I. THE RATE AND MECHANISM OF THE AIR OXIDATION OF PARTS-PER-MILLION CONCENTRATIONS OF NITRIC OXIDE.

II. THE QUANTITATIVE DETERMINATION OF PARTS-PER-MILLION QUANTITIES OF NITROGEN DIOXIDE IN NITROGEN, OXYGEN, AND UP TO 75 p.p.m. OF NITRIC OXIDE BY ELECTRON-CAPTURE DETECTION IN GAS CHROMATOGRAPHY.

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ABSTRACT

Part I

A study of the air oxidation of parts-per-million (p.p.m.) concentrations of nitric oxide was carried out in a constant-volume, batch reactor. The initial concentration of nitric oxide was varied from 2 to 75 p.p.m. while the oxygen concentration ranged from 3×10^4 to 25×10^4 p.p.m. The rate of the reaction was measured in the ambient temperature region from 17 to 37°C and at a pressure of one atmosphere. Gas analyses were made by means of chromatography.

The initial order of the oxidation reaction in the absence of nitrogen dioxide was 2.00 ± 0.09 for nitric oxide and 0.97 ± 0.11 for oxygen. From initial rate data at 26.5°C, a third-order rate constant of $(1.297 \pm 0.051) \times 10^4 \ell^2 \text{g.mole}^{-2} \text{sec}^{-1}$ was obtained. There were no measurable surface effects due to the Pyrex reaction vessel, but the addition of nitrogen dioxide did increase the initial oxidation rate. The initial third-order rate constant in the absence of nitrogen dioxide exhibited a small negative activation energy.

A mechanism was proposed which involved six reactions with NO_3, N_2O_3, and N_2O_5 as intermediates. When the rate equation which resulted from that mechanism for

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the oxidation of nitric oxide was integrated, the standard deviation of the predicted concentration of nitric oxide from the experimental data in the range from 2 to 75 p.p.m. of nitric oxide was 1.6 p.p.m.

Part II

A gas chromatograph was developed for the quantitative analysis of gas mixtures containing nitrogen dioxide at concentrations from 0.5 to 75 p.p.m. in nitrogen, less than 25×10^4 p.p.m. of oxygen, and up to 75 p.p.m. of nitric oxide. The chromatography column consisted of powdered Teflon, Fluoropak 80, which had been coated with a methyl silicone oil, SF-96. A parallel-plane electron-capture detector when operated in the pulse mode was found to be the most sensitive chromatography device available for the detection of nitrogen dioxide. The analysis was accurate to an absolute deviation of 3.4 percent, with a standard deviation of 1.3 p.p.m. in the concentration range from 3 to 75 p.p.m. of nitrogen dioxide when oxygen was present to the extent of 25 percent by volume in nitrogen. The detection limit for the method was 0.5 p.p.m. of nitrogen dioxide.

Studies were carried out to determine the optimum properties and operating conditions for the chromatography

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column. The parameters that affected the sensitivity of the electron-capture detector were examined. These included temperature, flow rate, cell geometry, size of tritium source, voltage, and the means of applying this potential to the cell.

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Part I

The Rate and Mechanism of the Air Oxidation of Parts-Per-Million Concentrations of Nitric Oxide

I. INTRODUCTION

Pollution of the air in metropolitan areas is an increasing problem. Nitric oxide and unburned hydrocarbons, formed by high-compression internal combustion engines and industrial plants, are of major importance in air pollution. Nitric oxide reacts in the atmosphere with molecular oxygen to form nitrogen dioxide, which oxidizes hydrocarbons photochemically to ketones, aldehydes, and alcohols. These compounds, nitrogen oxides and oxidized hydrocarbons, are the constituents of so-called "smog", which are detrimental to the health of both the human and plant population. However, the basic chemical reactions which occur in these atmospheres are not well understood. Because of the small amount of quantitative work which has been carried out on the air oxidation of nitric oxide in p.p.m.* concentrations, the rate of the reaction was measured and a mechanism proposed.

The mechanism of the oxidation of nitric oxide to nitrogen dioxide has been a subject of controversy ever since Raschig[21] found that the reaction was third order. He reported that the oxidation of nitric oxide was second order in nitric oxide and first order in oxygen, with N_2O_3 as an intermediate. Lunge and Berle[18]

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*Throughout this thesis p.p.m. is defined as mole fraction x 10^6.

found the same third-order dependence but reported the oxidation to involve no intermediate. They suggested that the reaction was truly termolecular and involved a three-body collision. Bodenstein[3] also assumed a three-body reaction, but later[4] proposed a mechanism involving an $(NO)_2$ intermediate. Sanfourche[27] explained the oxidation of nitric oxide with an intermediate N_2O_3, while Wourtzel[36] in substantiating the general third-order behavior reported that N_2O_3 was not an intermediate but a product of the several oxide reactions. Brown and Crist[5] found that the reaction was third order and postulated the existence of an NO_3 intermediate. Stoddart[31] reported that the oxidation of nitric oxide was a completely heterogeneous reaction involving adsorbed nitric oxide molecules on the glass reaction vessel. In all of the investigations discussed above either manometric or chemical methods of analysis were used. The total pressure of all the above investigations was approximately 20 mm of mercury. None of the investigators studied the effect of the initial addition of nitrogen dioxide, but some did obtain anamolous results if the gases were not dry.

Several investigators have noticed a departure from the third-order kinetics as the reaction approached completion or as the total pressure was reduced. Smith[29]

found that the third-order rate constant increased as the total pressure was reduced to near 1 mm of mercury. He attributed this phenomenon to a catalytic reaction involving adsorbed nitric oxide on the walls of the glass reaction vessel. Smith obtained erratic results upon the addition of water, but did not study the effect of nitrogen dioxide on the initial oxidation rate. Hasche and Patrick[11] found the general third-order behavior initially, but in several runs at 0°C the rate constants tended to increase as the reaction neared completion. In one run they found the third-order rate constant, after 80 percent of the initial nitric oxide had been oxidized, to be four times the initial third-order rate constant. They suggested the rate increase was due to the formation of N_2O_3. Treacy and Daniels[32] found that the apparent order was initially 2.3 in nitric oxide and slightly less than 1 in oxygen at total pressures near 1 mm of mercury. At higher pressures the reaction tended to third-order kinetics. They also found an increase in the third-order rate constant during any given run. The initial third-order rate constant was approximately one-half that found after 25 percent of the initial nitric oxide had been oxidized. They reported essentially no effect on the rate due to addition of glass beads, glass wool, or nitrogen dioxide. A mechanism was postulated which

involved NO_3, $NO \cdot NO_3$, and N_2O_5 as intermediates. All of the above investigations were carried out at total pressures of approximately 1 to 50 mm of mercury.

Recently two papers have been added to the literature on the oxidation of nitric oxide at low concentrations and atmospheric pressure. Glasson and Tuesday[9], using long path spectrophotometry, studied the air oxidation of nitric oxide between 2 and 50 p.p.m. They reported an initial third-order rate constant that was comparable to the initial rate constants obtained by previous investigators at high concentrations. The addition of nitrogen dioxide had no effect on the oxidation rate. Altshuller, et. al.[2], using chemical techniques, studied the air oxidation of 3 p.p.m. of nitric oxide. They obtained a value for the third-order rate constant which was approximately 200 percent of that reported by Glasson and Tuesday.

All investigators have reported a negative temperature coefficient for the initial termolecular oxidation of nitric oxide. Trotman-Dickenson[33] has correlated the results of several investigators and obtained an activation energy of -1.5 kcal/g.mole. Rice[23] presented a theoretical consideration of the possibility of a "negative activation energy". Gershnowitz and Eyring[8], using statistical techniques, calculated the rate constant for the oxidation reaction assuming a three-body reaction.

Their method predicts the negative temperature dependence.

In summary, the following statements can be made about the oxidation of nitric oxide:

1. Most studies have been carried out at total pressures below 50 mm of mercury.

2. Nearly all investigators, which have studied the oxidation reaction at total pressures below 50 mm of mercury, have reported an initial termolecular reaction and a rate constant of approximately 1.4 x $10^4 \ell^2 g.mole^{-2} sec^{-1}$ at 25^oC.

3. In the two studies[2, 9] carried out at low concentrations of nitric oxide but at atmospheric pressure, the initial termolecular rate constants differed by 200 percent.

4. Little work[9, 32] has been done on the effect of nitrogen dioxide on the initial oxidation rate.

5. A number of investigators have reported an increase in the termolecular rate constant as the reaction neared completion or as the initial partial pressure of nitric oxide was lowered.

6. Several mechanisms have been proposed which involve at least one of the intermediates NO_3, $(NO)_2$, $NO_3 \cdot NO$, N_2O_3, or N_2O_5.

7. All investigators have reported the initial termolecular rate constant in the absence of nitrogen dioxide to possess a small negative temperature coefficient. A temperature range from 140^oK to 650^oK has been studied.

In consideration of the inconsistencies in the reported rate and mechanism for the oxidation reaction at low concentrations, a study of the air oxidation of nitric oxide in the parts-per-million range was carried out. The initial concentration of nitric oxide was varied from 2 to 75 p.p.m., and the oxygen concentration ranged from 3×10^4 p.p.m. to 25×10^4 p.p.m. A system pressure of approximately one atmosphere was maintained. The effect of nitrogen dioxide on the initial rate was studied, and the change in the initial rate constant in the absence of nitrogen dioxide over the ambient temperature range of 17 to 37°C was measured. A mechanism and rate equation have been proposed.

II. NITROGEN OXIDES AND THEIR EQUILIBRIUM IN THE GAS PHASE

Before one begins to study the rate and mechanism of a gas phase reaction, the possible compounds that may exist in the solution and their approximate compositions should be postulated. This information is of great importance for two reasons. (1) The analytical technique should be suitable for the analysis of all compounds which are in measurable quantities. (2) It is of interest to know what compounds are in the solution and may be involved in the reaction mechanism. A literature survey was carried out to determine the nitrogen oxides which have been observed in the gas phase at room temperature and atmospheric pressure. NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5 are known to exist at these conditions.

The calculation of the equilibrium composition of a gas mixture is a relatively straightforward procedure[6]. One must postulate the number of species, N, which are present in the system at equilibrium. The minimum number of substances, c, which must be available initially in order to make up the equilibrium mixture must be determined. For the system in question N and c are equal to 8 and 2, respectively. N is the total number of nitrogen oxides plus oxygen and the two compounds required to make up this equilibrium system are nitric oxide and

oxygen. Therefore, the minimum number of chemical equations, M, which are sufficient to represent the stoichiometry of the system is N - c or 6. The following six reactions can be considered as the independent stoichiometric chemical equations for this system.

$$2NO + O_2 \rightleftharpoons 2NO_2 \quad (1)$$

$$2NO_2 + O_2 \rightleftharpoons 2NO_3 \quad (2)$$

$$4NO_2 \rightleftharpoons 2N_2O_3 + O_2 \quad (3)$$

$$2NO_2 \rightleftharpoons N_2O_4 \quad (4)$$

$$4NO_2 + O_2 \rightleftharpoons 2N_2O_5 \quad (5)$$

$$4NO_2 \rightleftharpoons 2N_2O + 3O_2 \quad (6)$$

By assuming ideal gas behavior and a standard state fugacity for the pure component at the system temperature as one atmosphere, the following equation results:

$$-\Delta F^{o}_{T} = RT \ \ell n \ K_p \quad (7)$$

Considering the stoichiometry of the six chemical equations as well as relation 7, the equilibrium composition was determined. Free energy data[1, 13, 25], which have been published in the literature, were used in the calculation. If an initial gas mixture at 25°C and 1 atmosphere pressure contains 0.2 atmosphere of oxygen,

0.8 atmosphere of nitrogen, and 0.000050 atmosphere or 50 p.p.m. of nitric oxide, at equilibrium the nitric oxide is almost quantitatively converted to nitrogen dioxide. The concentrations of the various oxides of nitrogen at equilibrium were found to be the following: NO, 10^{-4} p.p.m.; NO_2, 50 p.p.m.; NO_3, 10^{-10} p.p.m.; N_2O, 10^{-2} p.p.m.; N_2O_3, 10^{-7} p.p.m.; N_2O_4, 10^{-2} p.p.m.; and N_2O_5, 10^{-6} p.p.m.

The really important fact, though, is the concentration of the nitrogen oxides during any given oxidation run. This information can only be accurately obtained after the mechanism is known; but, if the following assumptions are made, a reasonable idea of the magnitude of the concentration of the various nitrogen oxides during any oxidation run can be obtained. (1) The only reaction for the production of N_2O_3 is the rapid[19, 34] equilibrium between NO and NO_2. (2) NO_2 is in rapid[10] equilibrium with N_2O_4 and is the only reaction for the production of N_2O_4. With these two assumptions, it can be shown that during any given test the concentrations of N_2O_4 or N_2O_3 would never be greater than 0.5 percent of the initial nitric oxide concentration. A prediction of the concentrations of NO_3, N_2O, and N_2O_5 can not accurately be made; however, no previous investigator has reported the concentrations to be sizable in relation to the concentrations of NO, NO_2, or N_2O_4. Therefore, the reaction can be

followed by monitoring the concentrations of NO or NO_2 and calculating the other from stoichiometry.

III. EXPERIMENTAL METHOD

Gas analysis

Three techniques were investigated for applicability in analyzing the gas system. These were (1) chemical analysis, (2) infrared analysis, and (3) gas chromatography.

The accepted chemical technique for the analysis of nitrogen dioxide in p.p.m. concentrations is the method developed by Saltzman [26]. This technique is sensitive to a few part-per-billion of nitrogen dioxide and is not hindered by the presence of other nitrogen oxides. The difficulty with using the method for studying the oxidation of nitric oxide lies in the fact that 1 liter samples are required. A sample of this quantity could only be obtained in a flow reactor. Since the reaction times were suspected to be of the order of hours, a flow reactor which would supply 1 liter samples was not considered applicable for the experimental study. Therefore, chemical analysis was not used.

The second analytical technique that was investigated involved the infrared analysis of the gaseous system for nitric oxide and nitrogen dioxide. Nightingale [20] has pointed out that nitric oxide and nitrogen dioxide can be analyzed in a gaseous mixture. The absorption bands do not completely overlap. By continuously reading the absorption of nitric oxide at 5.2 microns and nitrogen dioxide at 6.2

microns, the concentration-time profile can be determined. In 1961, at the time infrared analysis was being investigated for its applicability in the analysis of p.p.m. quantities of nitrogen dioxide, the detection limit for nitrogen dioxide was 6 p.p.m. with a 10 meter cell. Since the analysis of lower concentrations of nitrogen dioxide was desired, infrared spectrophotometry was not used.

Gas chromatography was the third analytical technique which was applicable. Through the use of an electron-capture detector[17], it appeared possible to analyze for the oxides of nitrogen below 1 p.p.m. Because of this high sensitivity with relatively simple equipment and the ease of use of gas chromatography, that method was used as the analytical technique in the oxidation studies.

Reactor

Two types of reactors were applicable, a constant-volume batch reactor and a constant-flow stirred-tank reactor. Because the latter required accurate metering of low feed flow rates and instantaneous mixing of the feed stream with the reactor composition, the constant-volume batch reactor was selected for use.

In the experimental study of the air oxidation of p.p.m. concentrations of nitric oxide the procedure was as follows: (1) The appropriate gases, nitric oxide,

nitrogen dioxide, nitrogen, and oxygen, were added to a constant-volume batch reactor. (2) Samples of the reaction mixture were analyzed for nitrogen dioxide as a function of time using the gas chromatograph described in Part II of this thesis. (3) The initial concentrations of the reactants were varied for different oxidation tests. (4) From the concentration-time data, the rate of the oxidation reaction was obtained and a mechanism proposed.

IV. EXPERIMENTAL APPARATUS

A photograph of the entire experimental apparatus is shown in Figure 1.

Reactor bay

A bay was constructed to house the reactor and hold tanks for the individual gases at a constant temperature. The enclosure was 1.5 ft by 2 ft by 5 ft. The frame was constructed of Unistrut. Fiberglass insulation, which had a thickness of 3 inches, was placed upon all but one side of the rectangular framework. An aluminum panel was attached to the Unistrut frame with Swenson locks. The panel could be removed from the bay, and so the reactor and hold tanks were easily accessible. Figure 2 is a photograph of the reactor bay with the aluminum panel removed showing the heater, temperature controller, fan, reactor, and hold tanks.

Four hold tanks of 416 stainless steel, which had a volume of approximately 4000 cc, were installed in the reactor bay. Stainless steel tubing with an inside diameter of 0.180 inch was used to connect these hold tanks to the gas manifold. Two-millimeter, high-vacuum stopcocks were used in the manifold. The gases were metered through this manifold and into the hold tanks or reactor. A Duo-Seal vacuum pump was connected to the

reactor and hold tanks for evacuation purposes. The pressure in the hold tanks and reactor was measured on a mercury manometer or McLeod gauge. Figure 3 is a flow diagram of the apparatus, excluding the chromatography unit. All connecting tubing was of 304 stainless steel or Pyrex glass. The stainless steel tubing was connected to the glass tubing with 304 stainless steel sleeves and adhered to the tubing by the use of Epoxy 220 (manufactured by Hughes Associates, Excelsior, Minnesota). These connections could be readily taken apart by heating with a flame. Thus they were inexpensive, leak-tight, and easy to construct or disassemble.

The reactor was a Pyrex vessel with an inside diameter of 7 inches, a length of 16 inches, and a volume of approximately 6000 cc. The reactor was evacuated from the top through Pyrex tubing having an i.d. of 3 mm. Gases were added from the hold tanks through Pyrex capillary tubing connected to the side of the reactor. Samples were removed from the reactor through a 3 mm stopcock placed on the side of the reactor and 90^{o} from the gas inlet. The reactor, being situated in the bay, was completely shielded from outside light. The reactor was shielded from the heaters by a copper base upon which it was seated.

A sixteen liter, 316 stainless steel tank was used as a standard tank. A mixture of approximately 50 p.p.m.

of nitrogen dioxide, 20 percent oxygen, and 80 percent nitrogen was added to this tank. This mixture was used each day to condition the chromatography column before the oxidation run was begun.

Temperature measurement and control

Copper-constantan thermocouples were used for temperature measurement. The junctions were silver soldered. These thermocouples were calibrated in an oil bath that has been described by Rinker[22]. The actual temperature of the oil bath was measured with a platinum resistance thermometer furnished by Leeds and Northrup that had been calibrated against a platinum resistance thermometer certified by the National Bureau of Standards. The resistance of the thermometer was measured by a Rubicon Bridge (Minneapolis-Honeywell). The voltage of the thermocouples was measured with a K-3 Leeds and Northrup Potentiometer. A stirred ice bath was used as the cold junction. The calibration data were fitted to a third-order polynomial by ordinary least-square techniques and gave a standard deviation about the polynomial of $0.02^{\circ}C$.

