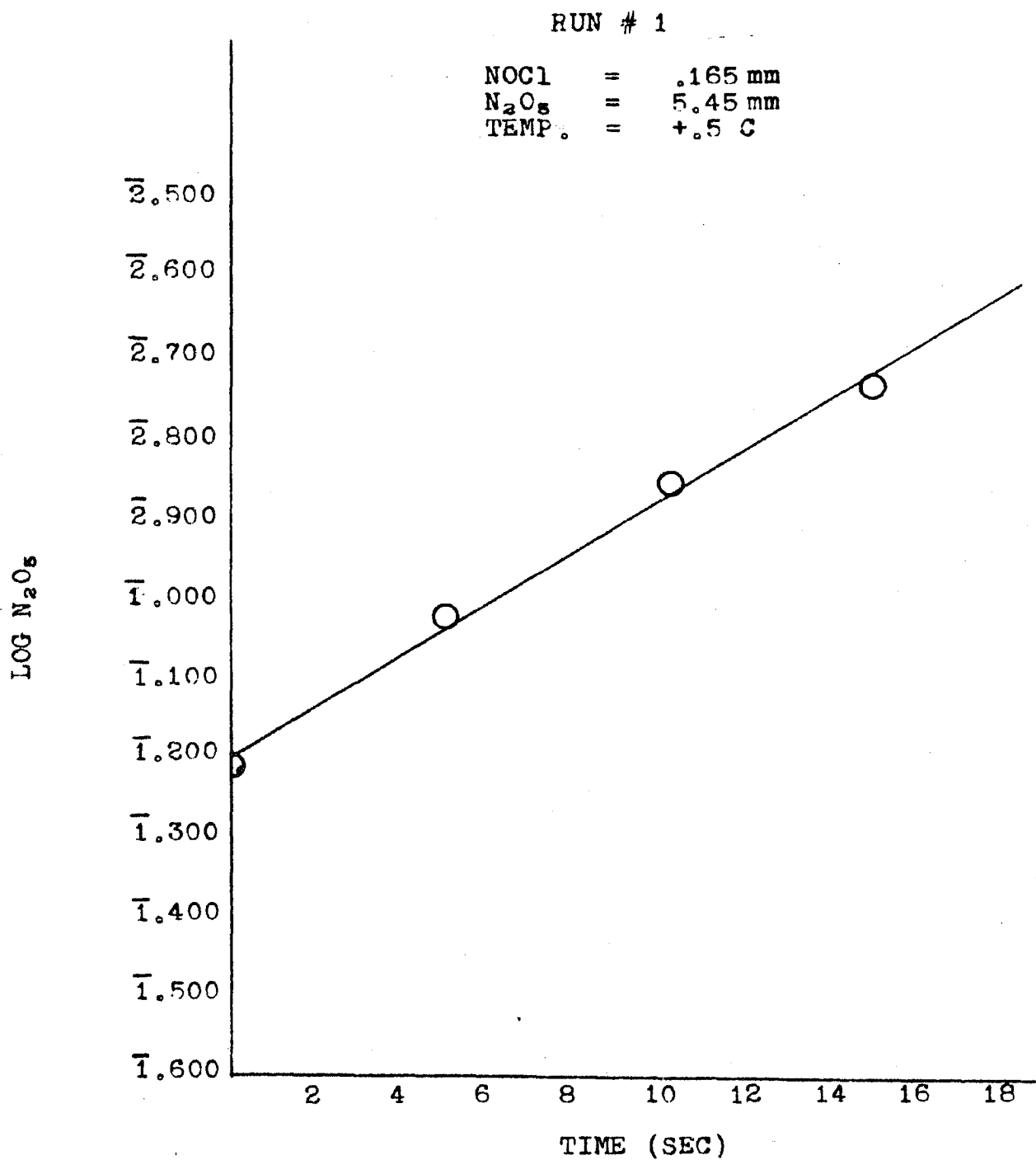
$$1/2 (\text{NO}_2)_{\text{final}} = (\text{N}_2\text{O}_5)_{\text{initial}}$$

The nitrogen pentoxide concentrations at any time "t" are calculated by dividing the corresponding nitrogen dioxide concentrations by two and subtracting this value from the initial concentration of nitrogen pentoxide.