A centrifugal fan, with a diameter of six inches, operating at 1750 r.p.m. was used to circulate the air in the reactor bay. Temperature control was maintained by a Fisher Thermoregulator placed 3 inches above the fan

outlet. A 500 watt nichrome resistance heater placed at the fan outlet was used for heating purposes for all tests at 27°C. When tests were made at higher temperatures, two 660 watt Glocoil heaters (Eagle Electric Manufacturing Co., Long Island City, N.Y.) were placed 12 inches above the fan outlet. When tests were made at 17°C, cooling was obtained from a one-ton Westinghouse air conditioner, while temperature control was maintained by the thermoregulator on the 500 watt nichrome resistance heater. A 10 KVA Stabiline Voltage Regulator maintained a regulated voltage of 115 ± 1 volt to all of the equipment used in this study.

Reaction gases

Commerical grade oxygen (purity of 99.5 percent) and hi-purity dry nitrogen (purity of 99.995 percent) furnished by Linde, were dried before use in the equipment. They were dried by passage through a 4 ft length of 1/4 inch i.d. copper tubing packed with 14/20 mesh 13X Molecular Sieve and mounted in a dry ice-acetone bath.

Nitrogen dioxide was obtained from a mixture furnished by Matheson containing nominally 1500 p.p.m. of nitrogen dioxide in nitrogen. Nitric oxide was also obtained from a mixture furnished by Matheson containing nominally 1000 p.p.m. of nitric oxide in nitrogen. The impurities in these mixtures were less than 10 p.p.m. water, 20 p.p.m. oxygen, and 20 p.p.m. hydrogen.

The recommended Matheson gas regulator was used on the outlet of all gas cylinders. A mercury manometer or a McLeod gauge was used to measure the pressure in the hold tanks or reactor. A cathetometer was employed for measuring the level of mercury in the manometer.

General

All equipment which contacted the nitrogen oxide gases was of stainless steel or Pyrex glass. The reactor, connecting lines, and four hold tanks were cleaned by evacuation below 0.01 mm of mercury while heating with heat lamps.

A timer manufactured by R. W. Cramer, Centerbrook, Connecticut, was used for timing the reaction. Using this timer, it was possible to read from 0 to 999.99 minutes with an accuracy of $\pm$ 0.01 minute.

Pyrex glass beads with a diameter of 3 mm were used to vary the surface to volume ratio in the reactor. The beads were cleaned by heating with a heat lamp while in the reactor under a vacuum of 0.01 mm of mercury.

Apiezon N was used as a stopcock grease.

V. EXPERIMENTAL PROCEDURE

The experimental study was designed such that all data which would be required to determine the order and mechanism could be obtained in a minimum of tests. To this goal, tests were made with initial concentrations of 2 to 75 p.p.m. of nitric oxide, 3 to 25 percent oxygen, and varying initial quantities of nitrogen dioxide. In order to determine the effect, if any, of the Pyrex surface on the reaction, 3 mm Pyrex beads were added to the reactor. By solving the differential equations describing a simultaneous catalytic and homogeneous reaction, it was found that diffusion from the glass beads into the sampling area was not a limiting factor. A discussion of the effect upon the reaction due to the addition of glass beads is included as Appendix A.

Oxidation tests

The general laboratory procedure for any given week was to carry out a calibration run for nitrogen dioxide on Monday and oxidation runs on Tuesday through Friday. The calibration runs are described in Part II of this thesis. In the oxidation runs the nitric oxide hold tank was evacuated below 0.05 mm of mercury. The Matheson mixture of nitric oxide and nitrogen and a quantity of nitrogen was added to this tank. In the process the

Matheson mixture was diluted to a concentration of nitric oxide between 150 and 300 p.p.m., such that when it was diluted approximately one-fifth in the reactor, the concentration would be the desired initial concentration of nitric oxide. If tests were to be made with very low initial concentrations of nitric oxide, the mixture in the hold tank was diluted by partial evacuation and the addition of nitrogen. The pressure in the hold tank was read on the mercury manometer and McLeod gauge. A cathetometer was used to read the mercury level. No pressure change less than 5 cm of mercury was ever read nor were more than three dilutions required. If an initial quantity of nitrogen dioxide was desired, the mixture was made up the same way in the hold tank for nitrogen dioxide.

After these gas mixtures were prepared in the hold tanks, the reaction mixture could be prepared. The reactor was pumped to less than 0.05 mm of mercury. Nitric oxide, nitrogen dioxide, and nitrogen were added from the hold tanks to the reactor in such a way as to obtain the desired initial quantities of nitric oxide, nitrogen dioxide, and nitrogen but leaving enough vacuum so that when oxygen was added, the desired initial concentration of oxygen would be obtained with a final total pressure of one atmosphere. No pressure changes

smaller than 5 cm of mercury were read with the cathetometer for the addition of nitric oxide, nitrogen, or nitrogen dioxide to the reactor. Therefore, the maximum error in the initial concentration of nitric oxide due to manometer measurement errors was 4 percent if three dilutions in the hold tank were required or 2 percent if only one dilution was needed. On most of the runs only one dilution was used. The maximum error in the initial concentration of nitrogen dioxide due to manometer measurement errors was 3 percent. The close agreement between the calculated initial concentrations of nitrogen dioxide and the measured initial concentrations of nitrogen dioxide shown in Table 3 for Tests 27 and 28 indicates that errors in sample make-up were indeed small. The maximum error due to inaccuracies in manometer measurement was 1.5 percent of the initial oxygen concentration.

Next, the chromatograph was prepared for the oxidation run. The background current in the electron-capture detector was measured. Several samples of a mixture of 50 p.p.m. nitrogen dioxide, 20 percent oxygen, and 80 percent nitrogen, were added to the column from the standard tank until reproducible results were obtained. Ten to twenty samples were required at five minute intervals. During the last sample from the standard tank, oxygen was added to the reactor and the timer started.

The timer was begun at the end of the oxygen addition, which required approximately twenty seconds. Samples were then taken from the reactor every five minutes and analyzed with the chromatograph. For runs lasting more than four hours, the reaction mixture was analyzed for a period of two to three hours at a time with prior conditioning of the column by the standard tank mixture. During the run thermocouple measurements were made approximately every thirty minutes. At the end of a given test the background current in the electron-capture detector and the reactor pressure were measured.

Mixing of initial reaction mixture

Before any oxidation tests were carried out, the time required for the gas mixture to become homogeneous after injection into the reactor was checked. A mixture of nitrogen and oxygen was added to the reactor until the pressure was 740 mm of mercury. The column was conditioned with the standard tank mixture. The nitrogen dioxide-nitrogen mixture containing 1627 p.p.m. of nitrogen dioxide was added to the reactor, until the total pressure was 760 mm of mercury, which gave a concentration of nitrogen dioxide of approximately 50 p.p.m. Thirty seconds after this addition, a sample was taken from the reactor. Three more samples were taken from the reactor at five minute intervals and analyzed. The peak height

for nitrogen dioxide showed all four samples to contain the same concentration of nitrogen dioxide, i.e., within the experimental error of 3.4 percent,which indicated almost immediate mixing of the gases in the reactor as well as acceptable conditioning of the column with the gas mixture from the standard tank.

Analysis of laboratory data

Ideal gas behavior was assumed in the calculation of the concentration of the initial reaction mixture. An error of less than 0.5 percent would be expected from the assumption of ideal behavior for the gases at the prevailing temperatures and pressures used in the oxidation study.

The concentration of nitrogen dioxide was calculated for each sample in the manner described in Part II of this thesis. An average background current, which never varied more than 5 percent during any given oxidation run, was used in the calculation. An initial pressure and average temperature during the run was employed in the calculation. During any given test the pressure never decreased more than 3 mm of mercury, and the temperature fluctuation was less than $0.05^{\circ}C$.

The concentration of nitric oxide as a function of time was obtained by subtraction of the concentration of nitrogen dioxide from the initial concentration of nitric

oxide. Plots of the concentration of nitric oxide as a function of time were prepared on 20 inch graph paper. The plots were smoothed by eye. Smoothed values of the nitric oxide concentration were read from these plots at even intervals of time. All concentration-time data were smoothed by eye for two reasons. (1) The first three or four points were more scattered than the rest of the data for any given test and thus had to be weighted accordingly. (2) The change in concentration with time was desired for the entire run, whereas laboratory data were not available for each five minute period for every test.

A program for fitting any seven data points in a two dimensional plane to a second-order polynomial by linear least-squares was written for an IBM 7094 Computer. For each test, the first seven smoothed data points were fitted to the polynomial, and the derivative, dC_{NO}/dt, was obtained at each of the first four points. Stepwise, the rest of the data for each test were fitted to the polynomial, and the derivative for the center point was calculated until the last seven data points in the test were fitted. The derivatives for the remaining three data points were obtained with the polynomial fitted to the last seven. After the derivatives were obtained, they were smoothed by the same program and plotted as a function of the concentration of nitrogen dioxide. From that

plot the rate for the oxidation of nitric oxide at zero concentration of nitrogen dioxide was determined.

VI. DISCUSSION OF RESULTS

Reaction order

The order of the oxidation of nitric oxide was determined by measuring the initial rate of the reaction in the absence of nitrogen dioxide at different concentrations of nitric oxide and oxygen. The results of these studies are presented in Table 1. The concentration of nitric oxide was varied from 2 to 75 p.p.m. and the oxygen concentration from 3×10^4 to 25×10^4 p.p.m. The data in the absence of nitrogen dioxide at $26.5 \pm 0.5^{\circ}C$ (Tests 1 through 15, excluding 10) were fitted by a non-linear least-squares technique[35] to the following equation:

$$\left(-\frac{dC_{NO}}{dt}\right)_o = k(C_{NO})_o^a \, (C_{O_2})_o^b \qquad (8)$$

The order with respect to nitric oxide, a, was found to be 2.00 ± 0.09 (0.09 is the 95 percent confidence limit for a), and the order for oxygen was 0.97 ± 0.11. Previous investigators[3,4,5,11,18,21] found the reaction to be second order in nitric oxide and first order in oxygen at higher concentrations of nitric oxide. Treacy and Daniels[29] found an apparent order in nitric oxide of 2.3 at lower pressures of nitric oxide which approached 2.0 at higher pressures. No such trend was found in the

present study. Since the order found in this work was essentially the same as that obtained by other investigators at higher concentrations of nitric oxide, a value for the third-order rate constant was determined. The value of the initial third-order rate constant, determined by the same least-squares technique, was found to be $(1.297 \pm 0.051) \times 10^4 \ell^2 g.mole^{-2} sec^{-1}$ at 26.5°C. The rate data are plotted in Figures 4 and 5. Figure 4 is a plot of the oxidation rate in the absence of nitrogen dioxide divided by the square of the concentration of nitric oxide as a function of the oxygen concentration. Shown in Figure 5 is the oxidation rate divided by the product of the concentration of nitric oxide and oxygen as a function of the concentration of nitric oxide. Both graphs show the fit of the data in the absence of nitrogen dioxide to the third-order rate expression.

Other investigators, with the exception of Treacy and Daniels[32] and Altshuller[2], have reported approximately the same value for the initial third-order rate constant in units of $10^4 \ell^2 g.mole^{-2} sec^{-1}$: Bodenstein[3], 1.49 (25°C); Glasson and Tuesday[9], 1.54 (23°C); Hasche and Patrick[11], 1.67 (27°C); Smith[29], 1.2 (25°C); Kornfeld and Klinger[16], 1.4 (21°C); Brown and Crist[5], 1.5 (25°C). Treacy and Daniels[32] report a value for the initial third-order rate constant of $0.75 \times 10^4 \ell^2 g.mole^{-2} sec^{-1}$ (25°C), while Altshuller, et. al.[2], report

$3.5 \times 10^4 \ell^2 g.mole^{-2} sec^{-1}$ (45^oC). All investigators other than Altshuller, et. al., and Glasson and Tuesday worked at total pressures below 50 mm of mercury, while Glasson and Tuesday and Altshuller studied the oxidation reaction at low concentrations of nitric oxide but at a total pressure of one atmosphere. Nitrogen was used as the diluent. The present study would support the findings of Glasson and Tuesday with respect to the initial third-order rate constant. A possible reason for the high value reported by Altshuller et. al., may be that some nitrogen dioxide was initially present.

Three millimeter Pyrex glass beads were added to the reactor in Tests 22 through 28. There were no noticeable surface effects. A discussion of the effect of the addition of glass beads to the non-stirred batch reactor is included in Appendix A.

The effect of the addition of nitrogen dioxide to the reaction mixture was to cause an increase in the oxidation rate. The reason for the increased oxidation rate when nitrogen dioxide was present is discussed in more detail in the next section.

The influence of temperature was slight which is in agreement with all previous investigators. The initial third-order rate constant in the absence of nitrogen dioxide over the ambient temperature region of 17 to 37^oC was nearly constant. In order to evaluate a meaningful

temperature coefficient, the temperature interval would have to be nearly 200°C.

Reaction mechanism

There are three areas that should be investigated in any kinetic study. They are the stoichiometry, order, and mechanism of the reaction. In Section II considerable time was spent in discussing the stoichiometry of the reaction. It was found that of the nitrogen oxides which have been found to exist in the gas phase at room temperature, i.e., NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5, the only compounds that would be in appreciable quantities during the oxidation reaction or at equilibrium were nitric oxide and nitrogen dioxide. In the previous section, it was shown that the initial rate for the oxidation of nitric oxide when no nitrogen dioxide was present was second order in nitric oxide and first order in oxygen with a slightly negative temperature coefficient. The presence of nitrogen dioxide increased the initial rate for the oxidation of nitric oxide. Therefore, the reaction schemes which were considered acceptable were those which met the following restrictions:

1. All reaction schemes had to make use of only the known nitrogen oxides, i.e., NO, NO_2, N_2O, N_2O_3, NO_3, N_2O_4, N_2O_5, or reaction intermediates for which a reasonable structure could be postulated.

2. The initial rate in the absence of nitrogen dioxide had to be second order in nitric oxide and first order in oxygen with a rate constant of $(1.297 \pm 0.051) \times 10^4 \ell^2 g.mole^{-2} sec^{-1}$.

3. The initial rate had to be increased by the addition of nitrogen dioxide.

4. The mechanism had to predict the oxidation rate within the experimental error.

A large number of reaction schemes were tested for their applicability in satisfying the above four restrictions. The assumption that the concentration of trace intermediates was essentially constant did not yield a rate equation which satisfied the above restrictions. The following reaction mechanism allowed the best prediction of the experimentally determined concentration-versus-time profile, satisfied the above four restrictions, and gave rate constants comparable to those which have been reported in the literature for reactions involving the nitrogen oxides.

$$2NO_2 \overset{K_9}{\rightleftharpoons} N_2O_4 \qquad (9)$$

$$NO + O_2 \overset{K_{10}}{\rightleftharpoons} NO_3 \qquad (10)$$

$$NO + NO_2 \overset{K_{11}}{\rightleftharpoons} N_2O_3 \qquad (11)$$

$$N_2O_3 + O_2 \overset{K_{12}}{\rightleftharpoons} N_2O_5 \qquad (12)$$

$$N_2O_5 \xrightarrow{k_{13}} NO_2 + NO_3 \qquad (13)$$

$$NO + NO_3 \xrightarrow{k_{14}} 2NO_2 \qquad (14)$$

Reactions 9 through 12 are assumed to be in rapid equilibrium and steps 13 and 14 considered to proceed at a measurable rate. The reverse reaction for Equation 13 is relatively unimportant since the reverse rate constant, k'_{13}, is approximately two orders of magnitude[12] smaller than k_{14}. Reactions 9 and 11 have been extensively studied [10, 34] and are known to be in nearly instantaneous equilibrium. Reaction 10 has been postulated by previous investigators[9, 32] of the oxidation of nitric oxide, but no measurement of the forward or reverse rates have been made. NO_3 has been found to be the primary intermediate in the decomposition of N_2O_5[12,19,28,30] and has been observed spectroscopically[15].

The proposed reaction scheme gives the following rate expression:

$$-\frac{dC_{NO}}{dt} = 2k_{14}K_{10}\,C^2_{NO}\,C_{O_2} + k_{13}K_{11}K_{12}\,C_{NO}\,C_{NO_2}\,C_{O_2} \qquad (15)$$

Rate equations for several reaction schemes were fitted to the smoothed data for dC_{NO}/dt for Tests 1 through 15 (excluding Test 10). Equation 15 gave the lowest standard deviation, 1.32×10^{-11} g.moles ℓ^{-1}sec^{-1}, for dC_{NO}/dt.

An F test on the ratio of the variances of the several rate equations showed that Equation 15 gave the best fit to the experimental data. The rate equations were fitted using the non-linear least-squares technique that has been previously described. The two constants, $2k_{14}K_{10}$ and $k_{13}K_{11}K_{12}$, were found to be equal to $(1.313 \pm 0.016) \times 10^4$ $\ell^2 g.mole^{-2} sec^{-1}$ and $(1.276 \pm 0.028) \times 10^4 \ell^2 g.mole^{-2} sec^{-1}$, respectively.

Table 2 gives a comparison between the experimental rate and the predicted rate for all tests at 26.5°C. There was no effect on the rate of oxidation due to the different surface to volume ratios. After integration of Equation 15, the predicted nitric oxide concentration-versus-time profile was obtained. Table 3 contains the predicted concentration of nitric oxide and the experimental concentration of nitric oxide as a function of time for all experimental tests. The same constants were used for the six tests at 17 and 37°C. There seemed to be a slight decrease in the rate for the oxidation of nitric oxide as the temperature was increased, but over the ambient temperature range which was studied, there was essentially no effect. Figures 6 through 12 are plots showing the experimental and predicted concentrations of nitric oxide as a function of time. With the exception of Tests 1 and 22, which are apparently bad experimental runs, the data

agree very well with the predicted theory. The standard deviation of the predicted concentration from the experimental at 26.5°C was 1.6 p.p.m., which is approximately equal to the error of 1.3 p.p.m. in the analytical method. Errors in the initial concentration of nitric oxide during sample make-up of approximately 1 p.p.m. place the deviation of the predicted concentrations within the experimental error.

Schott and Davidson[28], who studied the decomposition of nitrogen pentoxide, have suggested a value for the activation energy for reaction 14 of 1.4 ± 2.5 kcal/g.mole. Use of free energy data for NO_3[13] and NO[25] gives a value for K_{10} at 26.5°C of 3.18×10^{-4} ℓ/g.mole, which yields an experimental value for k_{14} of 2.06×10^{7} ℓ g.mole^{-1}sec^{-1}. The value for the steric factor, p, in the simple collision theory expression can now be calculated, where $k_{14} = p\ Z\ e^{-E_o/RT}$. When $E_{act} = 0 = E_o + \frac{1}{2}RT$, p is equal to 0.45×10^{-4}. When E_{act} = 1.4 kcal/g.mole, p is equal to 7.7×10^{-4}. For a reaction between one linear and one non-linear molecule a value for p of 10^{-4} has been both predicted by the transition state theory and found experimentally[7]. It would seem, therefore, that the activation energy for reaction 14 is small and positive, i.e., between 0 and 1.4 kcal/g.mole. Schott and Davidson have predicted a value of 6×10^{9} ℓ g.mole^{-1}sec^{-1} for

reaction 14, while Johnston[14] in studying the decomposition of nitrogen pentoxide has suggested a value of $\geq 10^{10}$ ℓ g.mole^{-1}sec^{-1}. Both values seem high since they are very close to the collision number, Z, of 2.8×10^{11} ℓ g.mole^{-1}sec^{-1} and would thus require a relatively high steric factor which has not been borne out by experiment for this type of reaction or a negative activation energy.