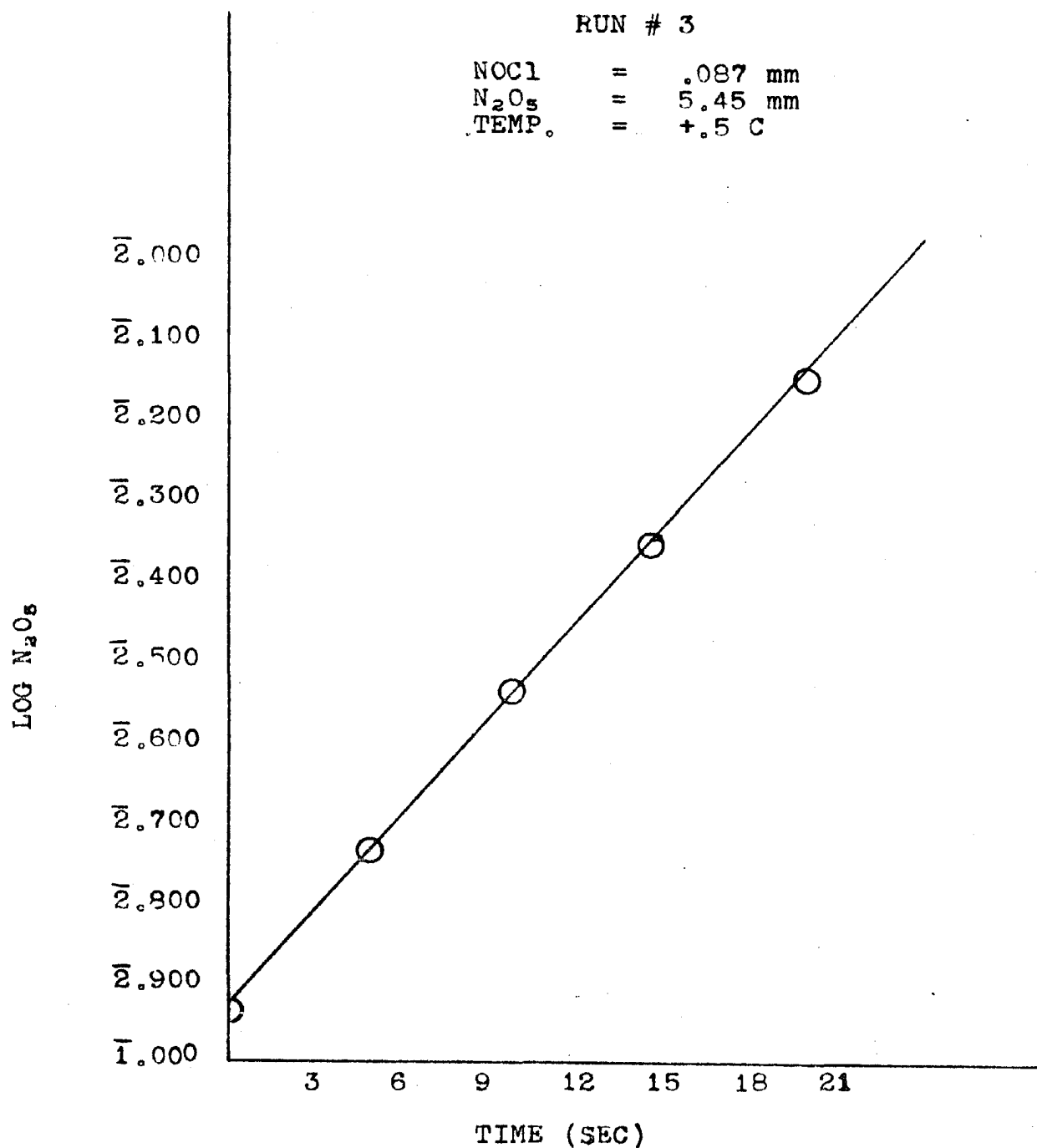
Time sec.	Conc. N_2O_5 mm pressure
0	.087
5	.055
10	.035
15	.024
20	.016

7) It is this concentration term which is used in the graphs of this thesis.

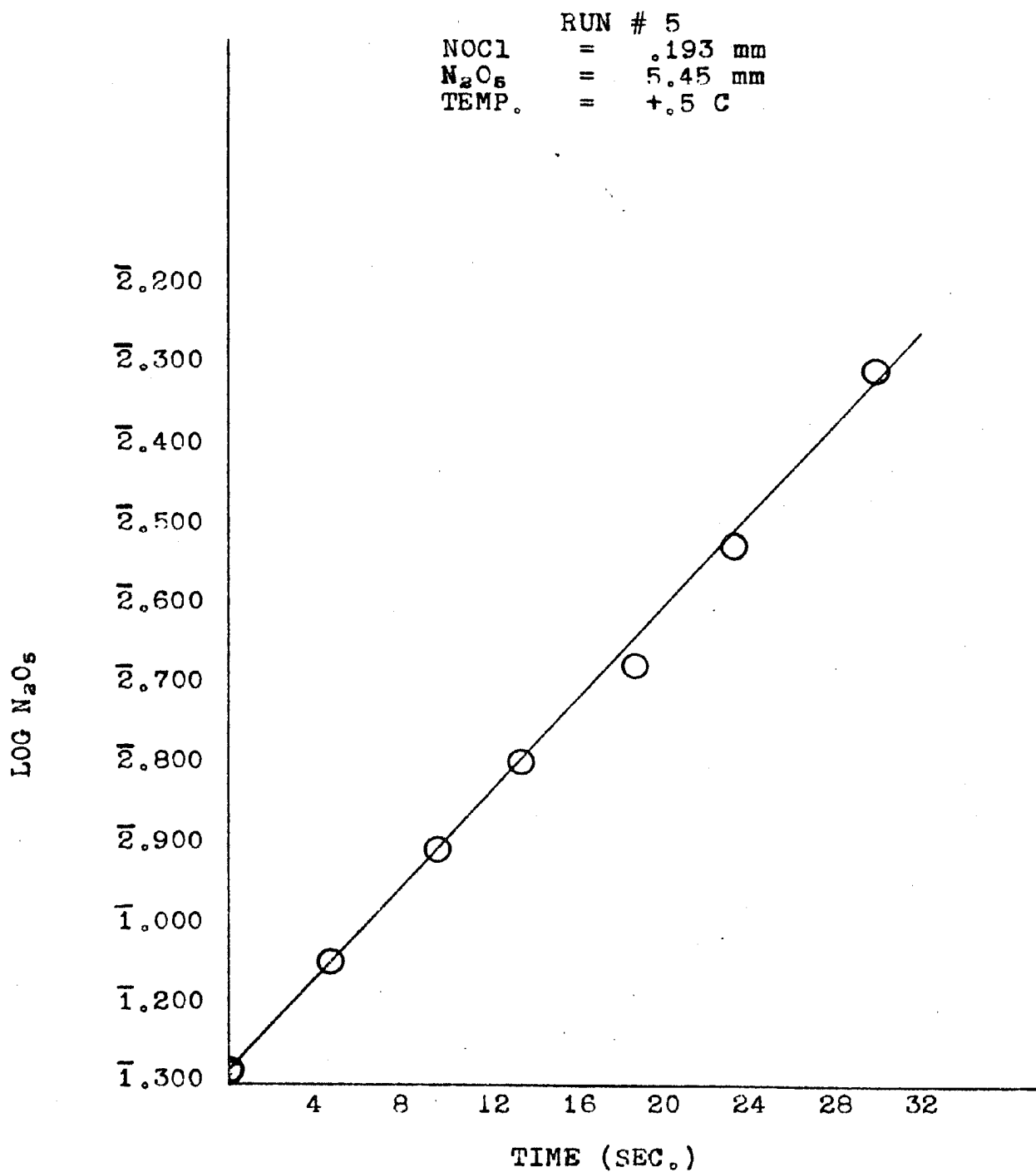
GRAPH # 1

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

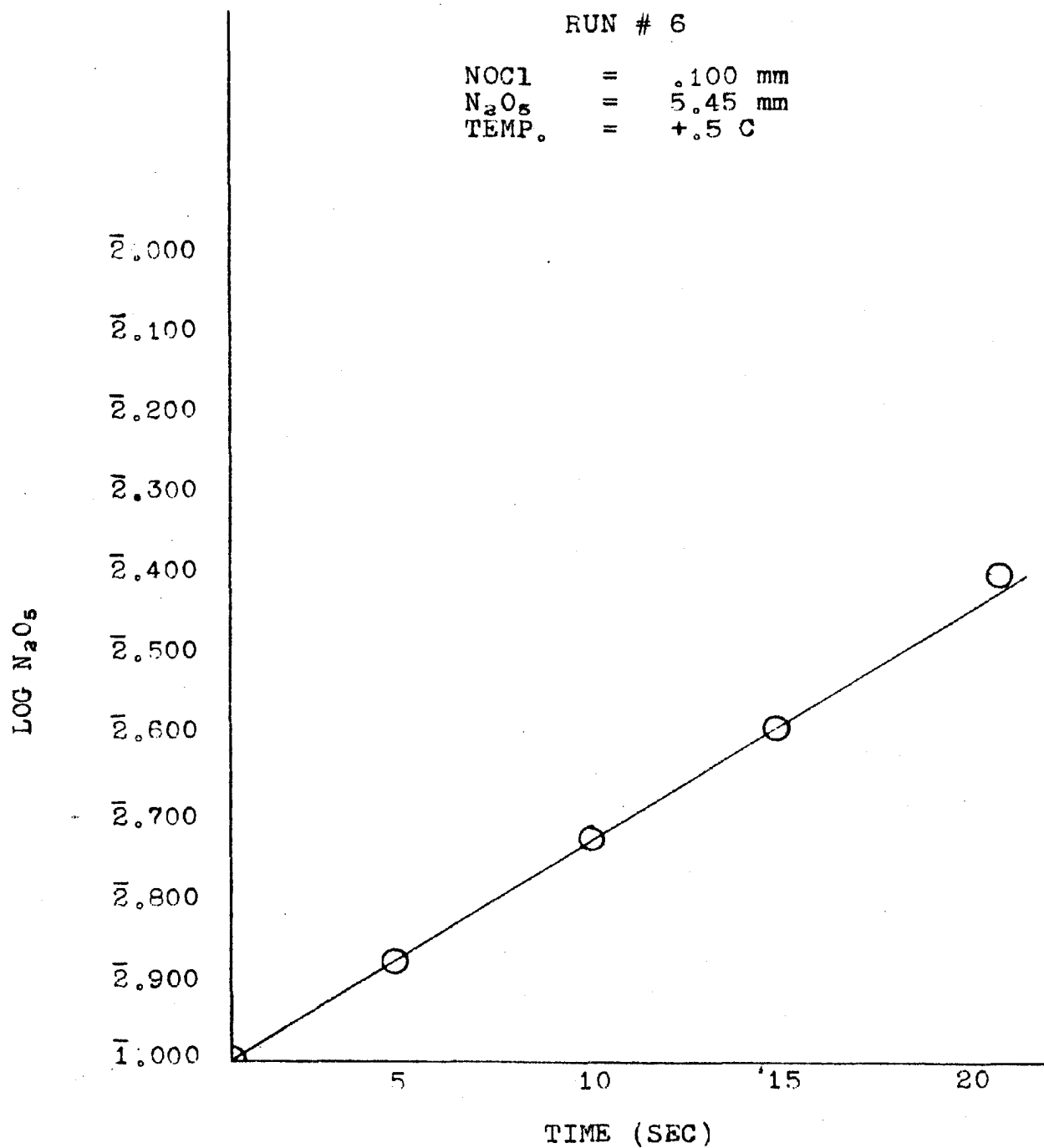
GRAPH # 2

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