A value for k_{13} at 26.5°C and 760 mm of mercury can be calculated from the experimental results and free energy data[1,13,25] for NO, NO_2, N_2O_3, and N_2O_5. The calculated value for k_{13} is 0.0062 sec^{-1}. This value compares with the experimental rate constants reported in the literature for the decomposition of nitrogen pentoxide by Hisatsune, Crawford, and Ogg[13] and Smith and Daniels[30] at 25°C of 0.09 sec^{-1}. A value of 0.14 sec^{-1} has been reported for k_{13} by Mills and Johnston[19] at 27°C.

The overall results of this investigation of the oxidation of nitric oxide at low concentrations agree quite well with previous investigators at higher concentrations but low total pressures. The initial order and rate of the reaction, which has been discussed above, agree very well with previous work[2,5,9,11,16,29]. Only Treacy and Daniels[32] have reported results which did not show an initial third-order behavior. Treacy and Daniels[32] suggested a mechanism involving two equilibrium steps and the steady-state approximation for NO_3,

$NO_3 \cdot NO$, and N_2O_5.

A negative temperature coefficient for the reaction rate has previously been explained either by a mechanism involving a three-body collision or a mechanism with either $(NO)_2$ or NO_3 as intermediates. In the latter mechanism involving $(NO)_2$ or NO_3, the intermediate is assumed to be formed rapidly, while the rate determining step is the reaction of the intermediate with either NO or O_2 to yield nitrogen dioxide. The resulting third-order constant involves the product of the rate constant for the rate determining step and the equilibrium constant for the production of the intermediate. If the equilibrium constant decreases more rapidly with temperature than the increase in the rate constant, the product will decrease with temperature. The mechanism of an intermediate formation has been the predominant reaction scheme that has been suggested for the oxidation of nitric oxide. Some[11,21,27] have suggested the intermediate N_2O_3, but have not formulated a mechanism.

Previous investigators[11,32] have found the third-order rate constant to increase as the reaction proceeded. Only two[9, 32] have studied the influence of the addition of nitrogen dioxide on the initial rate. Both reported essentially no effect. The reason some have not noticed the increase in the oxidation rate due to nitrogen dioxide

addition is that k_{13} is pressure dependent. It decreases an order of magnitude[19] in the range 760 to 10 mm of mercury. Since most of the work has been at a total pressure below 50 mm of mercury, it is understandable why the second term in Equation 15 was not important.

The mechanism that has been proposed is compatible with the data presented in the literature by most investigators for the oxidation of nitric oxide. More data should be obtained in order to substantiate two points in the mechanism. The first point is to check the importance of the reverse rate of the reaction shown in Equation 13. An experiment in which the ratio of the concentration of nitrogen dioxide to nitric oxide was of the order of ten should be carried out. The second point of the mechanism which requires more information is whether nitrogen pentoxide actually forms and then decomposes or whether nitrogen dioxide and nitrogen trioxide are immediately formed with no intermediate of nitrogen pentoxide. If more experiments were carried out over a temperature range of approximately 50°C, the activation energy for k_{13} could be measured and compared to the value of the activation energy for the decomposition of nitrogen pentoxide in the presence of nitric oxide that has been reported in the literature[19]. If the concentrations of dinitrogen trioxide and nitrogen pentoxide could be followed during the oxidation run by using long-path infrared spectro-

photometry[9], more information relative to the mechanism of the reaction would be obtained.

Another point that is of importance is the question of the formation of nitrogen dioxide and nitrogen trioxide from nitric oxide, nitrogen dioxide, and oxygen. That formation could be due to a three-body reaction[22] between nitric oxide, nitrogen dioxide, and oxygen or via dinitrogen trioxide and nitrogen pentoxide as suggested in this thesis. The latter path which involves bimolecular reactions in contrast to the three-body reaction seems more plausible, even though the oxidation of dinitrogen trioxide to nitrogen pentoxide is a reaction involving a change in the electronic multiplicity. The reason that the path involving the oxidation of dinitrogen trioxide seems more plausible is the following. The ratio of the ternary and binary collision frequencies in a gas at the conditions used for the research reported in this thesis is approximately 10^{-3}. K_{11} is equal to 12.4ℓ/g.mole. Therefore, the rate of formation of nitrogen trioxide would be approximately 10,000 times greater via the route proposed in this thesis in comparison to the three-body reaction. Of course this is assuming that the activation energies and steric factors are approximately the same. It would also seem that if the formation of nitrogen trioxide was due to the three-body collision, the steric factor would have to be very small because of the difficulty of orienting the three different molecules in an acceptable manner for reaction to occur.

VII. CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. The initial order and rate for the air oxidation of nitric oxide below 75 p.p.m. at one atmosphere pressure, in the absence of nitrogen dioxide, is the same as that reported at higher concentrations of nitric oxide but total pressures of 1 to 50 mm of mercury. At 26.5 $\pm$ 0.5°C the order for nitric oxide is 2.00 $\pm$ 0.09 and for oxygen is 0.97 $\pm$ 0.11. The third-order rate constant calculated from initial rate data is (1.297 $\pm$ 0.051) x 10^4 ℓ^2 g.mole^{-2} sec^{-1}.

2. The addition of nitrogen dioxide increases the rate of the oxidation of nitric oxide.

3. The initial third-order rate constant has a small negative activation energy.

4. There are no measurable surface effects due to the Pyrex surface.

5. A reaction mechanism is proposed which involves four equilibrium steps and two rate-determining steps. The six reactions are:

$$2NO_2 \overset{K_9}{\rightleftharpoons} N_2O_4 \qquad (9)$$

$$NO + O_2 \overset{K_{10}}{\rightleftharpoons} NO_3 \qquad (10)$$

$$NO + NO_2 \overset{K_{11}}{\rightleftharpoons} N_2O_3 \qquad (11)$$

$$N_2O_3 + O_2 \overset{K_{12}}{\rightleftharpoons} N_2O_5 \qquad (12)$$

$$N_2O_5 \xrightarrow{k_{13}} NO_2 + NO_3 \qquad (13)$$

$$NO + NO_3 \xrightarrow{k_{14}} 2NO_2 \qquad (14)$$

6. The rate equation which results from this reaction scheme is

$$-\frac{dC_{NO}}{dt} = 2k_{14}K_{10}\,C^2_{NO}\,C_{O_2} + k_{13}K_{11}K_{12}\,C_{NO}\,C_{NO_2}\,C_{O_2} \qquad (15)$$

The standard deviation of approximately 1000 experimental data points in the range from 2 to 75 p.p.m. of nitric oxide and 3 to 25 percent oxygen from the theoretical rate equation, 15, is 1.6 p.p.m. of nitric oxide.

7. The values for $2k_{14}K_{10}$ and $k_{13}K_{11}K_{12}$ at 26.5°C were found to be $(1.313 \pm 0.016) \times 10^4 \ell^2 \text{g.mole}^{-2}\text{sec}^{-1}$ and $(1.276 \pm 0.028) \times 10^4 \ell^2$ $\text{g.mole}^{-2}\text{sec}^{-1}$, respectively. Using free energy data, k_{14} was found to be equal to $2.06 \times 10^7 \ell$ g.mole^{-1} sec^{-1} with an activation energy of 0.7 ± 0.7 kcal/g.mole. k_{13} was found to be equal to 0.0062 sec^{-1}.

VIII. RECOMMENDATIONS

It would be of interest to study the oxidation of small quantities of nitric oxide at atmospheric pressure over a temperature range of 200°C. A study of this type would give added information on the effect of temperature on $2k_{14}K_{10}$ and $k_{13}K_{11}K_{12}$. Since the effect of temperature on k_{13} is known[19,28], more information would be obtained relative to the mechanism proposed in this thesis.

Experiments should be carried out for the oxidation of nitric oxide, when the ratio of the concentration of nitrogen dioxide to nitric oxide is of the order of ten. These experiments would yield information relative to the reverse of the reaction shown in Equation 13.

From a mechanistic standpoint, it would be helpful to follow the concentration of nitrogen pentoxide and dinitrogen trioxide during the course of a study of the air oxidation of nitric oxide at low concentrations. More spectroscopic information on dinitrogen trioxide would be required, though, as well as the use of long-path infrared spectrophotometry[9].

In order to understand reactions which occur in the atmosphere, the oxidation of nitric oxide at low concentrations should be studied in the presence of water vapor. Very little data have been reported on the oxidation of nitric oxide in the presence of water vapor.

More studies on the photochemical reactions which occur between nitrogen dioxide, water vapor, and hydrocarbons should be carried out. Long-path infrared spectrophotometry could be used for the analysis of a reaction system of this type.

IX. REFERENCES

1. Altshuller, A. P., J. Phys.Chem., 61, 251 (1957).

2. Altshuller, A. P., et. al., Science, 138, 442 (1962).

3. Bodenstein, M., Z. Electrochem., 24, 183 (1918).

4. Bodenstein, M., Helv. Chim Acta., 18, 743 (1935).

5. Brown, F. B. and Crist, R. H., J. Chem. Phys., 9, 804 (1941).

6. Denbigh, K.,"The Principles of Chemical Equilibrium", p. 264, Butterworths Scientific Publications, London, England (1955).

7. Frost, A. A. and Pearson, R. G., "Kinetics and Mechanism", John Wiley and Sons, Inc., New York, New York (1961).

8. Gershnowitz, H. and Eyring,H., J. Am. Chem. Soc., 57, 985 (1935).

9. Glasson, W. A. and Tuesday, C. S., ibid., 85, 2901 (1963).

10. Gray, P. and Yoffe, A. D., Chem. Rev. 55, 1069 (1955).

11. Hasche, R. L. and Patrick, W. A., J. Am. Chem. Soc., 47, 1207 (1925).

12. Hisatsune, I. C., Crawford, G., Jr., and Ogg, R. A., Jr., ibid., 79, 4648 (1957).

13. Hisatsune, I. C., J. Phys. Chem., 65, 2249 (1961).

14. Johnston, H. S., J. Am. Chem. Soc., 73, 4542 (1951).

15. Jones, E. J. and Wulf, O. R., J. Chem. Phys., 5, 873 (1937).

16. Kornfeld, G. and Klinger, E., Z. physik. Chem., B4, 37 (1929).

17. Lovelock, J. E., Anal. Chem., 33, 162 (1961).

18. Lunge, G. and Berle, E., Z. Angew. Chem., 19, 861 (1906).

REFERENCES (contd.)

19. Mills, R. L. and Johnston, H. S., J. Am. Chem. Soc., 73, 938 (1951).

20. Nightingale, R. E., J. Phys. Chem., 58, 1047 (1954).

21. Raschig, F., Z. Angew. Chem., 18, 1281 (1905).

22. Ray, J. D. and Ogg, R. A., Jr., J. Chem. Phys., 26, 984 (1957).

23. Rice, O. K., J. Chem. Phys., 4, 53 (1936).

24. Rinker, R. G., Ph.D. thesis, "A Preliminary Study of the Catalyzed Addition of Hydrogen Chloride to Vinyl Chloride in a Stirred Reactor", California Institute of Technology (1959).

25. Rossini, F. D., et. al., "Selected Values of Properties of Hydrocarbons", NBS Circular C461, Nov., 1947.

26. Saltzmann,B. E., Anal. Chem., 26, 1949 (1954).

27. Sanfourche, M. A., Comptes Rendus., 168, 307 (1919).

28. Schott, G. and Davidson, N., J. Am. Chem. Soc., 80, 1841 (1958).

29. Smith, J. H., J. Am. Chem. Soc., 65, 74 (1943).

30. Smith, J. H. and Daniels, F., J. Am. Chem. Soc., 69, 1735 (1947).

31. Stoddart, E. M., J. Chem. Soc. (London), 5 (1939).

32. Treacy, J. C. and Daniels, F., J. Am. Chem. Soc., 77, 2033 (1955).

33. Trotman-Dickenson, A. F., "Gas Kinetics", p. 264, Butterworths Scientific Publications, London, England, (1955).

34. Verhoek, F. H. and Daniels, F., J. Am. Chem. Soc., 53, 1250 (1931).

REFERENCES (contd.)

35. Woodward, J. W., Ph.D. thesis, "A Study of Dislocation Density and Crystal Orientation on the Kinetics of the Catalyzed Oxidation of Ethylene over a Single Crystal of Silver", California Institute of Technology, (1965).

36. Wourtzel, M. E., Comptes Rendus., 170, 229 (1920).

X. NOMENCLATURE

C	Concentration, g.moles/liter.
E_o	Minimum relative kinetic energy between two molecules for reaction to occur, cal/g.mole.
ΔF^o	Standard state free energy change, cal/g.mole.
k	Rate constant, appropriate units.
K_p	Equilibrium constant defined in terms of partial pressures.
p	Steric factor.
R	Gas constant, 1.987 cal/(g.mole)(^oK).
S	Pyrex surface area in reactor, cm^2.
t	Time, seconds.
T	Temperature, ^oK.
V	Reactor volume, cm^3.
Z	Collision number, liter/(g.mole)(sec).

Subscripts

NO_2	Refers to nitrogen dioxide
NO	Refers to nitric oxide
O_2	Refers to oxygen
1,2,3...	Refers to reactions 1,2,3....
o	In the absence of nitrogen dioxide.

LIST OF TABLES

Table 1. Experimental Results for the Oxidation of Nitric Oxide in the Absence of Nitrogen Dioxide.

Test[+]	Initial Pressure, mm.Hg.	Average Temperature, °C.	p.p.m.	Initial Nitric Oxide Concentration g. mole $\ell^{-1} \times 10^{7}$	Initial Oxygen Concentration p.p.m.$\times 10^{-4}$	Initial Oxygen Concentration g.mole $\ell^{-1} \times 10^{5}$	Initial Nitric Oxide Oxidation Rate p.p.m.$min^{-1} \times 10^{2}$	Initial Nitric Oxide Oxidation Rate g.mole $\ell^{-1} sec^{-1} \times 10^{12}$	Initial Third* Order Rate Constant p.p.m.$^{-2} min^{-1} \times 10^{9}$	Initial Third* Order Rate Constant ℓ^{2} g.mole$^{-2} sec^{-1} \times 10^{-4}$
1	769.8	26.9	39.81	16.38	5.807	2.389	-14.51	-99.50	1.577	1.552
2	757.4	26.7	57.35	23.23	3.248	1.315	-13.23	-89.30	1.238	1.259
3	750.6	26.6	28.74	11.54	10.48	4.209	- 9.637	-64.50	1.113	1.151
4	751.6	26.5	77.12	31.02	14.91	5.997	-110.4	-740.0	1.245	1.283
5	752.8	26.2	20.28	8.177	10.14	4.089	-47.92	-32.20	1.149	1.178
6	749.6	27.1	30.84	12.35	20.16	8.070	-23.38	-156.0	1.219	1.268
7	751.7	27.1	42.17	16.93	12.44	4.994	-23.76	-159.0	1.074	1.111
8	755.6	26.9	5.53	2.23	13.05	5.270	- 5.49	- 3.70	1.377	1.408
9	770.4	26.8	52.99	21.82	10.23	4.213	-37.74	-259.0	1.314	1.291
10	755.7	26.4	2.21	0.894	12.37	5.004	- 0.132	- 0.893	2.192	2.233
11	754.2	26.3	44.91	18.14	25.03	10.11	-63.82	-429.5	1.264	1.292
12	749.9	26.1	15.16	6.092	8.321	3.344	- 2.756	-18.46	1.441	1.487
13	748.7	26.2	25.57	10.26	16.15	7.280	-14.69	-98.70	1.238	1.283
14	754.6	26.1	10.68	4.319	13.04	5.273	- 1.512	-10.19	1.016	1.036
15	754.0	26.5	36.91	14.89	22.02	8.884	-40.15	-270.0	1.339	1.371
16	759.0	17.4	27.45	11.50	14.86	6.225	-15.78	-110.2	1.410	1.339
17	759.5	17.2	41.94	17.59	9.620	4.035	-20.81	-145.5	1.230	1.165
18	755.2	17.3	39.30	16.38	9.971	4.157	-24.80	-172.3	1.610	1.544
19	752.2	37.5	42.61	16.54	18.88	7.330	-37.09	-240.0	1.082	1.197
20	752.0	37.6	41.59	16.14	10.09	3.915	-18.43	-119.2	1.056	1.169
21	757.2	37.5	31.30	12.23	14.67	5.733	-14.23	-92.70	0.990	1.081
22	754.0	26.9	32.90	13.26	19.73	7.950	-18.76	-126.00	0.879	0.902
23	754.4	26.8	40.49	16.33	4.971	2.005	-10.62	-71.40	1.303	1.335
24	747.8	26.8	40.05	16.01	10.15	4.057	-25.40	-169.2	1.560	1.627
25	763.5	26.6	31.15	12.72	11.29	4.611	-16.10	-109.6	1.470	1.469
26	753.9	27.0	75.14	30.26	14.64	5.896	-120.4	-808.0	1.456	1.497

[+]For Tests 1 through 21, S/V = 0.31cm^{-1}. For Tests 22 through 26, S/V = 1.6 cm^{-1}.

* Initial Third Order Rate Constant = $\left(-\frac{dC_{NO}}{dt}\right)_0 \Big/ (C_{NO})_0^2 \, (C_{O_2})_0$

Table 2. Experimental and Predicted Oxidation Rates for Nitric Oxide in the Presence of Nitrogen Dioxide.

Test[+]	Initial Pressure, mm. Hg.	Average Temperature, °C.	Nitric Oxide Concentration, p.p.m.	Nitrogen Dioxide Concentration, p.p.m.	Oxygen Concentration p.p.m. x 10^{-4}	Nitric Oxide Oxidation Rate, p.p.m./min. Experimental x 10^{3}	*Predicted x 10^{3}
1	769.8	26.9	34.32	5.49	5.807	136.3	105.4
2	757.4	26.7	52.65	4.70	3.248	129.0	126.4
3	750.6	26.6	25.41	3.33	10.48	94.43	96.92
4	751.6	26.5	69.53	7.54	14.91	1011.	1017.
5	752.8	26.2	17.56	2.72	10.14	44.69	46.07
6	749.6	27.1	27.65	3.19	20.16	213.9	216.4
7	751.7	27.1	38.08	4.09	12.44	223.3	252.9
8	755.6	26.9	4.75	0.77	13.05	5.19	4.40
9	770.4	26.8	49.62	3.37	10.23	355.8	358.7
10	755.7	26.4	2.00	0.21	12.37	1.27	0.703
11	754.2	26.3	40.83	4.08	25.03	570.8	588.1
12	749.9	26.1	13.24	1.92	8.321	26.70	21.17
13	748.7	26.2	23.05	2.52	18.15	135.2	135.2
14	754.6	26.1	9.93	0.75	13.04	14.69	17.73
15	754.0	26.5	34.08	2.83	22.02	365.9	354.4
22	754.0	26.9	25.82	7.08	19.73	160.5	213.3
23	754.4	26.8	36.27	4.22	4.971	95.06	93.28
24	747.8	26.3	37.56	2.49	10.15	226.2	191.9
25	763.5	26.6	29.03	2.12	11.29	1437.	1339.
26	753.9	27.0	68.08	7.08	14.64	1029.	954.1
27	750.7	27.0	20.00	32.31	19.41	272.3	252.8
28	758.8	27.0	20.08	33.01	11.27	176.9	152.8

[+] For Tests 1 through 15, $S/V = 0.31\ cm^{-1}$. For Tests 22 through 28, $S/V = 1.6\ cm^{-1}$.

* Predicted from Equation 15.

Table 3. Experimental and Predicted Nitric Oxide Concentration as a Function of Time.

NOTE:

1. The predicted nitric oxide concentration was evaluated from the integral of Equation 15.
2. The term "INITIAL NITRIC OXIDE CONCENTRATION" refers to the total nitrogen oxides at zero time, i.e., $C_{NO} + C_{NO_2}$.
3. In Tests 1 through 21, S/V was equal to 0.31 cm^{-1}.
4. In Tests 22 through 28, S/V was equal to 1.6 cm^{-1}.
5. The concentrations of nitric oxide and nitrogen dioxide at zero time for Tests 1 through 26 were obtained by smoothing the experimental nitric oxide versus time plots back through zero time. All other experimental data were obtained from the chromatograph analysis and initial concentrations of nitric oxide, nitrogen dioxide, oxygen, and nitrogen.

Table 3 (contd.)

TEST 1
NOV 5, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 39.81 PPM
INITIAL OXYGEN CONCENTRATION= 0.5807E 05 PPM
REACTOR PRESSURE= 769.8 MM OF MERCURY
REACTOR TEMPERATURE= 300.01 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	34.32	34.32
4.27	33.09	33.87
9.27	32.70	33.36
14.29	32.24	32.85
19.30	31.68	32.35
24.34	31.15	31.85
29.34	30.41	31.37
34.37	29.80	30.89
39.39	29.06	30.41
44.44	28.49	29.95
49.46	27.82	29.49
54.50	27.35	29.04
59.53	26.65	28.60
64.58	26.14	28.16
69.62	25.44	27.73
74.64	24.79	27.31
83.67	23.93	26.56
88.71	23.35	26.16
93.74	22.84	25.76
98.76	22.21	25.37
103.81	21.89	24.98
108.86	21.38	24.60
113.86	20.85	24.22
118.87	20.25	23.86
123.90	19.84	23.49
128.94	19.35	23.14
133.96	18.93	22.78
138.99	18.48	22.44
143.98	18.08	22.10
149.02	17.91	21.76
154.04	17.41	21.43
159.06	16.85	21.11
164.10	16.39	20.79
169.13	16.01	20.47
174.14	15.69	20.16
179.16	15.28	19.86
184.20	15.07	19.56
189.22	14.79	19.26
194.24	14.45	18.97

Table 3 (contd.)

TIME, MIN	CNO EXPERIMENTAL, PPM	CNO PREDICTED, PPM
199.26	13.96	18.68
204.31	13.57	18.40
209.32	13.48	18.12
214.34	12.92	17.84
219.37	12.91	17.57
224.39	12.43	17.31
372.19	8.83	11.07
377.21	8.87	10.90
382.25	8.51	10.73
387.28	8.17	10.57
392.31	7.44	10.41
397.34	7.28	10.26
402.37	6.39	10.10
407.44	6.61	9.95
412.47	6.59	9.80
417.50	6.39	9.65
422.54	6.10	9.51
427.58	5.94	9.36
432.62	5.87	9.22
437.64	5.25	9.08
442.68	5.32	8.94
447.71	5.13	8.81
452.76	5.13	8.68
457.78	4.91	8.55

Table 3 (contd.)

TEST 2
NOV 7, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 57.35 PPM
INITIAL OXYGEN CONCENTRATION= 0.3248E 05 PPM
REACTOR PRESSURE= 757.4 MM OF MERCURY
REACTOR TEMPERATURE= 299.90 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	52.65	52.65
6.36	51.43	51.85
11.33	50.99	51.24
16.34	50.54	50.63
21.32	49.95	50.02
26.32	49.38	49.43
31.33	48.70	48.84
36.33	48.18	48.26
41.34	47.74	47.68
46.34	47.03	47.11
51.33	46.33	46.55
56.34	45.77	46.00
61.36	45.18	45.45
66.35	44.65	44.91
71.33	43.65	44.38
76.34	43.32	43.85
81.33	42.47	43.33
86.35	42.05	42.81
91.36	41.61	42.30
96.34	41.02	41.80
101.33	39.52	41.31
106.35	39.99	40.82
111.34	39.29	40.33
116.33	38.82	39.86
121.33	38.45	39.38
126.35	38.34	38.91
131.38	37.29	38.45
136.35	36.99	38.00
141.33	36.85	37.55
146.33	35.99	37.10
151.33	35.64	36.66
156.37	35.14	36.23
161.38	34.74	35.80
166.38	33.85	35.37
171.36	33.32	34.96
176.38	33.20	34.54
181.37	32.63	34.13
186.38	32.63	33.73
196.37	31.35	32.94

Table 3 (contd.)

TIME, MIN	CNO EXPERIMENTAL, PPM	CNO PREDICTED, PPM
201.37	31.19	32.55
206.39	30.62	32.16
211.38	30.32	31.78
216.42	30.32	31.40
221.38	29.67	31.04
226.38	29.25	30.67
231.39	29.25	30.31
246.38	28.12	29.25
251.38	27.84	28.90
256.37	27.25	28.56

Table 3 (contd.)

TEST 3
NOV 10, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 28.74 PPM
INITIAL OXYGEN CONCENTRATION= 0.1048E 06 PPM
REACTOR PRESSURE= 750.6 MM OF MERCURY
REACTOR TEMPERATURE= 299.72 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	25.41	25.41
6.37	24.61	24.80
11.38	24.24	24.33
16.40	23.89	23.87
21.43	23.44	23.42
26.47	23.03	22.97
31.50	22.60	22.54
36.52	22.18	22.11
41.56	21.75	21.69
46.56	21.37	21.28
51.57	20.85	20.88
56.60	20.44	20.49
61.62	19.97	20.10
66.64	19.62	19.72
71.66	19.16	19.35
76.70	18.73	18.98
81.72	18.31	18.63
86.74	17.95	18.27
91.76	17.64	17.93
96.76	17.05	17.59
101.81	16.76	17.26
106.83	16.24	16.94
111.87	16.08	16.62
116.89	15.63	16.30
121.91	15.28	16.00
126.96	14.93	15.70
132.00	14.52	15.40
137.02	14.26	15.11
142.04	13.77	14.83
147.07	13.56	14.55
152.07	13.10	14.28
157.15	12.72	14.01
162.16	12.54	13.74
167.18	12.22	13.49
240.28	9.86	10.24
245.32	9.44	10.05
250.35	9.34	9.86
255.36	8.88	9.68
260.38	8.74	9.50

Table 3 (contd.)

TIME, MIN	CNO EXPERIMENTAL, PPM	CNO PREDICTED, PPM
265.41	8.51	9.32
270.44	8.36	9.15
275.46	8.07	8.98
280.50	8.07	8.81
285.52	7.74	8.64
290.55	7.41	8.48
295.56	7.27	8.32
300.58	7.13	8.17
305.60	6.77	8.02
310.61	6.77	7.87
315.64	6.69	7.72
320.68	6.61	7.58
325.69	6.23	7.43
330.71	6.23	7.30
335.73	5.98	7.16

Table 3 (contd.)

TEST 4
NOV 11, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 77.12 PPM
INITIAL OXYGEN CONCENTRATION= 0.1491E 06 PPM
REACTOR PRESSURE= 751.6 MM OF MERCURY
REACTOR TEMPERATURE= 299.66 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	69.58	69.58
0.81	70.92	68.76
5.83	64.12	63.90
10.84	59.70	59.40
15.87	55.54	55.21
20.88	51.80	51.34
25.90	48.40	47.73
30.91	44.80	44.39
35.93	42.32	41.28
40.95	39.76	38.39
45.98	37.36	35.70
51.00	35.22	33.21
56.02	33.48	30.89
61.05	31.22	28.73
66.08	28.86	26.73
71.09	26.72	24.87
76.12	26.42	23.13
81.14	25.12	21.53
86.17	23.32	20.03
91.17	20.42	18.64
96.20	19.66	17.34
101.24	18.54	16.13
106.27	17.54	15.01
111.30	16.92	13.97
116.32	15.12	13.00
121.34	13.82	12.10

Table 3 (contd.)

TEST 5
NOV 12, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 20.28 PPM
INITIAL OXYGEN CONCENTRATION= 0.1014E 06 PPM
REACTOR PRESSURE= 752.8 MM OF MERCURY
REACTOR TEMPERATURE= 299.39 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	17.56	17.56
51.33	15.02	15.35
56.35	15.02	15.15
61.40	14.92	14.95
66.40	14.82	14.76
71.41	14.58	14.57
76.43	14.30	14.38
81.44	14.14	14.19
86.46	13.98	14.00
91.48	13.89	13.82
96.50	13.63	13.64
101.52	13.41	13.46
106.52	13.24	13.29
111.55	13.09	13.12
116.57	12.82	12.95
121.59	12.60	12.78
126.61	12.47	12.61
131.65	12.38	12.45
136.65	12.14	12.29
141.66	11.87	12.13
146.67	11.74	11.97
151.69	11.56	11.81
156.71	11.40	11.66
161.74	11.27	11.51
166.76	11.06	11.36
171.80	10.78	11.21
176.80	10.58	11.07
181.83	10.56	10.92
186.87	10.18	10.78
191.89	10.08	10.64
196.93	10.05	10.50
360.77	7.55	6.87
365.79	7.23	6.78
370.81	7.12	6.69
375.83	6.88	6.61
380.86	6.75	6.52
385.91	6.46	6.44
390.92	6.34	6.36
395.93	5.99	6.27

Table 3 (contd.)

TIME, MIN	CNO EXPERIMENTAL, PPM	CNO PREDICTED, PPM
400.96	5.88	6.19
405.95	5.68	6.11
410.98	5.61	6.03
416.00	5.62	5.96
421.05	5.68	5.88
426.08	5.49	5.80
431.11	5.11	5.73
436.12	5.03	5.66
441.13	4.87	5.58
446.16	4.77	5.51
451.16	4.59	5.44
456.20	4.62	5.37
461.24	4.31	5.30
466.30	4.43	5.23
471.30	4.37	5.16
476.31	4.22	5.10
481.34	4.32	5.03

Table 3 (contd.)

TEST 6
NOV 13, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 30.84 PPM
INITIAL OXYGEN CONCENTRATION= 0.2016E 06 PPM
REACTOR PRESSURE= 749.6 MM OF MERCURY
REACTOR TEMPERATURE= 300.27 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	27.65	27.65
6.28	26.23	26.32
11.30	25.34	25.31
16.31	24.54	24.34
21.32	23.58	23.41
26.34	22.71	22.51
31.36	21.92	21.65
36.37	21.04	20.82
41.39	20.19	20.02
46.41	19.45	19.26
51.44	18.74	18.52
56.40	18.10	17.82
61.49	17.34	17.13
66.50	16.61	16.48
71.52	16.10	15.85
76.54	15.37	15.25
81.56	14.88	14.67
86.58	14.13	14.11
91.60	13.73	13.57
96.64	13.25	13.05
101.64	12.60	12.56
106.66	12.37	12.08
111.68	11.72	11.62
116.70	11.31	11.18
121.71	10.90	10.76
126.75	10.56	10.35
131.75	9.96	9.96
136.79	9.88	9.58
141.80	9.64	9.22
146.80	9.06	8.87
151.82	8.76	8.53
156.84	8.41	8.21
161.86	8.14	7.90
166.87	7.80	7.60
171.80	7.64	7.32
176.91	7.24	7.04
181.90	6.81	6.77
186.93	6.70	6.52

Table 3 (contd.)

TEST 7
NOV 17, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 42.17 PPM
INITIAL OXYGEN CONCENTRATION= 0.1244E 06 PPM
REACTOR PRESSURE= 751.7 MM OF MERCURY
REACTOR TEMPERATURE= 300.25 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	38.08	38.08
0.94	37.24	37.84
5.94	36.65	36.61
11.30	35.37	35.33
16.31	34.65	34.17
21.33	33.65	33.06
26.35	32.59	31.98
31.35	31.72	30.94
36.36	30.77	29.93
41.36	29.85	28.96
46.37	28.94	28.02
51.39	28.01	27.10
56.39	27.20	26.22
61.40	26.34	25.37
66.42	25.48	24.55
71.42	24.85	23.75
76.43	24.07	22.98
81.44	23.46	22.24
86.46	22.61	21.52
91.52	21.80	20.81
96.52	21.27	20.14
101.52	20.89	19.49
106.54	19.80	18.86
111.57	19.43	18.25
116.56	18.87	17.66
121.59	18.50	17.09
126.62	17.76	16.54
131.63	17.15	16.00
136.66	16.65	15.48
141.67	16.35	14.98
146.70	15.67	14.50
151.71	15.28	14.03
156.73	14.81	13.58
161.76	14.31	13.14
166.79	13.82	12.72
171.79	13.44	12.31
176.80	12.84	11.91
181.82	12.05	11.53

Table 3 (contd.)

TEST 8
NOV 18, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 5.53 PPM
INITIAL OXYGEN CONCENTRATION= 0.1305E 06 PPM
REACTOR PRESSURE= 755.6 MM OF MERCURY
REACTOR TEMPERATURE= 300.03 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	4.76	4.76
267.18	3.48	3.72
272.20	3.48	3.70
277.20	3.49	3.69
719.40	2.01	2.46
1349.18	0.96	1.39
1354.17	1.09	1.38
1581.33	0.72	1.12
1586.33	0.81	1.12
1830.15	0.57	0.90
1835.17	0.57	0.89
2180.54	0.83	0.65

Table 3 (contd.)

TEST 9
NOV 20, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 52.99 PPM
INITIAL OXYGEN CONCENTRATION= 0.1023E 06 PPM
REACTOR PRESSURE= 770.4 MM OF MERCURY
REACTOR TEMPERATURE= 300.00 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	49.62	49.62
0.42	48.97	49.47
5.43	47.54	47.71
10.44	45.62	46.02
15.46	44.47	44.38
20.48	42.53	42.80
25.50	41.36	41.28
35.50	38.18	38.42
40.52	36.90	37.06
45.54	35.53	35.75
50.55	34.29	34.49
55.56	33.10	33.27
60.60	31.98	32.09
65.62	30.76	30.96
70.61	29.69	29.87
75.62	28.83	28.82
80.65	27.59	27.80
85.65	27.04	26.83
90.66	25.79	25.88
95.67	25.19	24.98
100.67	24.84	24.10
105.67	23.93	23.26
110.68	22.99	22.44
115.71	22.29	21.65
120.72	21.49	20.89
125.73	20.89	20.16
130.74	20.19	19.45
135.75	19.39	18.77
140.76	19.10	18.12
145.78	18.23	17.48
150.80	17.79	16.87

Table 3 (contd.)

TEST 10
NOV 24, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 2.21 PPM
INITIAL OXYGEN CONCENTRATION= 0.1237E 06 PPM
REACTOR PRESSURE= 755.7 MM OF MERCURY
REACTOR TEMPERATURE= 299.55 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	2.00	2.00
719.35	1.14	1.55
1430.84	0.62	1.21
1746.52	0.63	1.09
2823.11	0.28	0.75

Table 3 (contd.)

TEST 11
NOV 27, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 44.91 PPM
INITIAL OXYGEN CONCENTRATION= 0.2503E 06 PPM
REACTOR PRESSURE= 754.2 MM OF MERCURY
REACTOR TEMPERATURE= 299.49 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	40.83	40.83
1.02	40.19	40.23
6.00	37.79	37.45
11.02	35.35	34.85
16.03	33.01	32.43
21.04	30.94	30.19
26.05	29.14	28.10
31.06	27.40	26.16
36.08	25.95	24.35
41.09	24.41	22.68
46.11	23.24	21.11
51.12	21.93	19.66
56.13	20.76	18.31
61.14	19.98	17.05
66.15	19.05	15.88
71.16	18.30	14.79
76.17	17.48	13.78
81.19	16.81	12.84
86.21	16.06	11.96
91.22	15.24	11.14

Table 3 (contd.)

TEST 12
DEC 1, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 15.16 PPM
INITIAL OXYGEN CONCENTRATION= 0.8321E 05 PPM
REACTOR PRESSURE= 749.9 MM OF MERCURY
REACTOR TEMPERATURE= 299.24 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	13.24	13.24
93.93	10.85	11.40
98.94	10.76	11.31
128.96	9.90	10.78
133.99	9.92	10.69
163.97	9.29	10.19
168.99	9.27	10.11
198.99	8.47	9.64
229.06	7.71	9.19
407.37	5.90	6.93
412.38	5.88	6.88
417.39	5.82	6.82
422.40	5.83	6.77
427.40	5.65	6.72
432.42	5.59	6.66
437.79	5.53	6.61
442.78	5.56	6.55
447.80	5.48	6.50
452.80	5.39	6.45
457.81	5.37	6.40
462.82	5.37	6.35
467.83	5.26	6.30
472.84	5.22	6.25
477.85	5.15	6.20
482.87	5.21	6.15
487.90	5.09	6.10
492.91	5.07	6.06

Table 3 (contd.)

TEST 13
DEC 2, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 25.57 PPM
INITIAL OXYGEN CONCENTRATION= 0.1815E 06 PPM
REACTOR PRESSURE= 748.7 MM OF MERCURY
REACTOR TEMPERATURE= 299.34 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	23.05	23.05
8.82	21.35	21.89
13.84	21.21	21.29
18.86	20.61	20.64
23.87	20.10	20.04
28.88	19.48	19.47
33.90	18.98	18.90
38.91	18.45	18.36
43.92	17.88	17.83
48.93	17.35	17.32
53.94	16.76	16.82
58.95	16.37	16.33
63.97	15.88	15.86
68.99	15.37	15.41
73.99	15.01	14.97
78.99	14.53	14.54
84.00	14.12	14.12
89.03	13.68	13.71
94.04	13.25	13.32
99.05	13.04	12.94
104.06	12.69	12.57
109.08	12.36	12.21
114.10	11.98	11.86
119.12	11.60	11.52
124.13	11.57	11.19
129.14	10.98	10.87
134.16	10.62	10.56
139.17	10.35	10.26
144.18	10.08	9.96
149.20	9.73	9.68
154.21	9.44	9.40
159.22	9.30	9.14
164.23	9.00	8.87
169.24	8.66	8.62
174.25	8.50	8.38
179.26	8.31	8.14
184.27	8.20	7.91

Table 3 (contd.)