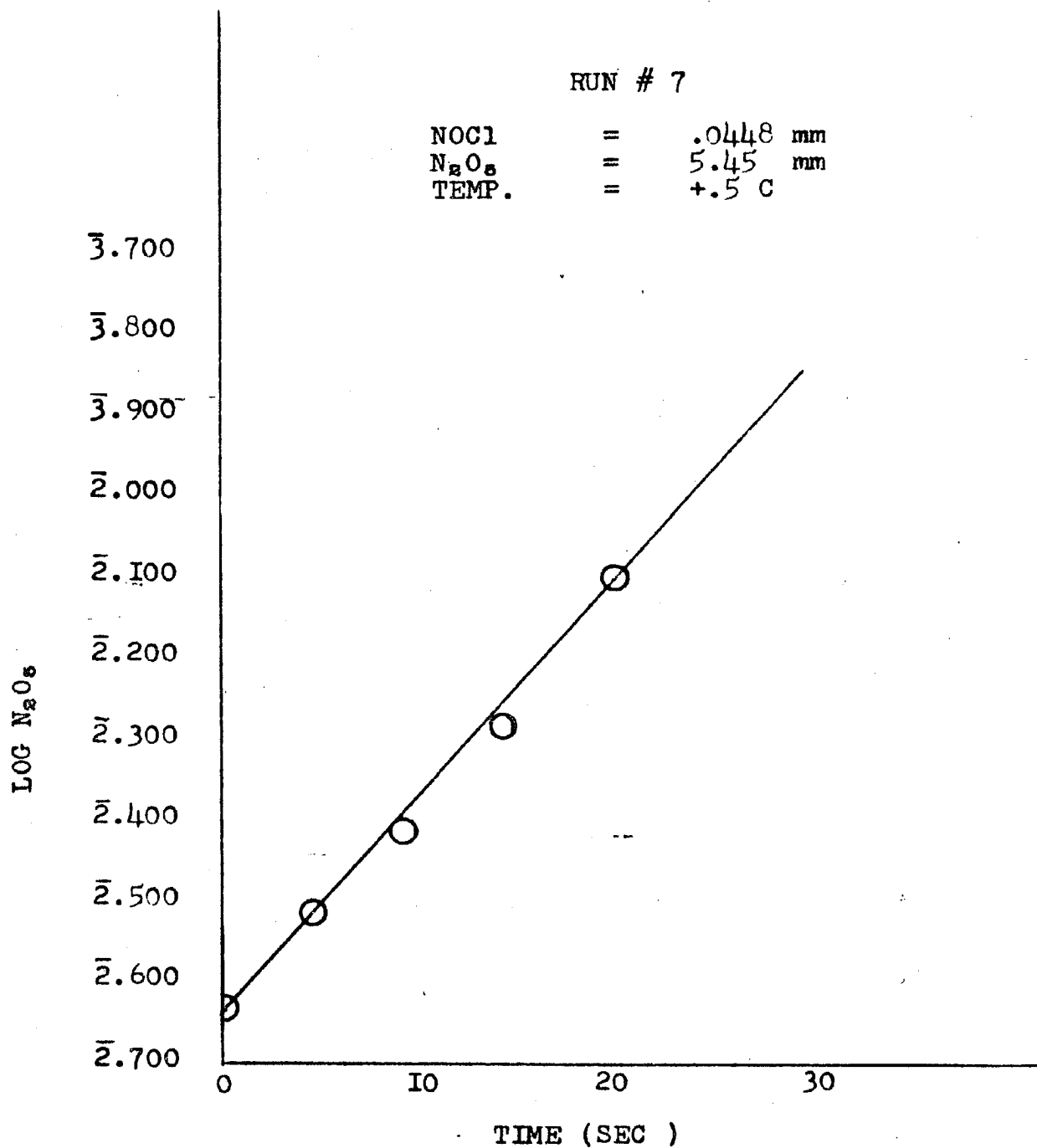
GRAPH # 3

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

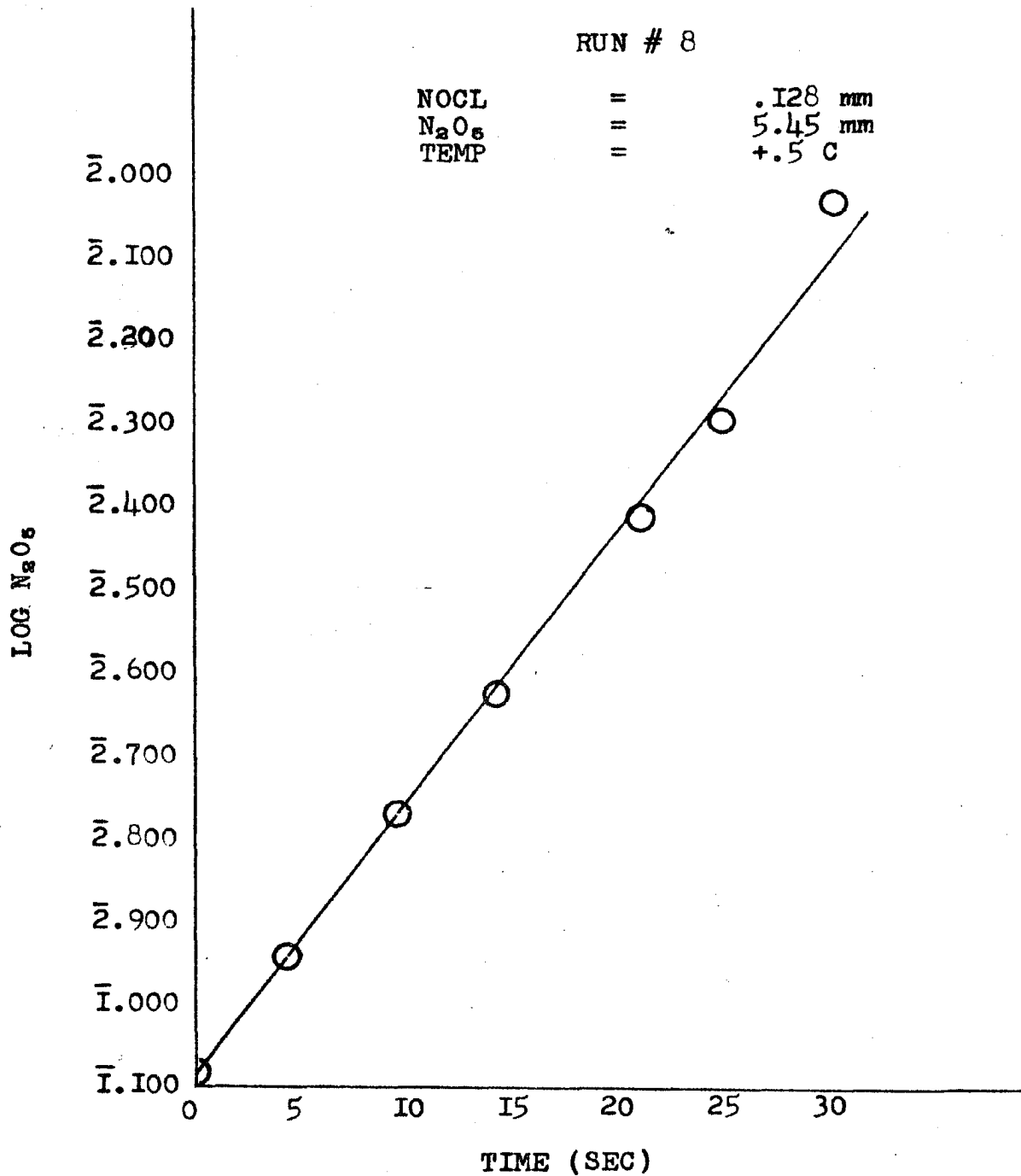
GRAPH # 4