TEST 14
DEC 4, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 10.68 PPM
INITIAL OXYGEN CONCENTRATION= 0.1304E 06 PPM
REACTOR PRESSURE= 754.6 MM OF MERCURY
REACTOR TEMPERATURE= 299.22 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	9.93	9.93
263.55	6.42	6.21
298.53	5.98	5.84
303.53	5.95	5.79
308.54	6.05	5.73
313.55	5.95	5.68
318.57	6.00	5.63
323.58	5.89	5.58
524.07	4.05	3.92
529.08	4.00	3.88
534.08	4.10	3.85
539.09	3.98	3.82
544.11	4.02	3.78
549.12	3.98	3.75
554.13	3.96	3.72
559.15	3.88	3.68
564.15	3.87	3.65
569.16	3.82	3.62
574.16	3.82	3.59
579.17	3.78	3.56
584.17	3.84	3.52
589.17	3.72	3.49
594.18	3.68	3.46
599.19	3.73	3.43
604.19	3.71	3.40
609.20	3.65	3.37
614.21	3.56	3.34
619.20	3.56	3.31
624.22	3.57	3.29

Table 3 (contd.)

TEST 15
DEC 7, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 36.91 PPM
INITIAL OXYGEN CONCENTRATION= 0.2202E 06 PPM
REACTOR PRESSURE= 754.0 MM OF MERCURY
REACTOR TEMPERATURE= 299.69 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	34.08	34.08
0.82	33.45	33.79
5.82	31.70	32.08
10.82	31.20	30.46
15.83	29.65	28.92
20.83	27.48	27.46
25.82	26.14	26.08
30.83	25.01	24.76
35.84	23.80	23.51
40.84	22.81	22.33
45.84	21.81	21.21
50.84	21.11	20.15
55.85	20.12	19.14
60.86	19.38	18.18
65.86	18.60	17.27
70.86	17.92	16.40
75.88	17.32	15.58
80.88	16.62	14.80
85.89	15.83	14.06
90.91	15.39	13.36
95.93	14.73	12.69
100.92	14.39	12.06
105.93	13.93	11.45
110.93	13.55	10.88
115.94	13.22	10.34
120.94	12.54	9.83

Table 3 (contd.)

TEST 16
DEC 11, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 27.45 PPM
INITIAL OXYGEN CONCENTRATION= 0.1486E 06 PPM
REACTOR PRESSURE= 759.0 MM OF MERCURY
REACTOR TEMPERATURE= 290.56 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	25.39	25.39
20.65	22.50	22.61
25.65	21.98	21.98
30.66	21.07	21.37
35.66	20.55	20.78
40.68	20.12	20.21
45.68	19.47	19.65
50.68	19.00	19.11
55.66	18.67	18.58
60.65	18.08	18.07
65.63	17.40	17.58
70.62	17.18	17.10
75.61	16.89	16.63
80.62	16.42	16.17
85.62	15.66	15.72
90.62	15.42	15.29
95.62	15.02	14.87
100.62	14.37	14.46
105.61	14.27	14.07
110.60	14.06	13.68
115.62	13.79	13.31
120.60	13.47	12.94
125.60	13.40	12.59
130.59	12.98	12.25
135.59	12.84	11.91
140.59	12.05	11.58
145.59	11.89	11.27
150.58	11.76	10.96
155.58	11.55	10.66
160.60	11.03	10.37
165.60	11.06	10.09
170.60	10.26	9.81
175.60	10.38	9.54
180.60	10.23	9.28

Table 3 (contd.)

TEST 17
DEC 10, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 41.94 PPM
INITIAL OXYGEN CONCENTRATION= 0.9620E 05 PPM
REACTOR PRESSURE= 759.5 MM OF MERCURY
REACTOR TEMPERATURE= 290.34 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	39.60	39.60
0.72	39.30	39.44
5.73	38.54	38.35
10.73	37.20	37.30
15.74	36.39	36.27
20.75	35.50	35.27
25.75	34.91	34.31
30.75	34.17	33.36
35.75	33.60	32.45
40.75	32.88	31.56
45.76	32.06	30.70
50.76	30.86	29.86
55.76	30.62	29.04
60.76	29.72	28.24
65.76	28.88	27.47
70.78	28.37	26.72
75.76	27.34	25.99
90.75	25.14	23.93
95.76	24.26	23.27
100.72	23.63	22.64
105.72	23.69	22.03
110.75	23.13	21.43
115.72	22.36	20.85
120.72	21.43	20.28

Table 3 (contd.)

TEST 18
DEC 12, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 39.30 PPM
INITIAL OXYGEN CONCENTRATION= 0.9971E 05 PPM
REACTOR PRESSURE= 755.2 MM OF MERCURY
REACTOR TEMPERATURE= 290.48 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	37.14	37.14
4.17	36.07	36.32
9.17	35.11	35.36
19.17	32.34	33.52
24.16	31.73	32.64
29.17	31.04	31.78
34.16	30.21	30.94
39.17	29.48	30.13
44.17	28.44	29.33
49.16	27.44	28.57
54.17	26.89	27.81
59.16	26.14	27.08
64.15	25.54	26.38
69.15	24.84	25.68
74.15	24.18	25.01
79.15	23.49	24.36
84.15	23.04	23.72
89.17	22.05	23.09
94.17	21.66	22.49
99.17	21.24	21.90
104.18	20.61	21.33
109.18	20.31	20.77
114.20	19.81	20.23
119.20	19.33	19.70

Table 3 (contd.)

TEST 19
DEC 16, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 42.61 PPM
INITIAL OXYGEN CONCENTRATION= 0.1888E 06 PPM
REACTOR PRESSURE= 752.2 MM OF MERCURY
REACTOR TEMPERATURE= 310.69 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	38.17	38.17
1.44	37.17	37.65
6.43	37.09	35.90
11.43	34.95	34.24
16.43	33.71	32.65
26.42	31.29	29.70
31.43	30.21	28.32
36.43	29.36	27.02
41.42	28.15	25.77
46.43	27.31	24.58
51.42	26.52	23.45
56.42	25.43	22.37
61.42	24.76	21.34
66.42	24.09	20.36
71.43	23.26	19.42
76.43	22.58	18.53
81.43	21.92	17.68
86.43	21.35	16.87
91.43	20.95	16.10
96.43	20.21	15.36
101.42	19.82	14.66
106.43	19.14	13.98
111.43	18.87	13.34
116.43	18.26	12.73
121.43	17.86	12.15

Table 3 (contd.)

TEST 20
DEC 17, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 41.59 PPM
INITIAL OXYGEN CONCENTRATION= 0.1009E 06 PPM
REACTOR PRESSURE= 752.0 MM OF MERCURY
REACTOR TEMPERATURE= 310.79 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	37.42	37.42
1.67	36.69	37.11
6.67	36.57	36.20
11.66	35.88	35.32
16.66	35.27	34.45
21.66	34.54	33.61
26.66	33.92	32.79
31.66	33.28	31.99
36.66	32.61	31.21
41.65	31.95	30.45
46.66	31.33	29.70
51.66	30.56	28.98
56.67	30.00	28.27
61.66	29.41	27.58
66.66	28.74	26.91
71.66	28.35	26.26
76.66	27.60	25.62
81.66	27.33	25.00
86.67	27.20	24.39
91.67	26.57	23.80
96.66	26.34	23.22
101.66	25.57	22.66
106.66	25.27	22.11
111.67	24.89	21.57
116.67	24.37	21.05
121.67	23.83	20.54
126.67	23.58	20.04
131.67	23.07	19.55
136.67	22.69	19.08
141.67	22.35	18.62
146.66	21.98	18.17
151.66	21.52	17.73
156.66	21.27	17.30
161.66	20.89	16.88
166.66	20.59	16.47
171.66	20.21	16.08
176.66	19.93	15.69
181.66	19.92	15.31

Table 3 (contd.)

TEST 21
DEC 18, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 31.30 PPM
INITIAL OXYGEN CONCENTRATION= 0.1467E 06 PPM
REACTOR PRESSURE= 757.2 MM OF MERCURY
REACTOR TEMPERATURE= 310.69 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	27.49	27.49
1.63	27.15	27.24
6.62	26.81	26.51
11.62	26.31	25.79
16.62	25.78	25.09
21.62	25.26	24.41
26.62	24.63	23.75
31.62	24.22	23.11
36.62	23.65	22.48
41.62	23.16	21.87
46.62	22.58	21.28
51.62	22.12	20.71
56.62	21.66	20.15
61.62	21.24	19.61
66.62	20.81	19.08
71.62	20.29	18.56
76.61	19.89	18.06
81.61	19.40	17.58
86.61	19.14	17.10
91.61	18.69	16.64
96.61	18.28	16.20
101.61	18.10	15.76
106.60	17.63	15.34
111.60	17.26	14.93
116.61	16.97	14.53
121.60	16.64	14.14
126.61	16.44	13.76
131.61	16.12	13.39
136.61	15.78	13.03
141.61	15.63	12.68
146.61	15.46	12.34
151.61	14.04	12.01

Table 3 (contd.)

TEST 22
DEC 31, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 32.90 PPM
INITIAL OXYGEN CONCENTRATION= 0.1973E 06 PPM
REACTOR PRESSURE= 754.0 MM OF MERCURY
REACTOR TEMPERATURE= 300.05 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	25.82	25.82
19.08	23.16	22.06
24.07	22.54	21.18
29.07	21.82	20.32
34.07	21.20	19.51
39.07	20.44	18.72
44.07	19.79	17.97
49.08	19.10	17.25
54.08	18.48	16.56
59.08	17.90	15.89
64.08	17.42	15.25
69.09	16.99	14.64
74.09	16.47	14.06
79.09	15.95	13.49
84.09	15.49	12.95
89.09	14.94	12.44
94.09	14.54	11.94
99.09	14.29	11.46
104.08	14.00	11.01
109.09	13.60	10.57
114.09	13.30	10.14
119.09	12.83	9.74
124.09	12.79	9.35
129.08	12.54	8.98
134.10	12.20	8.62
139.10	11.89	8.28
144.10	11.82	7.95
149.10	11.59	7.63

Table 3 (contd.)

TEST 23
JAN 6, 1965
INITIAL NITRIC OXIDE CONCENTRATION= 40.49 PPM
INITIAL OXYGEN CONCENTRATION= 0.4971E 05 PPM
REACTOR PRESSURE= 754.4 MM OF MERCURY
REACTOR TEMPERATURE= 299.93 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	36.27	36.27
26.49	33.76	33.88
31.51	33.47	33.45
36.51	33.06	33.02
41.51	32.69	32.60
46.51	32.28	32.19
51.52	31.77	31.78
56.55	31.47	31.37
61.55	30.96	30.97
66.55	30.59	30.57
71.55	30.30	30.19
76.57	29.77	29.80
81.57	29.42	29.42
86.57	29.07	29.05
91.59	28.71	28.68
96.59	28.17	28.31
101.59	27.96	27.95
106.62	27.40	27.60
111.62	27.37	27.24
116.66	26.99	26.90
121.67	26.66	26.55
126.68	26.29	26.22
131.69	25.92	25.88
136.68	25.54	25.56
141.68	25.29	25.23
146.68	24.94	24.91
151.68	24.54	24.60
156.69	24.30	24.28
161.69	23.96	23.98
166.69	23.70	23.67
171.69	23.53	23.37
176.69	23.23	23.08
181.69	22.99	22.78
186.72	22.48	22.49
191.72	22.39	22.21
196.73	22.06	21.93
201.72	21.70	21.65
206.73	21.37	21.38

Table 3 (contd.)

TIME, MIN	CNO EXPERIMENTAL, PPM	CNO PREDICTED, PPM
211.73	21.12	21.11
216.73	20.89	20.84
221.73	20.69	20.58
226.74	20.32	20.32
231.73	19.81	20.06
236.73	19.70	19.81
241.73	19.65	19.56

Table 3 (contd.)

TEST 24
JAN 7, 1964
INITIAL NITRIC OXIDE CONCENTRATION= 40.05 PPM
INITIAL OXYGEN CONCENTRATION= 0.1015E 06 PPM
REACTOR PRESSURE= 747.8 MM OF MERCURY
REACTOR TEMPERATURE= 299.98 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	37.56	37.56
6.77	36.19	36.28
11.77	35.19	35.37
16.77	34.25	34.48
21.77	33.37	33.61
26.77	32.65	32.77
31.77	31.65	31.94
36.77	30.93	31.14
41.77	30.16	30.36
46.77	29.52	29.60
51.78	28.82	28.85
56.78	28.24	28.13
61.78	27.73	27.43
66.78	27.04	26.74
71.78	26.32	26.07
76.79	25.80	25.42
81.79	25.35	24.78
86.80	24.94	24.16
91.80	24.26	23.56
96.80	23.64	22.97
101.80	23.35	22.40
106.81	22.79	21.84
111.81	21.85	21.29
116.81	21.45	20.76
121.81	21.53	20.24

Table 3 (contd.)

TEST 25
JAN 8, 1965
INITIAL NITRIC OXIDE CONCENTRATION= 31.15 PPM
INITIAL OXYGEN CONCENTRATION= 0.1129E 06 PPM
REACTOR PRESSURE= 763.5 MM OF MERCURY
REACTOR TEMPERATURE= 299.79 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	29.03	29.03
11.49	27.15	27.53
16.49	26.85	26.91
21.49	26.36	26.29
26.50	25.79	25.70
31.51	25.39	25.11
36.51	24.85	24.54
41.52	24.27	23.98
46.53	23.60	23.44
51.53	23.09	22.91
56.53	22.66	22.39
61.53	22.26	21.88
66.57	21.76	21.38
71.52	21.26	20.90
76.52	20.89	20.43
81.53	20.51	19.96
86.53	20.12	19.51
91.53	19.63	19.07
96.53	19.27	18.64
101.54	18.55	18.22
106.54	18.57	17.81
111.54	18.38	17.41
116.54	18.04	17.01
121.53	17.87	16.63
126.53	17.61	16.26
131.54	17.30	15.89
136.53	16.89	15.53
141.53	16.63	15.18
146.53	16.19	14.84
151.53	16.14	14.51
156.54	15.86	14.18
161.54	15.62	13.86
166.54	15.31	13.55
171.54	15.24	13.24
176.54	14.93	12.95
181.54	14.63	12.66
186.54	14.36	12.37
191.53	14.27	12.09

Table 3 (contd.)

TIME, MIN	CNO EXPERIMENTAL, PPM	CNO PREDICTED, PPM
196.52	14.00	11.82
201.53	13.75	11.56
206.52	13.50	11.30
211.52	13.36	11.05

Table 3 (contd.)

TEST 26
JAN 12, 1965
INITIAL NITRIC OXIDE CONCENTRATION= 75.14 PPM
INITIAL OXYGEN CONCENTRATION= 0.1464E 06 PPM
REACTOR PRESSURE= 753.9 MM OF MERCURY
REACTOR TEMPERATURE= 300.18 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	68.06	68.06
5.88	62.56	62.68
10.88	58.72	58.45
15.89	54.76	54.50
20.89	51.42	50.83
25.89	48.36	47.42
30.90	45.87	44.23
35.91	43.02	41.25
40.91	41.08	38.49
45.91	38.60	35.91
50.92	36.92	33.51
55.92	34.50	31.27
60.93	33.36	29.18
65.94	31.28	27.23
70.94	30.44	25.41
75.94	28.74	23.72
80.94	26.76	22.14
85.93	25.36	20.67
90.92	24.62	19.30
95.92	23.54	18.01
100.92	22.44	16.82
105.91	21.70	15.70
110.92	20.92	14.66
115.91	20.16	13.69
120.90	19.14	12.78

Table 3 (contd.)

TEST 27
JAN 13, 1965
INITIAL NITRIC OXIDE CONCENTRATION= 52.31 PPM
INITIAL OXYGEN CONCENTRATION= 0.1941E 06 PPM
REACTOR PRESSURE= 750.7 MM OF MERCURY
REACTOR TEMPERATURE= 300.19 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	20.00	20.00
0.63	20.25	19.84
5.63	19.19	18.63
10.63	17.93	17.49
15.63	17.19	16.42
20.63	16.01	15.41
25.63	14.75	14.47
30.63	14.07	13.59
35.63	13.45	12.76
40.63	12.87	11.98
45.63	11.87	11.25
50.63	11.31	10.57
55.63	10.51	9.92
60.63	10.33	9.32
65.64	8.71	8.75
70.63	8.71	8.22
75.64	8.43	7.72
80.64	8.31	7.25
85.64	7.71	6.81
90.64	6.51	6.39
95.64	7.23	6.00
100.64	6.33	5.64
105.64	6.19	5.30
110.65	6.01	4.97
115.65	5.71	4.67
120.65	4.99	4.39

Table 3 (contd.)

TEST 28
JAN 14, 1965
INITIAL NITRIC OXIDE CONCENTRATION= 53.09 PPM
INITIAL OXYGEN CONCENTRATION= 0.1127E 06 PPM
REACTOR PRESSURE= 758.8 MM OF MERCURY
REACTOR TEMPERATURE= 300.20 DEGREES KELVIN

TIME,MIN	CNO EXPERIMENTAL,PPM	CNO PREDICTED,PPM
0.	20.08	20.08
0.48	19.51	20.01
5.48	19.09	19.26
10.48	18.25	18.54
15.49	17.49	17.85
20.50	17.05	17.18
25.50	16.27	16.54
30.51	15.39	15.92
35.50	14.57	15.33
40.51	14.09	14.76
45.51	13.57	14.21
50.51	12.79	13.68
55.52	12.65	13.17
60.52	12.09	12.68
65.52	11.65	12.21
70.52	11.03	11.76
75.52	10.97	11.32
80.52	9.89	10.90
85.52	9.93	10.50
90.52	9.49	10.11
95.52	8.99	9.73
100.52	8.83	9.37
105.52	8.09	9.02
110.53	8.21	8.69
115.53	7.75	8.36
120.53	7.19	8.05

LIST OF FIGURES

LIST OF FIGURES (contd.)

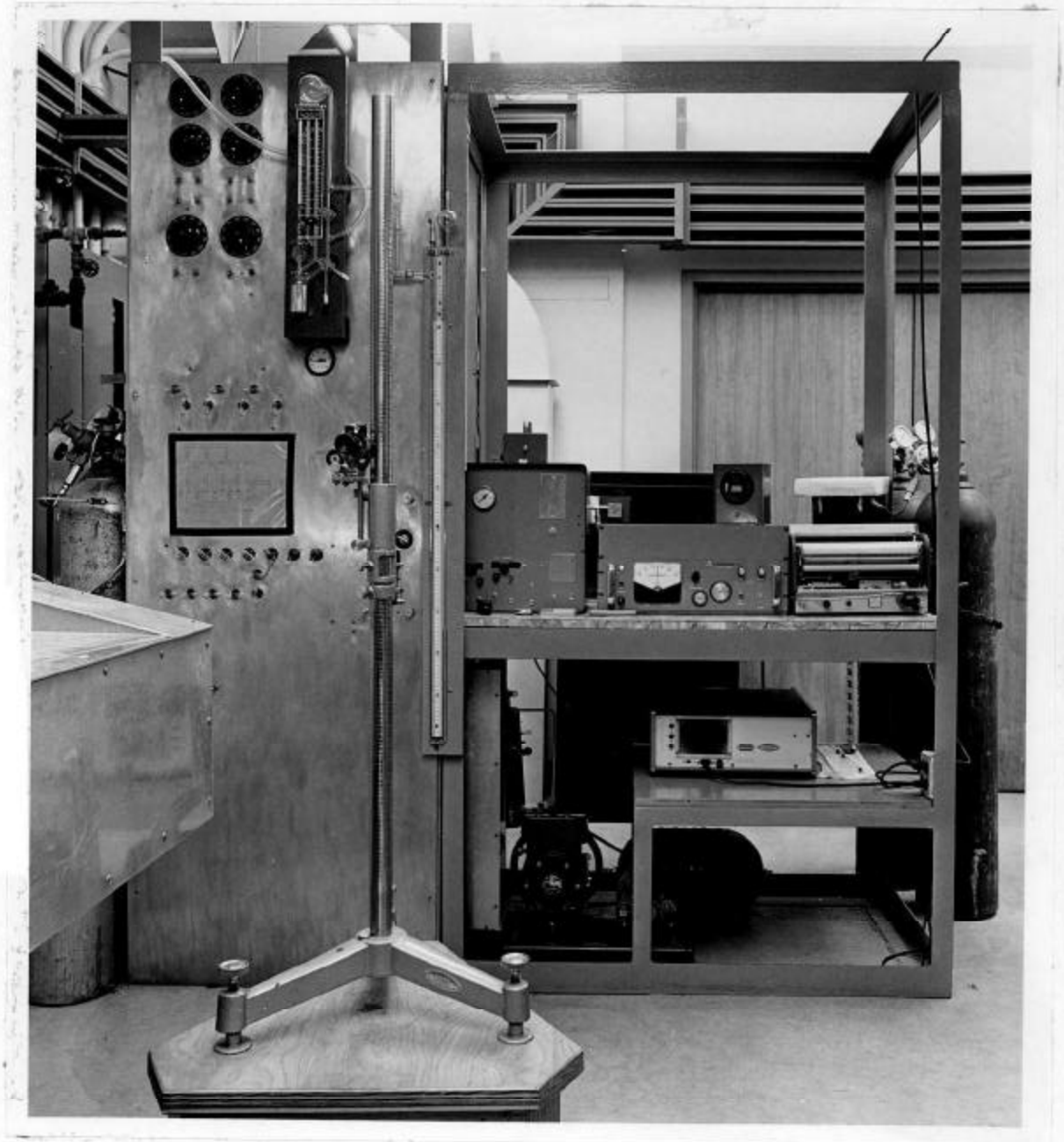


Figure 1. Photograph of the complete experimental apparatus for the oxidation study.

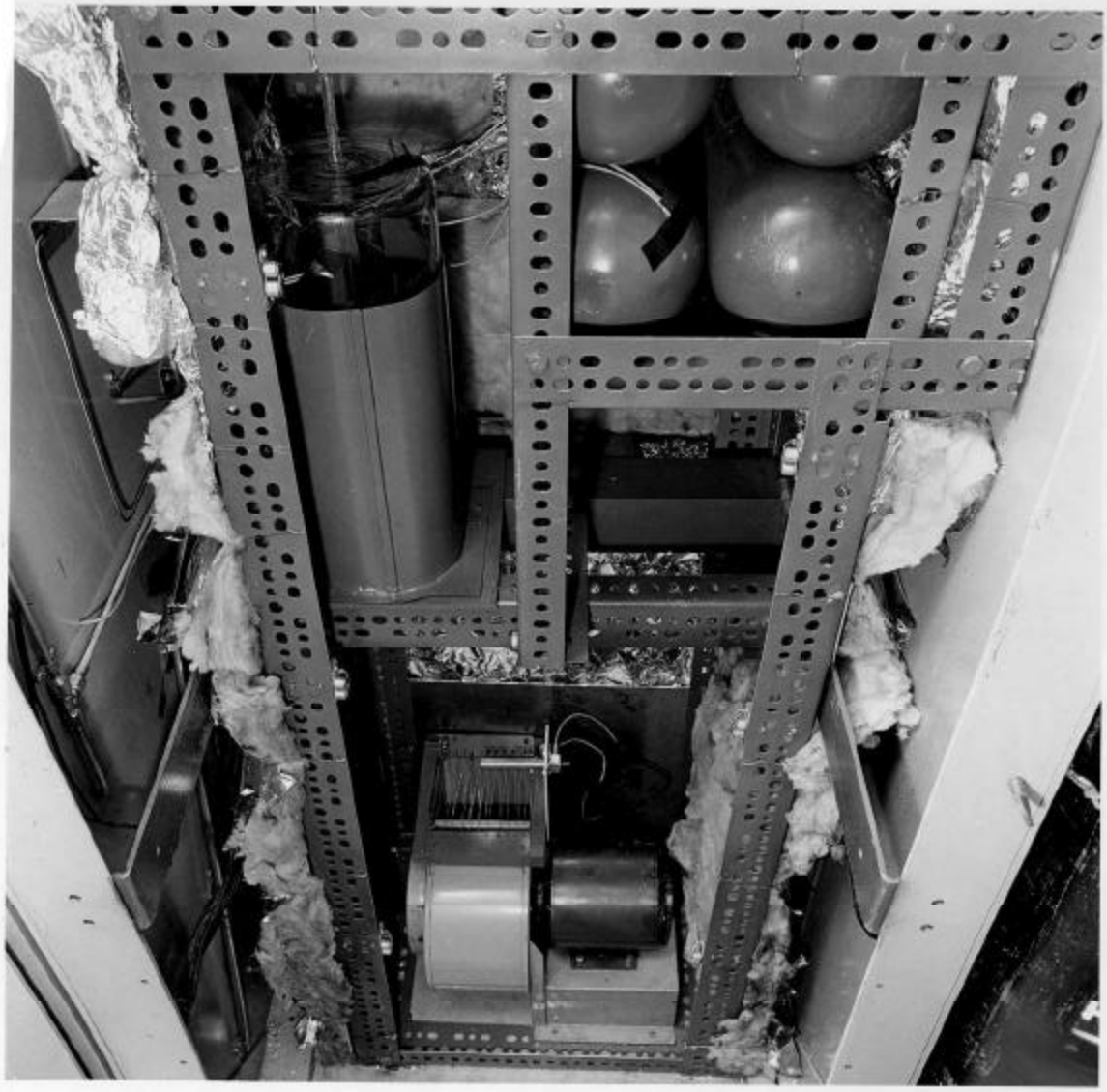
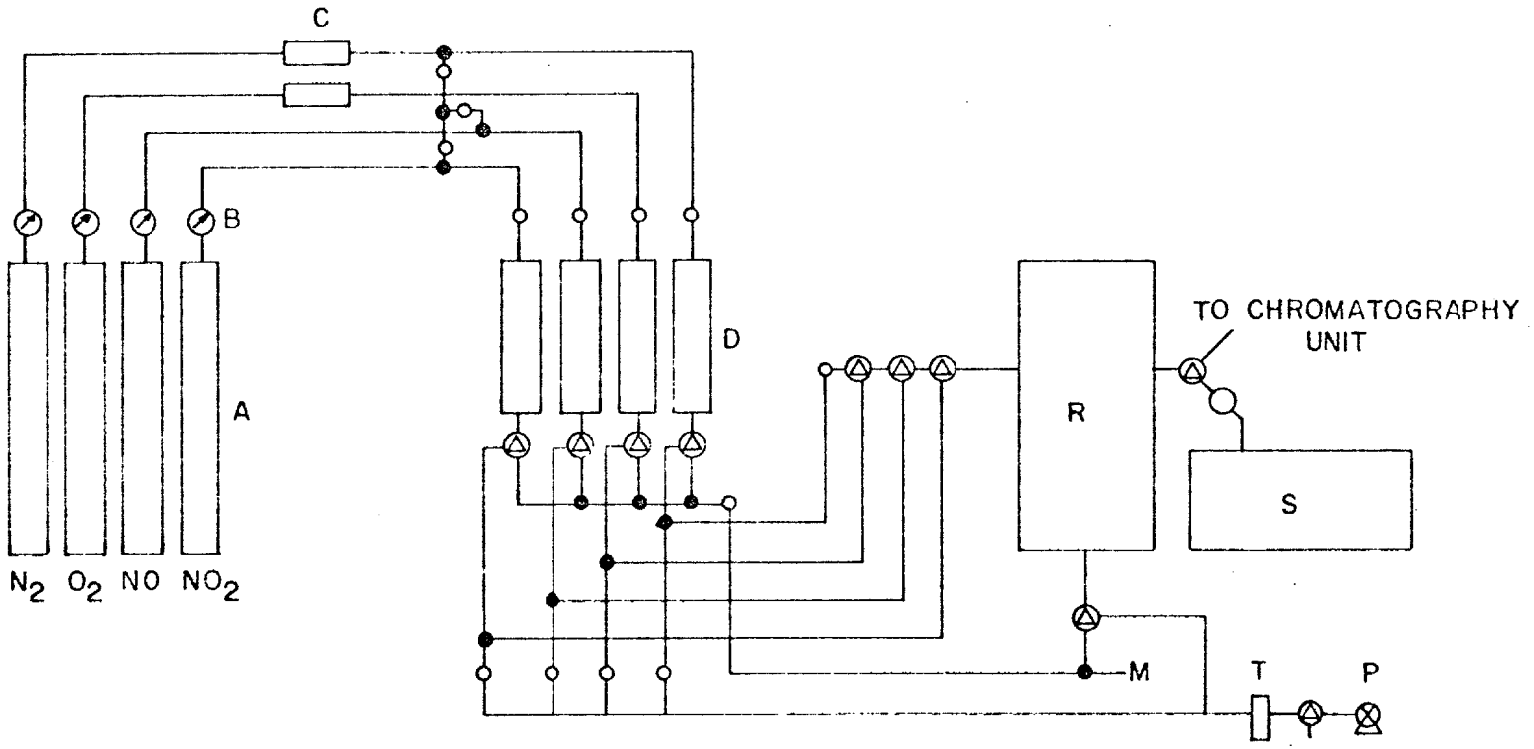


Figure 2. Photograph of the reactor bay for the oxidation study.



⊛	Three-way, 2 mm high vacuum stopcock	D	Hold tanks
○	Straight-bore, 3 mm high vacuum stopcock	R	Reactor
o	Straight-bore, 2 mm high vacuum stopcock	S	Standard tank
A	Gas cylinders	M	Mercury manometer and McLeod Gauge
B	Pressure regulators	T	Liquid nitrogen trap
C	Dry ice-acetone traps	P	Vacuum pump

Figure 3. Flow diagram for the experimental equipment used in the oxidation study.

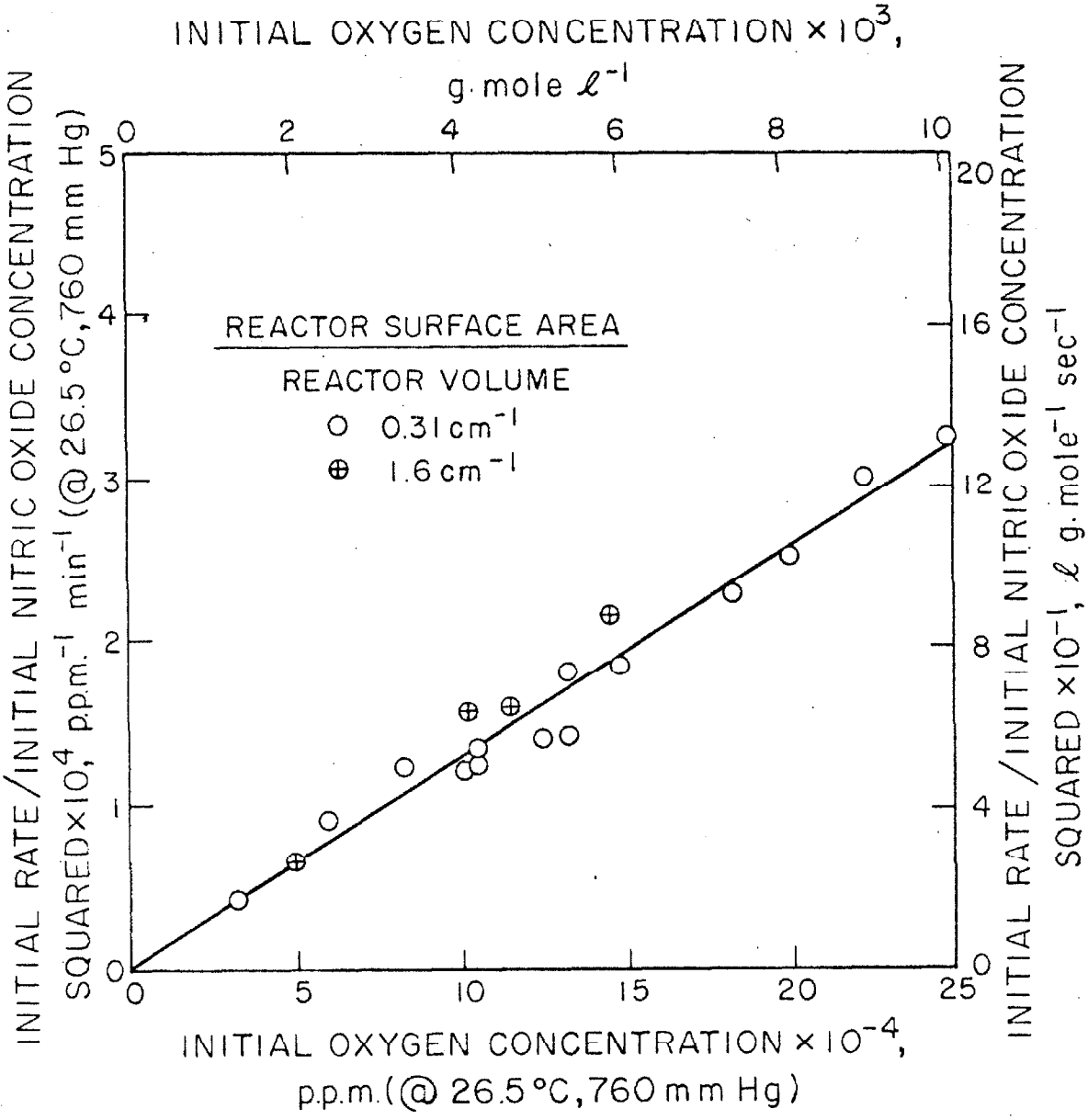


Figure 4. Plot of initial rate data for third order kinetics in the air oxidation of nitric oxide with oxygen as the abscissa.

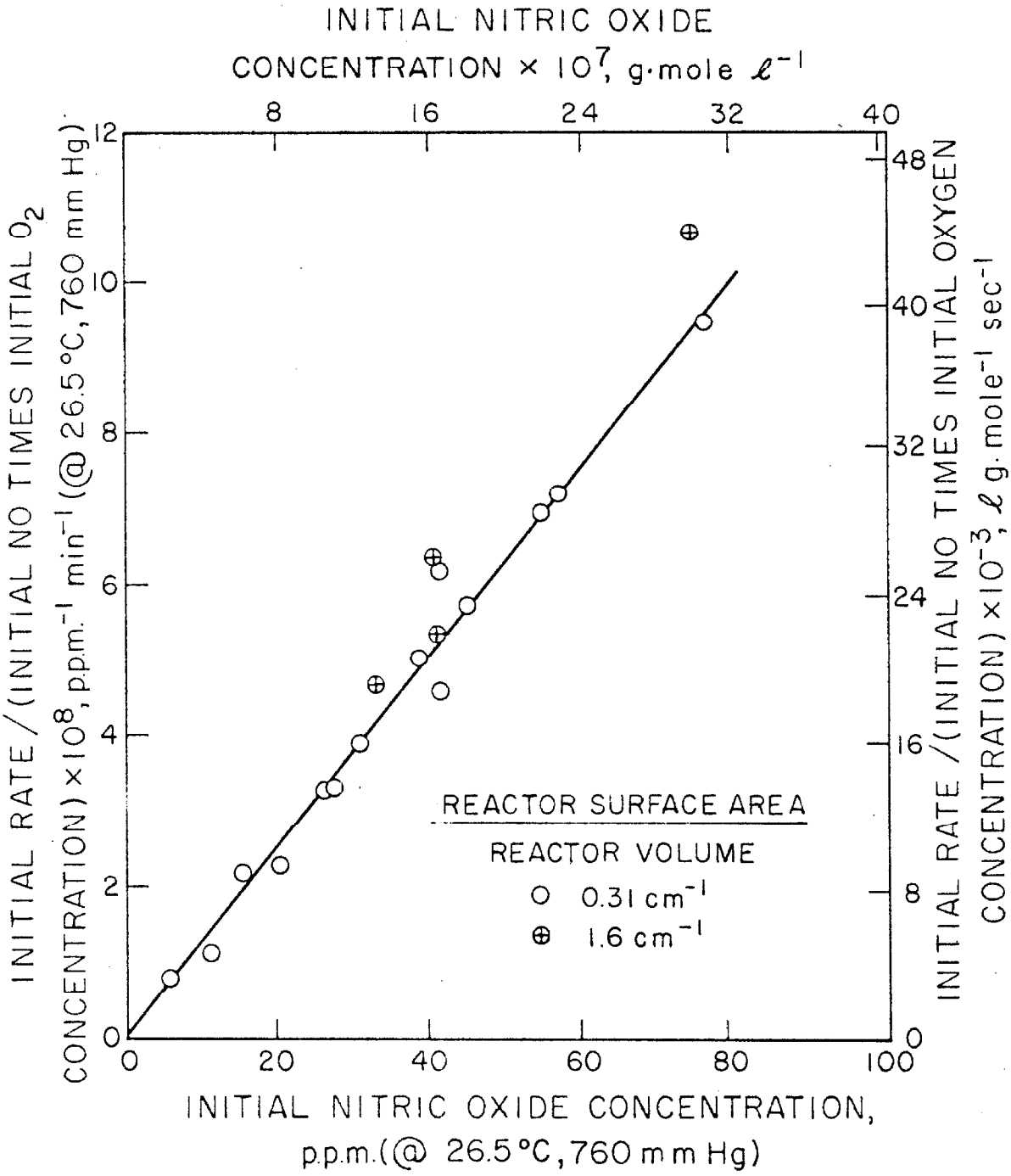


Figure 5. Plot of initial rate data for third order kinetics in the air oxidation of nitric oxide with nitric oxide as the abscissa.