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

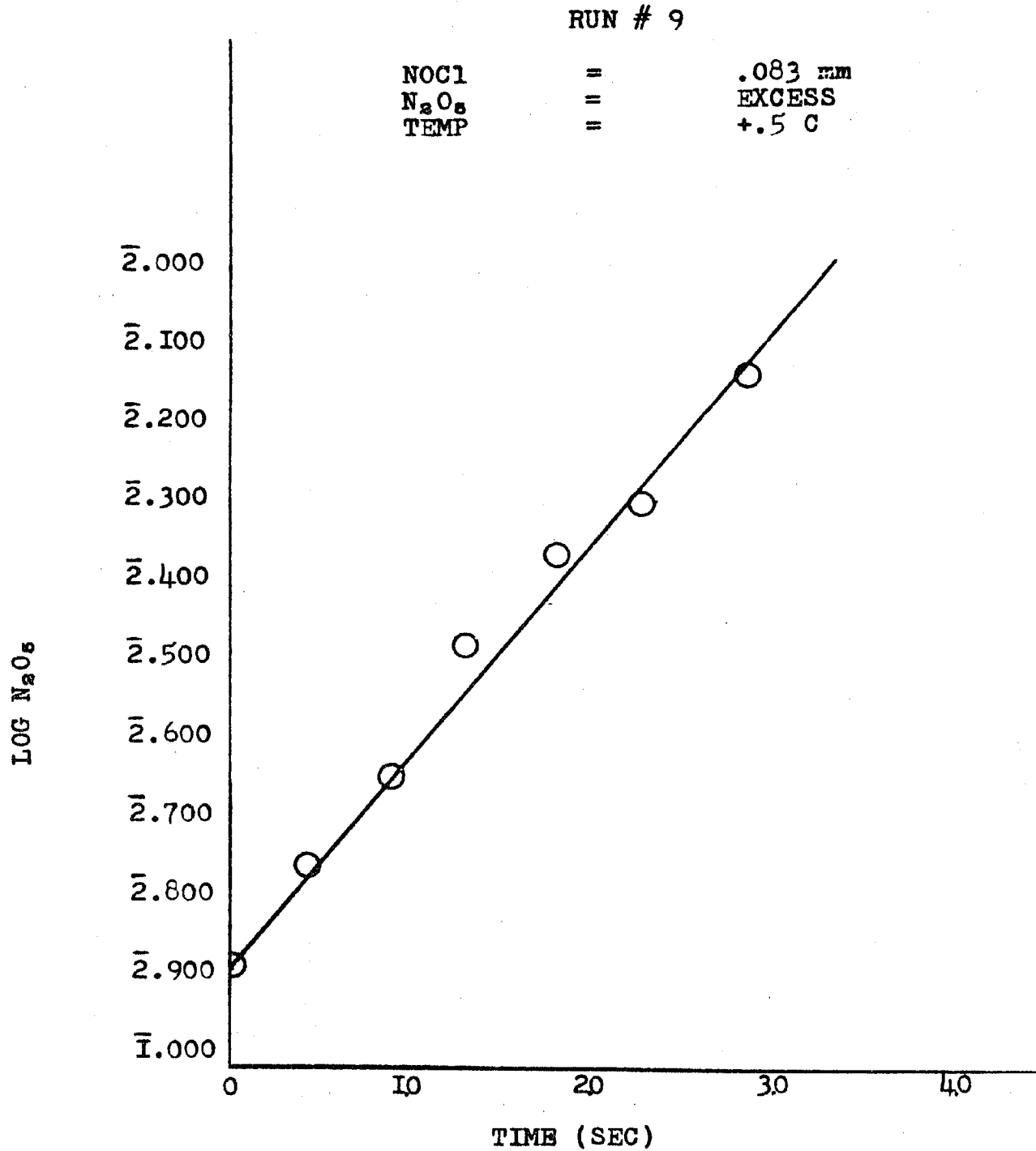
GRAPH # 5

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

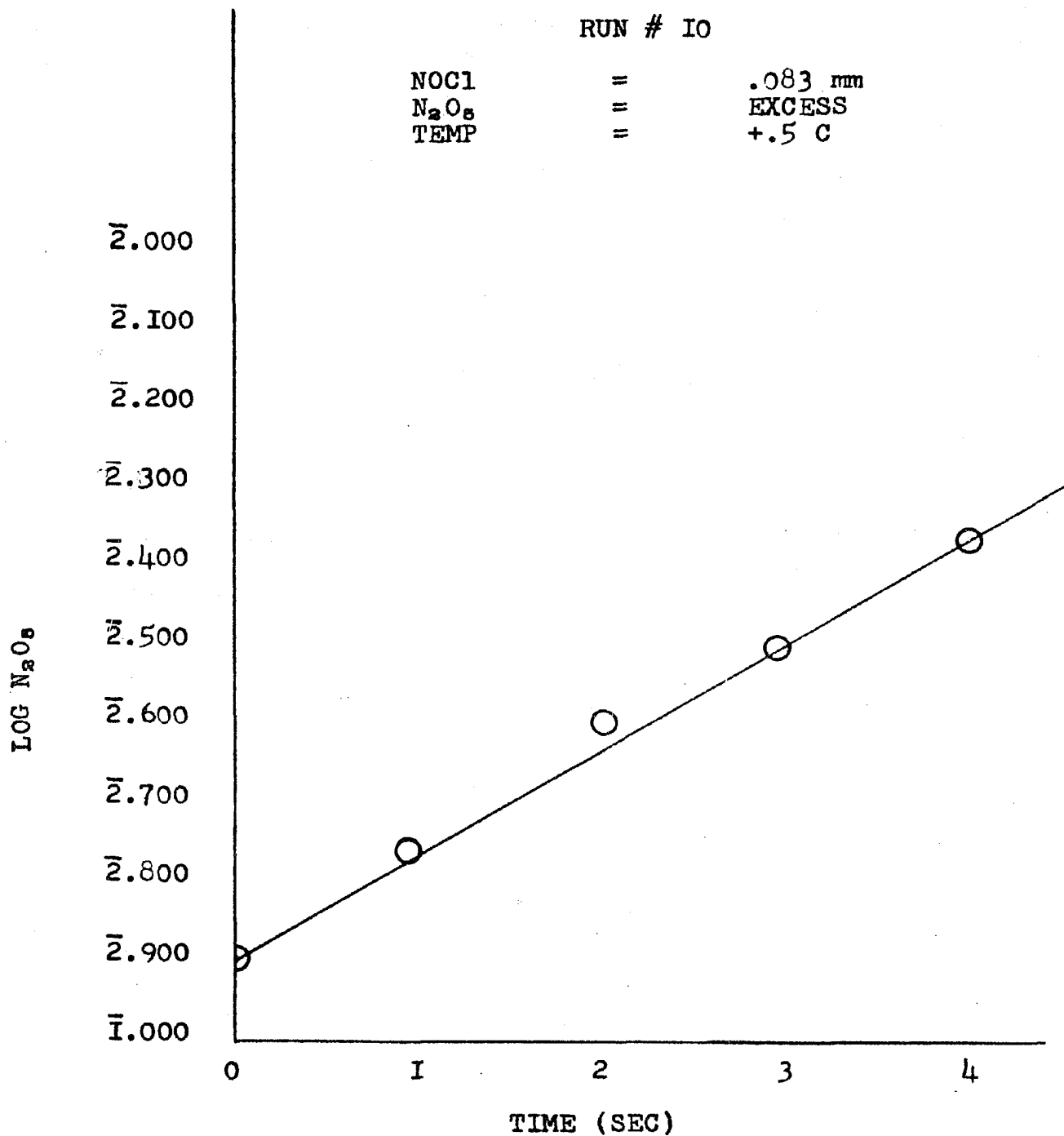