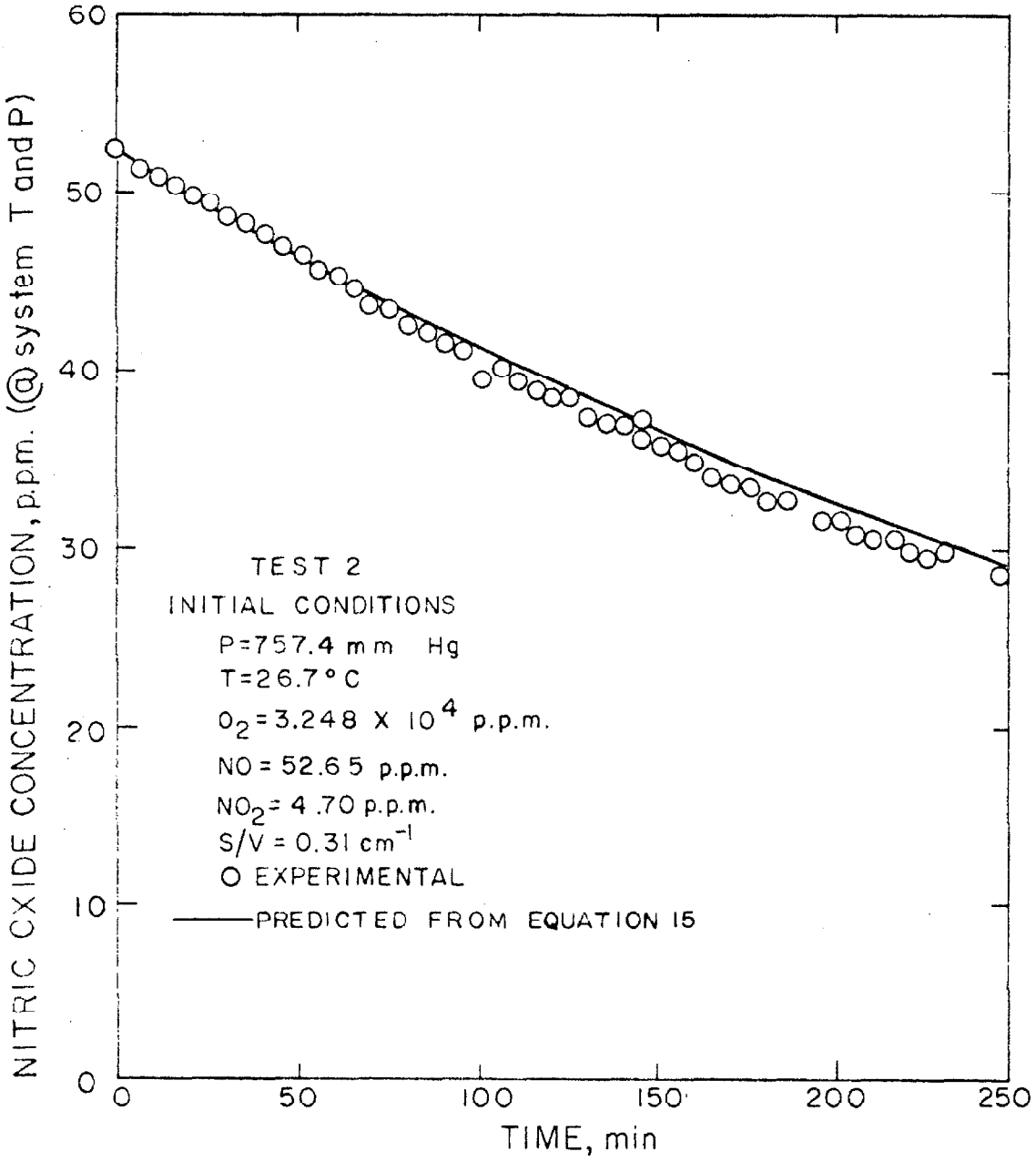


Figure 6. Nitric oxide concentration as a function of time for an initial reactor composition of 3.248 x 10^4 p.p.m. oxygen, 52.65 p.p.m. nitric oxide, and 4.70 p.p.m. nitrogen dioxide.

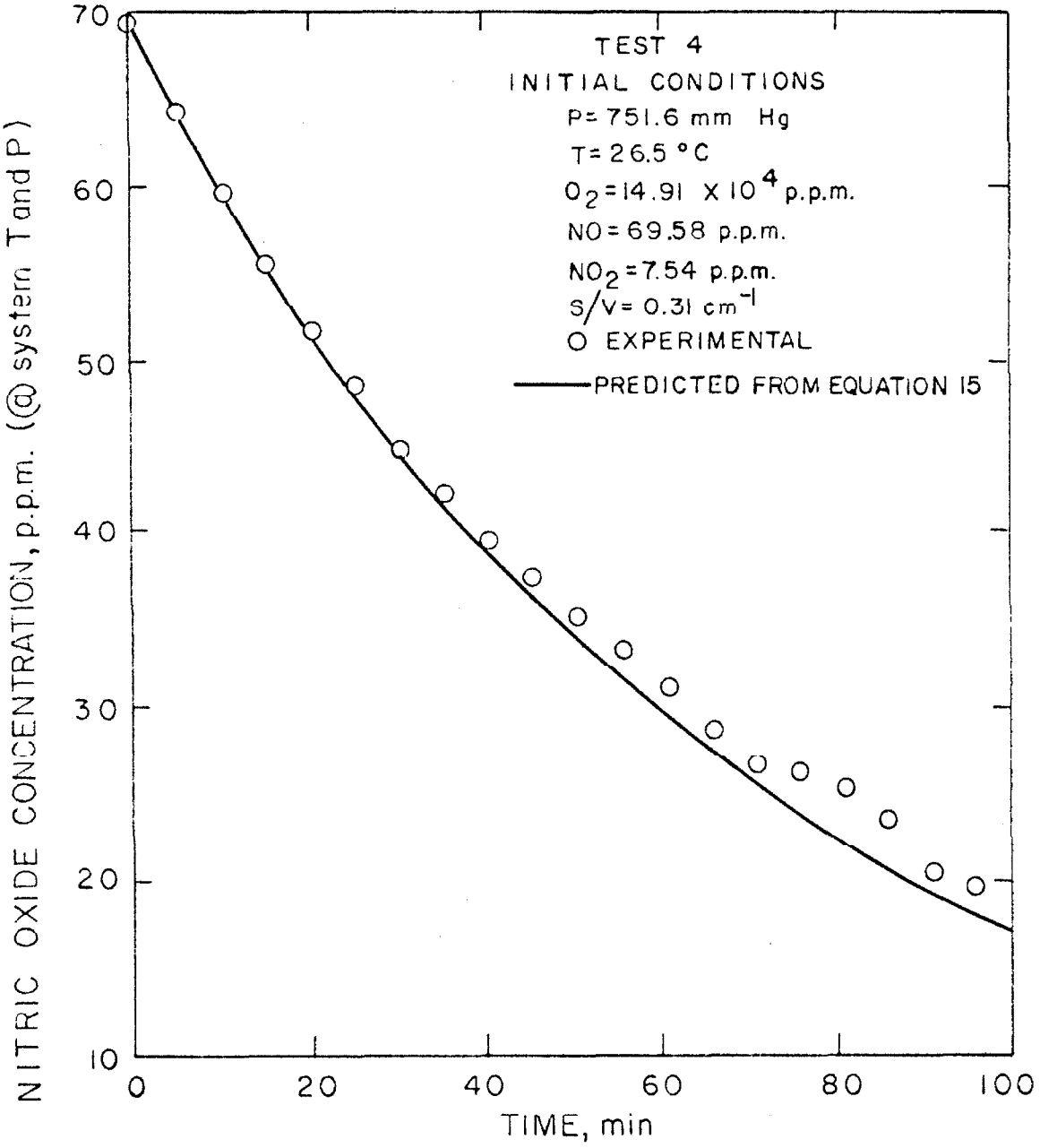


Figure 7. Nitric oxide concentration as a function of time for an initial reactor composition of 14.91 x 10^4 p.p.m. oxygen, 69.58 p.p.m. nitric oxide, and 7.54 p.p.m. nitrogen dioxide.

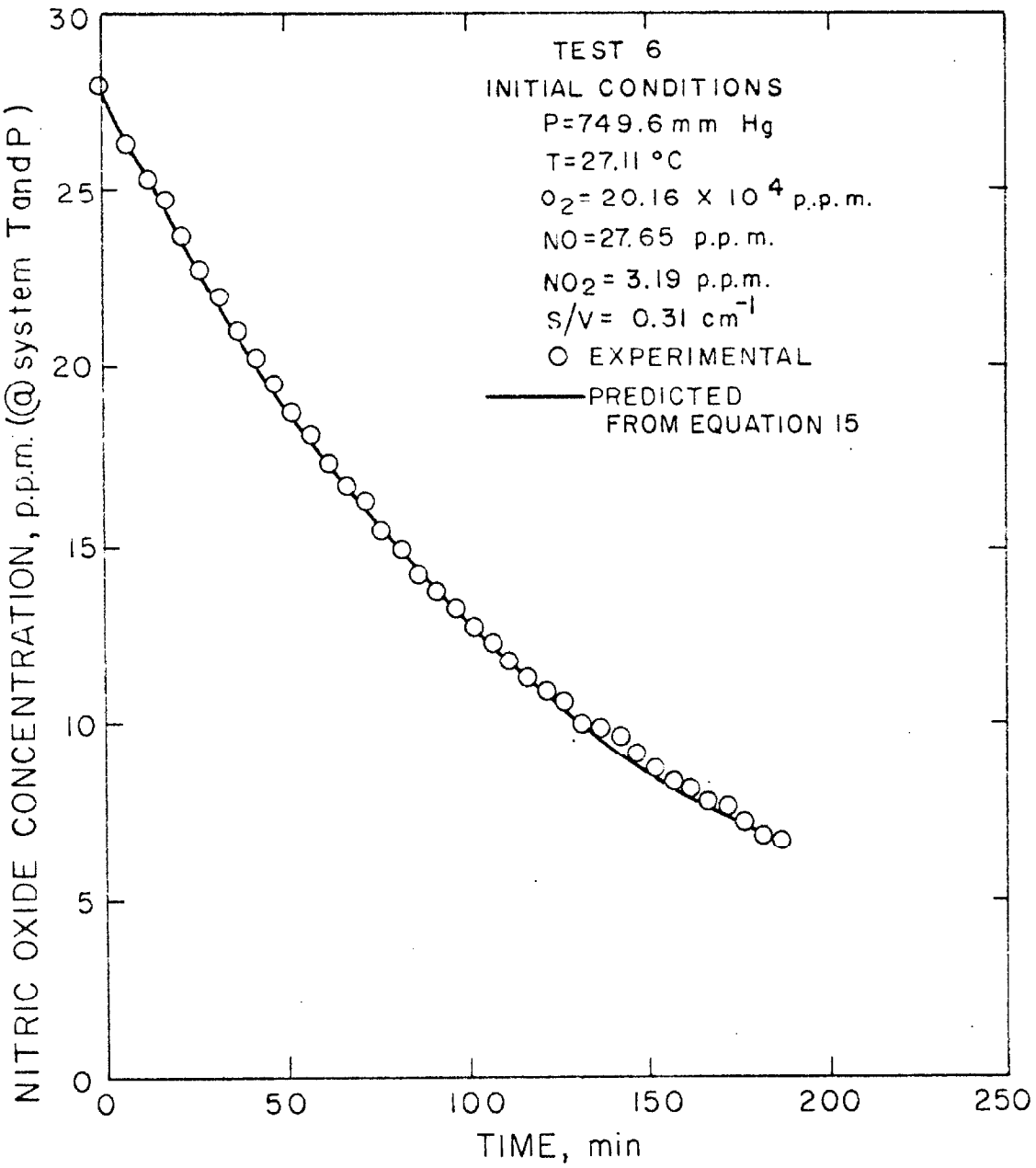


Figure 8. Nitric oxide concentration as a function of time for an initial reactor composition of 20.16 x 10^4 x 10 p.p.m. oxygen, 27.65 p.p.m. nitric oxide, and 3.19 p.p.m. nitrogen dioxide.

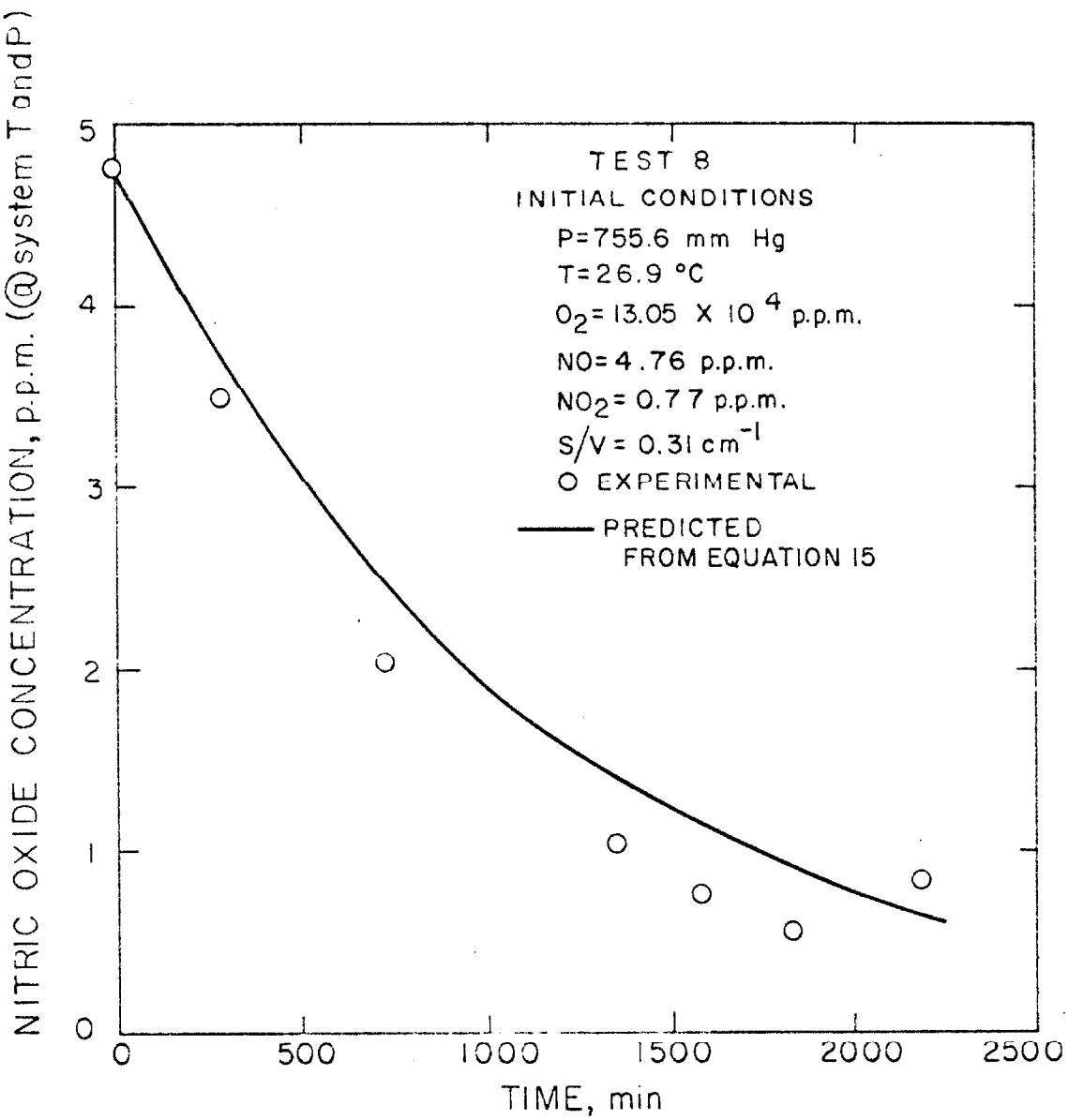


Figure 9. Nitric oxide concentration as a function of time for an initial reactor composition of 13.05 x 10^4 p.p.m. oxygen, 4.76 p.p.m. nitric oxide, and 0.77 p.p.m. nitrogen dioxide.

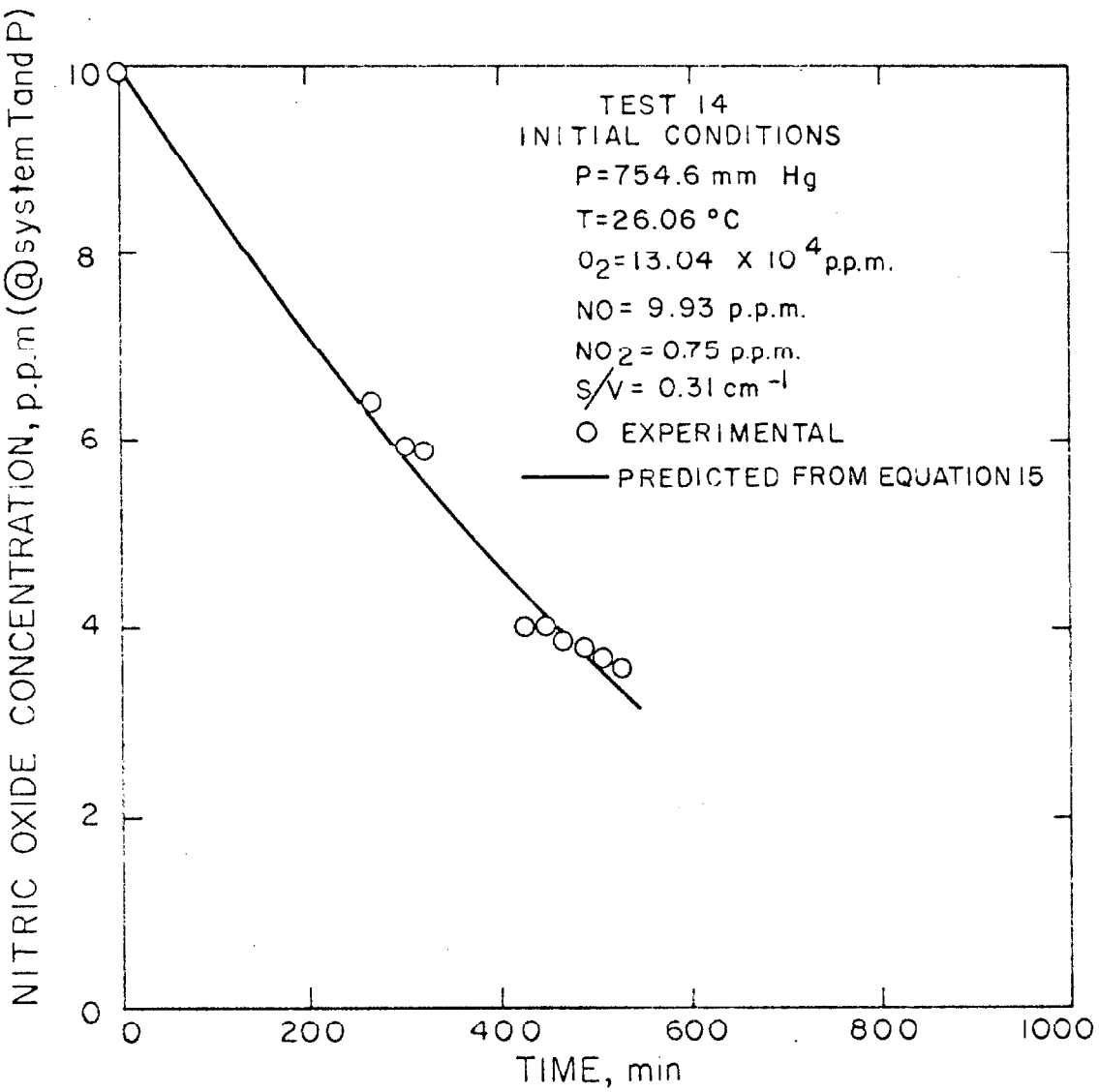


Figure 10. Nitric oxide concentration as a function of time for an initial reactor composition of 13.04 x 10^4 p.p.m. oxygen, 9.93 p.p.m. nitric oxide, and 0.75 p.p.m. nitrogen dioxide.