GRAPH # 6

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

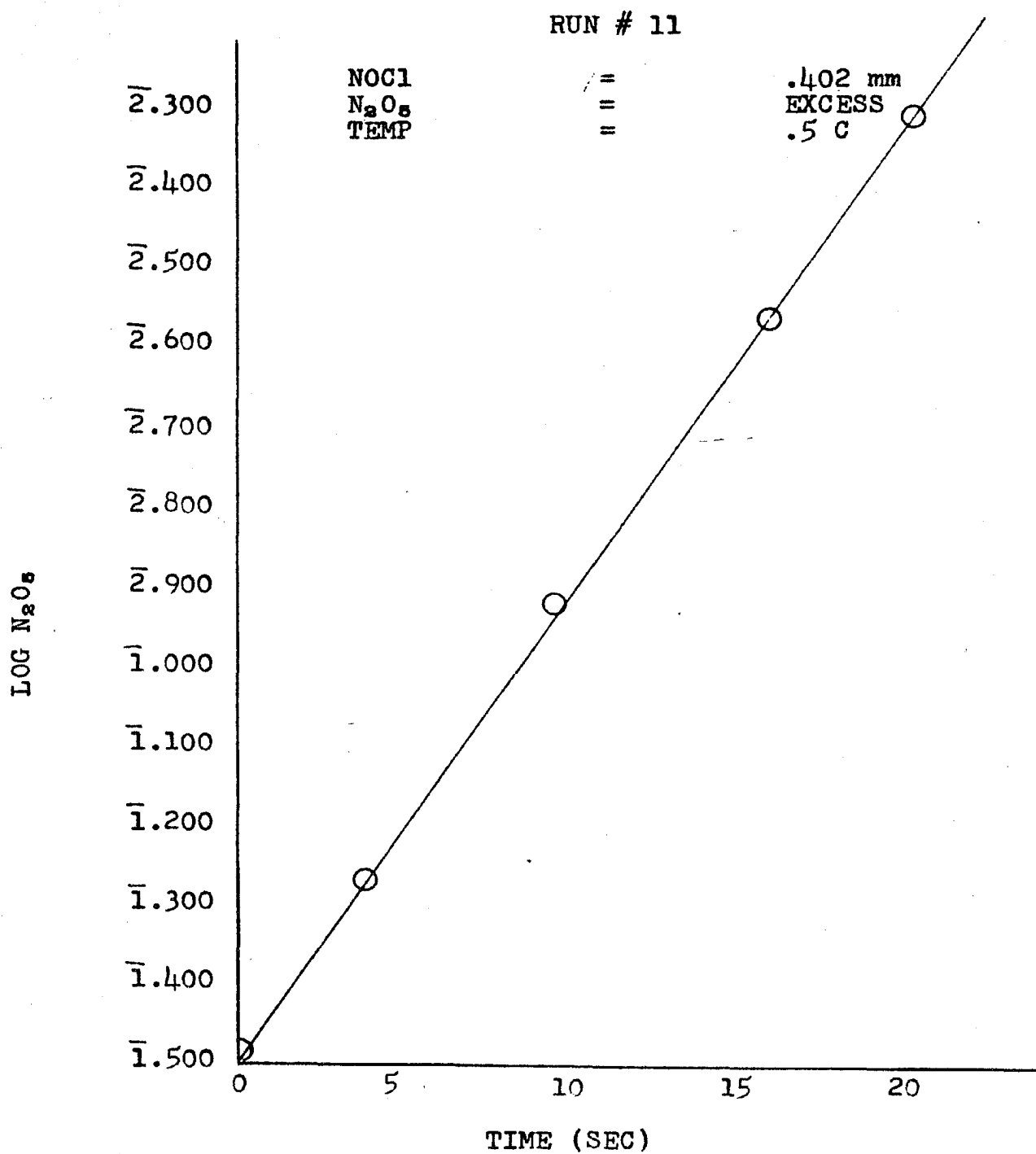
GRAPH # 7

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

GRAPH # 8

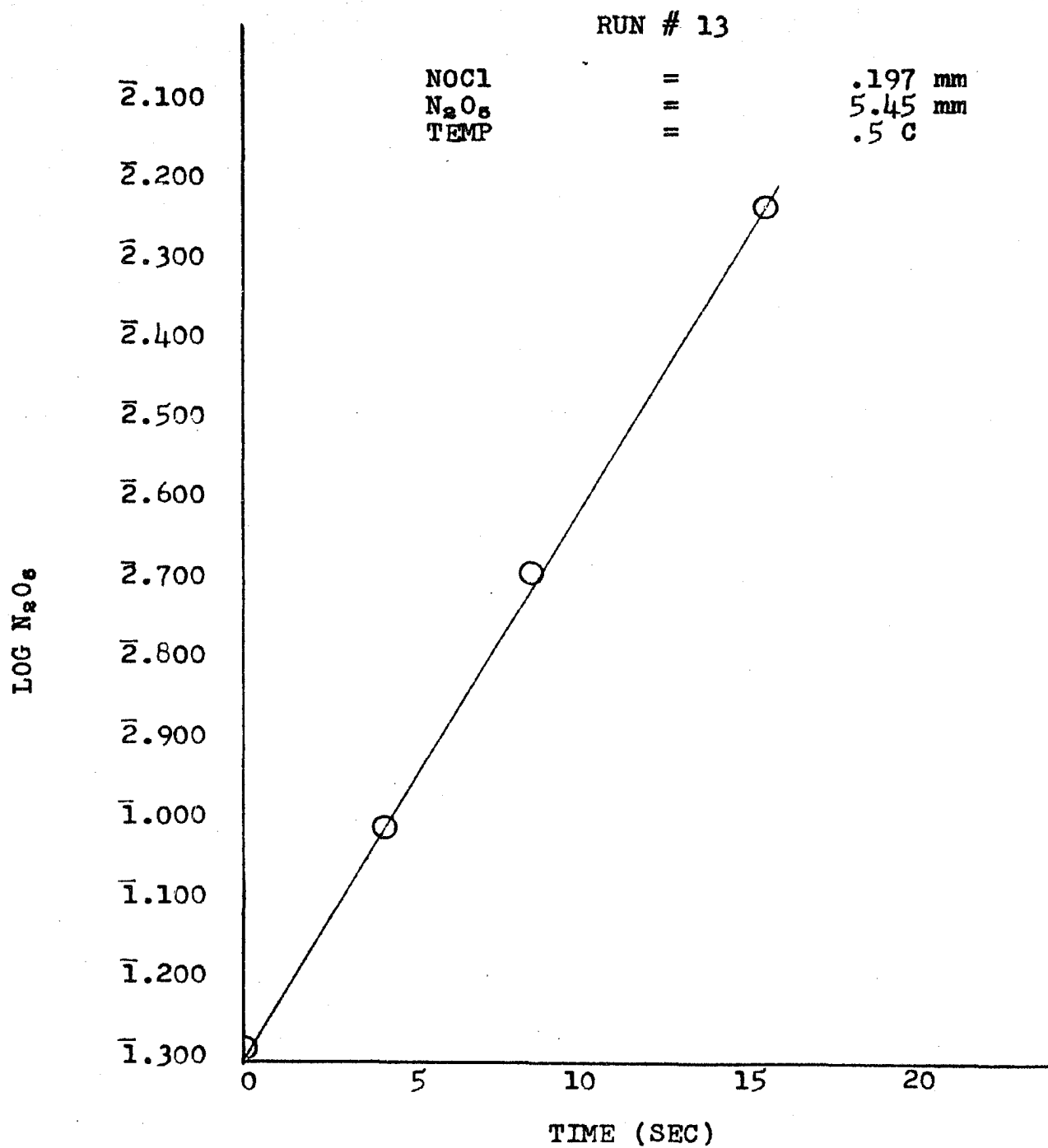
DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

GRAPH # 9

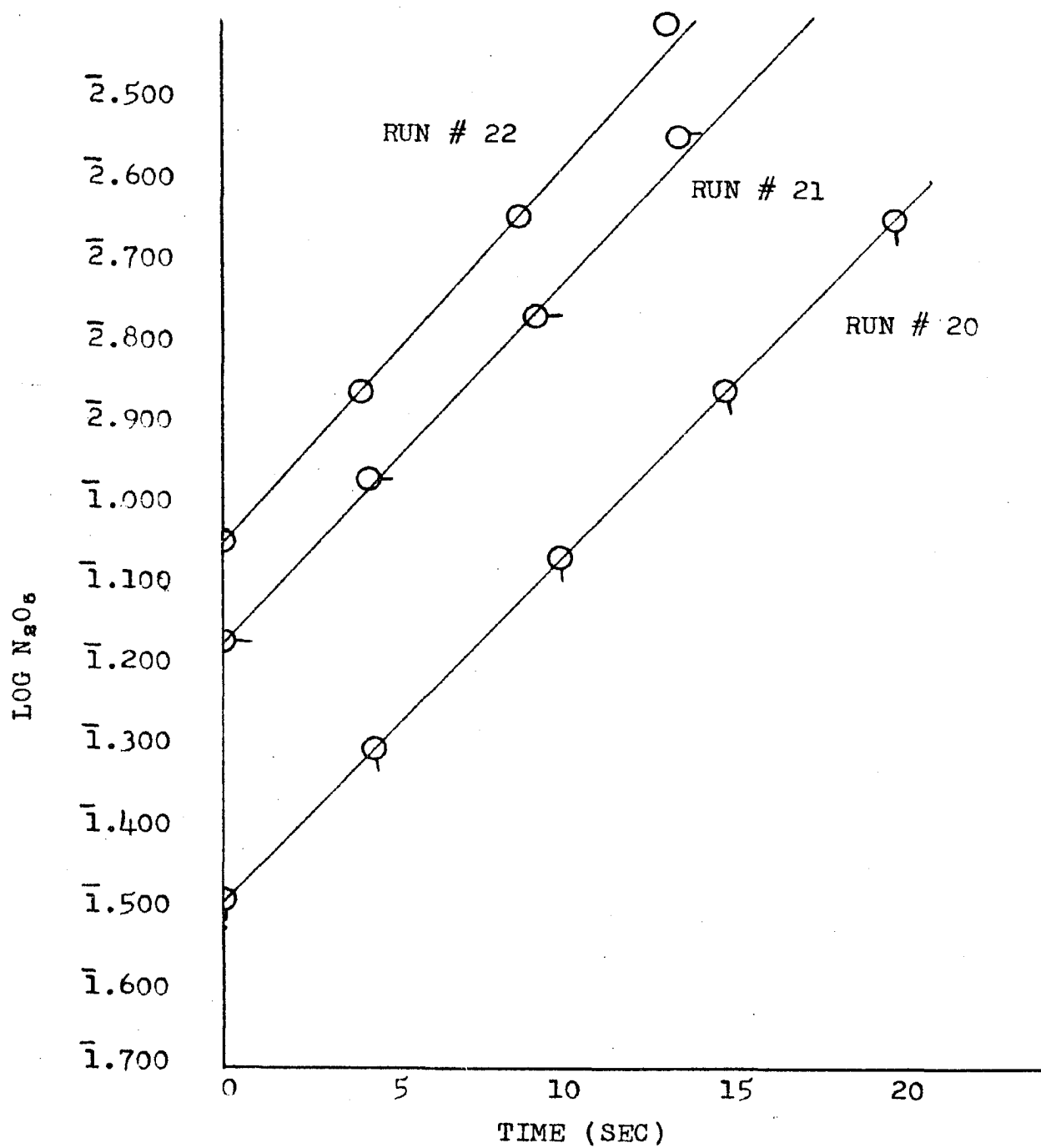
DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME

GRAPH # 10

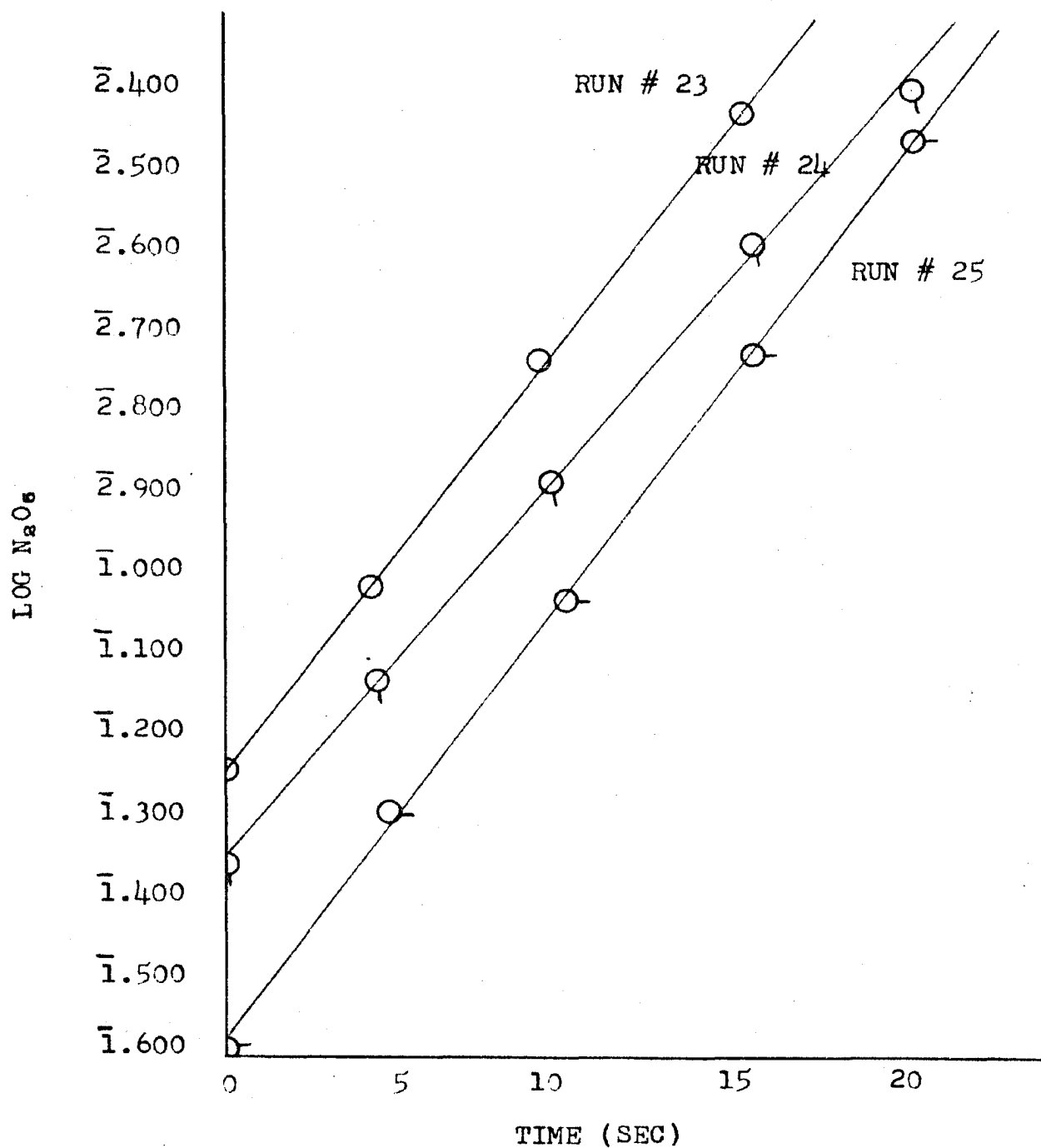
DEPENDENCE OF THE LOG CONCENTRATION ON TIME



GRAPH # 13

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 ON TIME AT 10 C

GRAPH # 14

DEPENDENCE OF THE LOG CONCENTRATION N_2O_5 AT 20 C

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APPENDIX

In total about seventy-five experimental runs were made on the rates of various reactions for this thesis. About thirty of the runs are included in this thesis. The rest are omitted or only briefly mentioned for two reasons. First many of the runs were qualitative attempts to ascertain the range of concentrations of reactants and temperatures which could be most easily and most accurately determined on the limited experimental apparatus used in this work. Consequently they were of minor interest. Secondly, several of the runs ended in failure for one reason or another. The investigator has understandably omitted these but they are mentioned in his experimental thesis book.

As was mentioned in the experimental section of this thesis, the glass tubing leading to the reaction vessel was of the microbore type. In order that fast complete mixing of the reactants be accomplished, it was necessary to add an inert gas, nitrogen, to one of the reactants so that the reactant could be carried quickly through the microbore tubing into the reactant vessel. It should be remembered that all the runs recorded in this thesis were carried out at a total pressure of approximately 8 mm.