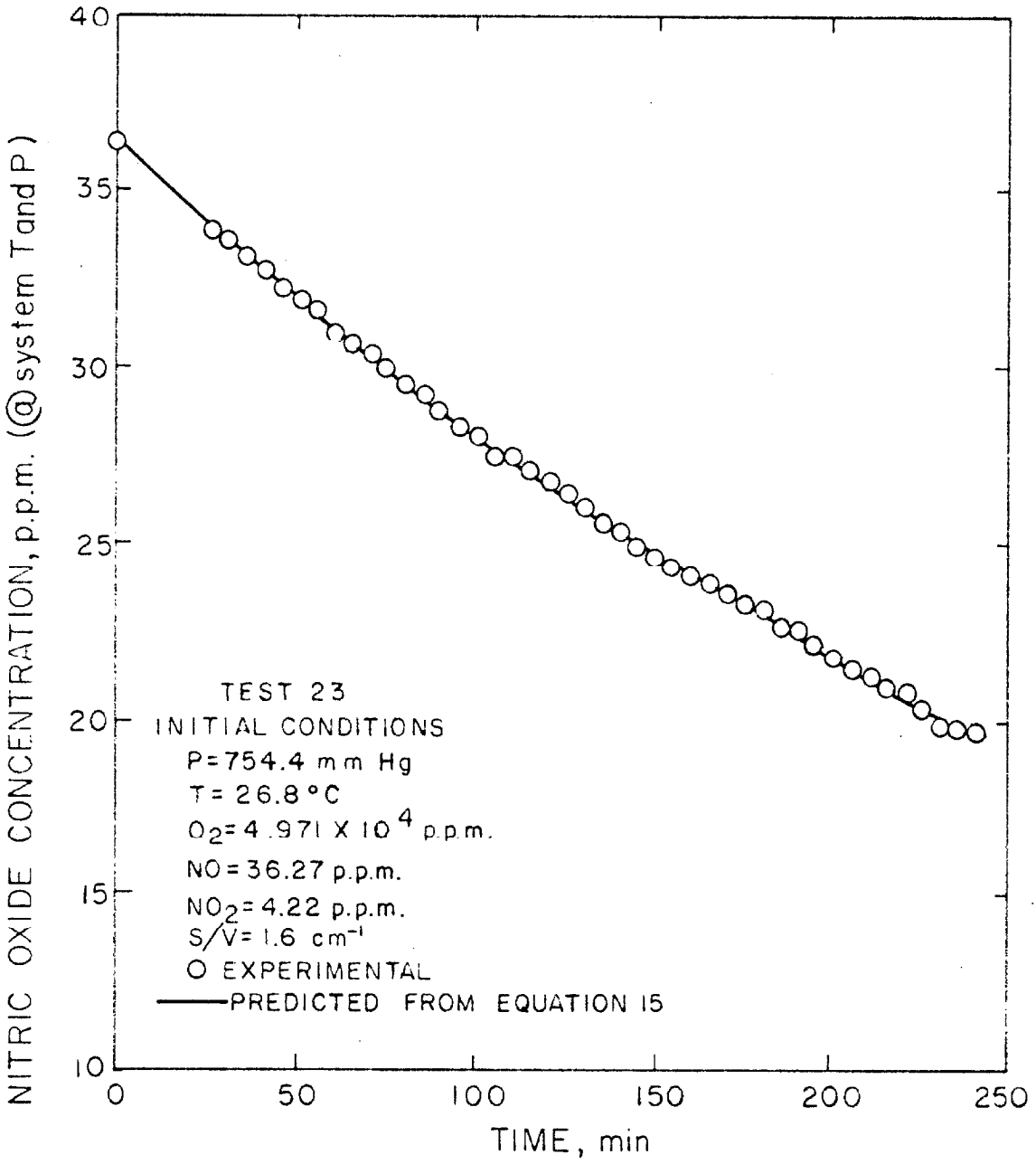


Figure 11. Nitric oxide concentration as a function of time for an initial reactor composition of 4.971 x 10^4 p.p.m. oxygen, 36.27 p.p.m. nitric oxide, and 4.22 p.p.m. nitrogen dioxide.

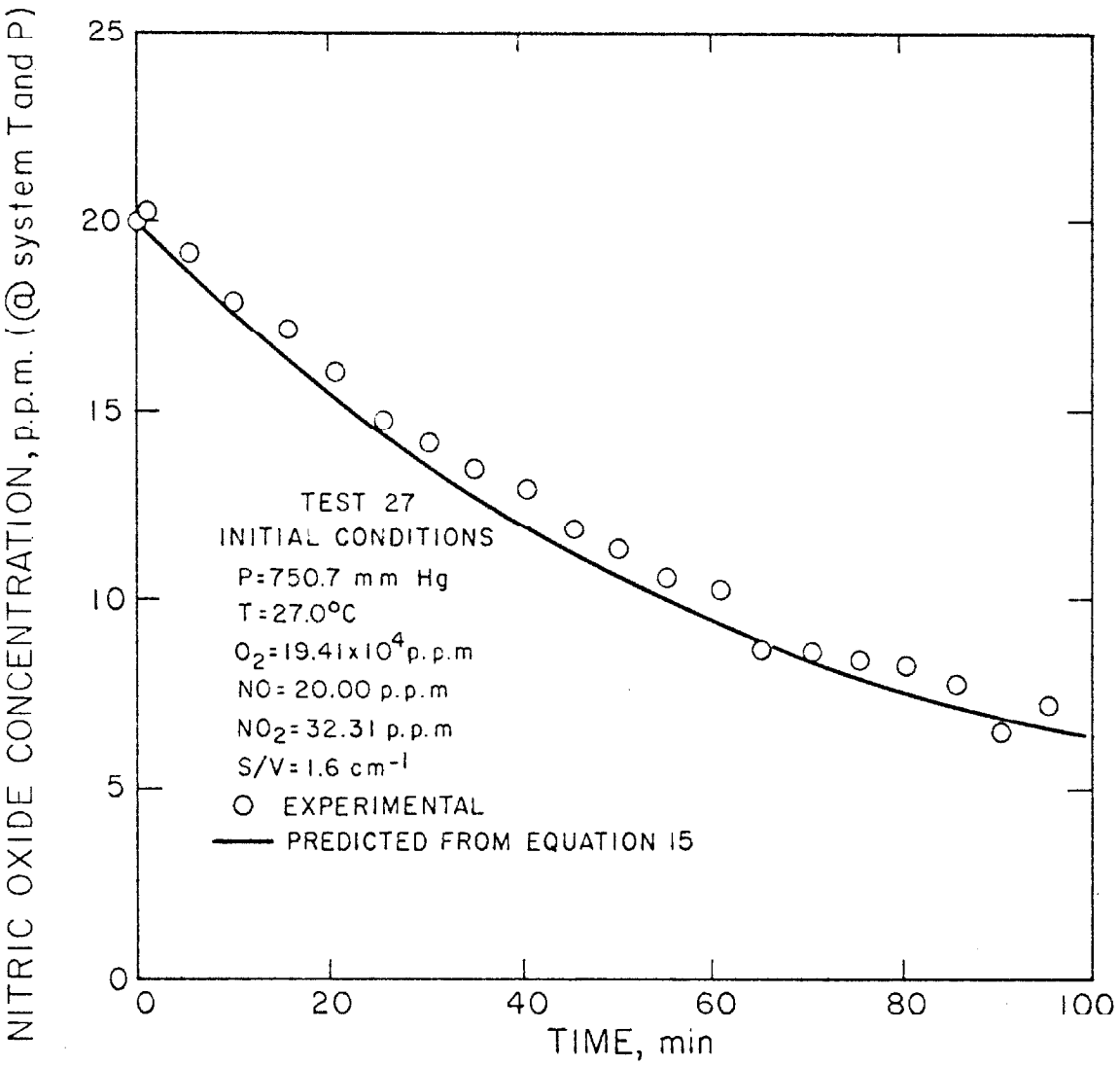


Figure 12. Nitric oxide concentration as a function of time for an initial reactor composition of 19.41 x 10^4 p.p.m. oxygen, 20.00 p.p.m. nitric oxide, and 32.31 p.p.m. nitrogen dioxide.

Appendix A

Diffusion in an Unstirred Constant-Volume Batch Reactor

INTRODUCTION

It is important to know the influence of diffusion in any unstirred reactor. This is especially important when one must determine the effect of the reactor surface upon a given reaction by varying the surface to volume ratio. In this study of the oxidation of nitric oxide the effect of the Pyrex surface was determined by the addition of 3 mm Pyrex glass beads to the reactor.

The reactor was a Pyrex cylinder with a diameter of 7 inches and a height of 16 inches. A gas sample line was connected to the side of the reactor 11 inches from the bottom. The evaluation of the concentration profile for nitric oxide produced by a simultaneous catalytic reaction on Pyrex glass beads at the bottom of the reactor and a homogeneous gas phase reaction is the problem discussed in this Appendix.

REACTOR ANALYSIS

A schematic of the reactor is shown in Figure 1-A. In the derivation of the differential equations which describe the physical problem, the following assumptions were made:

1. There were no radial concentration gradients.
2. There were no angular concentration gradients.
3. The transport of nitric oxide by bulk motion of the gases can be neglected.

4. The change in reactor volume upon addition of glass beads was negligible.
5. The diffusion rate through the packing of glass beads was the same as in the gas phase.
6. There were no temperature gradients.

If a material balance is written over a differential element of the reactor and the assumptions listed above are used, Equation 1-A results

$$D_{v_{NO}} \frac{\partial^2 C_{NO}}{\partial Z^2} - k_h \left(C_{NO}^2 \, C_{O_2}\right) = \frac{\partial C_{NO}}{\partial t} \qquad (1\text{-A})$$

The boundary conditions for the problem are:

$$@ \; Z = 0, \quad - D_{v_{NO}} \frac{\partial C_{NO}}{\partial Z} = \frac{k_c \, A}{V} \; C_{NO}^2 \, C_{O_2} \qquad (2\text{-A})$$

$$@ \; Z = L, \quad \frac{\partial C_{NO}}{\partial Z} = 0 \qquad (3\text{-A})$$

$$@ \; t = 0, \quad C_{NO} = C_{NO_i} \qquad (4\text{-A})$$

Equation 1-A with its three boundary conditions can be solved numerically. If n is the increment in the Z direction and m the increment in time, the following numerical equations result.

$$(C_{m+1,n} - C_{m,n})_{NO} = \frac{D_{V_{NO}} \Delta t}{\Delta Z^2} (C_{m,n+1} - 2C_{m,n} + C_{m,n-1})_{NO}$$

$$- k_h (C_{NO}^2 C_{O_2})_{m,n} \Delta t \qquad (5\text{-A})$$

$$@ \quad Z = 0, \quad - D \frac{(C_{m,1} - C_{m,o})_{NO}}{\Delta Z} = \frac{k_c A}{V} (C_{NO}^2 C_{O_2})_{m,o} \qquad (6\text{-A})$$

$$@ \quad Z = L, \quad (C_{m,k} - C_{m,k-1})_{NO} = 0 \qquad (7\text{-A})$$

$$@ \quad t = 0, \quad (C_{o,n} - C_i)_{NO} = 0 \qquad (8\text{-A})$$

Equations 5-A through 8-A were solved on an IBM 7094 Computer. The rate of the catalytic reaction was varied, as well as the initial concentrations of nitric oxide and oxygen. It was found that if the total production of nitrogen dioxide by the catalytic reaction were the same as for the total homogeneous production for a surface to volume ratio of 0.31 cm^{-1}, then the measured concentration profile would exhibit an apparent increase of 60 percent in the initial third-order rate constant if the surface to volume ratio were increased to 0.62 cm^{-1}, which was definitely greater than the experimental error in the kinetic studies.

CONCLUSION

On the basis of the results presented above, an increase of the surface to volume ratio from 0.31 cm^{-1} to 1.6 cm^{-1} would be more than sufficient to check for surface effects.

NOMENCLATURE

A	Reactor surface area, cm^2.
c	Concentration, g. moles/cm^3.
D_v	Volumetric diffusion coefficient, cm^2/sec.
k_c	Catalytic rate constant, $cm^7/(g.mole)^2(sec)$.
k_h	Homogeneous rate constant, $cm^6/(g.mole)^2(sec)$.
L	Length of reactor in z direction, cm.
r	Radial coordinate, cm.
t	Time, seconds.
V	Reactor volume, cm^3
z	Longitudinal coordinate, cm.
θ	Angular coordinate, radians.

Subscripts

NO	Refers to nitric oxide.
O_2	Refers to oxygen.
m	Increment in time.
n	Increment in z.

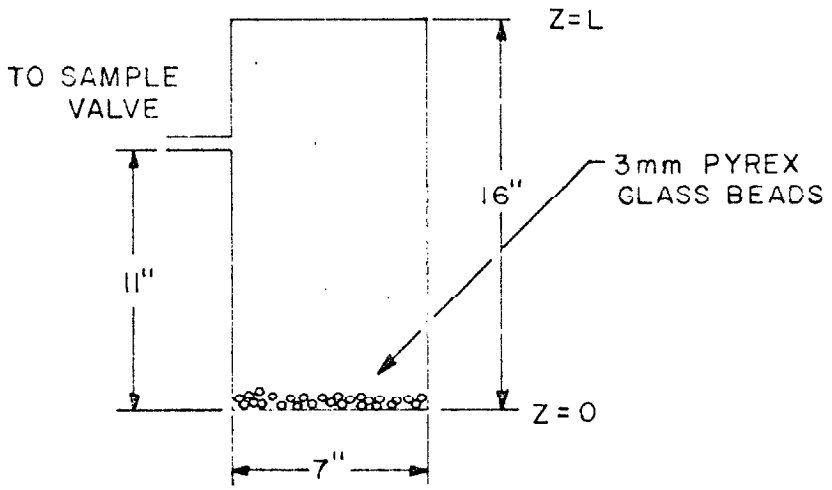


Figure 1-A. Schematic of reactor.

Part II

The Quantitative Determination of Parts-per-Million Quantities of Nitrogen Dioxide in Nitrogen, Oxygen, and up to 75 p.p.m. of Nitric Oxide by Electron-Capture Detection in Gas Chromatography*

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* A portion of the material presented in this part of the thesis has been published by M. E. Morrison, R. G. Rinker, and W. H. Corcoran, Anal. Chem., 36, 2256 (1964). The published article is included as Appendix A.

I. INTRODUCTION

The use of gas chromatography for analysis of nitrogen dioxide below 1000 p.p.m. has not been described in the literature, but Greene and Pust[3] did use a wetted molecular sieve column to analyze for nitrogen dioxide at relatively high concentrations. The dearth of literature for work at low concentrations is probably because of the difficulty in development of a chromatography column to separate nitrogen dioxide reproducibly from its diluents and the lack of acceptable means for detection of parts-per-million (by volume) quantities of nitrogen dioxide. The purpose of the research described here was to develop a chromatography unit that would be capable of quantitative analysis of parts-per-million quantities of nitrogen dioxide and which could be used in a study of the air oxidation of nitric oxide when present in concentrations below 75 p.p.m.

Ionization detectors[1, 4, 5, 9, 11, 14, 18] have recently been developed which have a very high sensitivity to specific compounds. In particular, the electron-capture detector[10] has been shown to be very sensitive to compounds with high affinities for free electrons. Because of the relatively high electronegativity of the nitrogen oxides, an electron-capture detector was studied for its applicability in the detection of parts-per-million

quantities of nitrogen dioxide.

Subsequent to the first description of electron capture for the identification of components of a mixture resolved by gas chromatography[13] the number of applications of the method has been quite small. Specifically, the electron-capture detector has only been used for the detection of small quantities of highly chlorinated materials such as insecticides[2], polycyclic hydrocarbons[12], lead alkyls[18], and aliphatic monohalides[7]. The area of greatest exploitation has been in the detection of picagram quantities of insecticides. Presently the electron-capture detector provides the only satisfactory means for determination of pollution by insecticides of food for human and animal consumption. Even though the electron-capture detector has had practical application, little has been published on the effect of operating parameters on its sensitivity and performance. Therefore, a study of these parameters has been included as part of the present work. The effects of temperature, flow rate, cell geometry, tritium-source size, voltage, and the means of applying voltage to the cell have been studied. In the study of the methods for applying voltage, direct current and pulse modes were used.

II. THEORY OF ELECTRON-CAPTURE DETECTION

Electron-capture detection[10] can be considered as the reaction between a dilute solution of free electrons and reactive molecules both suspended in an inert gas. The reaction is ordinarily carried on in a cylindrical volume with a diameter and length of one centimeter into which has been placed a tritium source of approximately 200 mc. This volume is continually swept with a stream of inert gas, I_g, which does not absorb electrons; nitrogen, hydrogen, and the noble gases are inert in this sense. The chamber is connected to a source of low potential and to some means of measuring the resulting current flow. The potential applied across the cell is just sufficient to collect all of the electrons produced by the following reaction:

$$\beta^- + aI_g \longrightarrow aI_g^+ + (a + 1)\, e^- \qquad (1)$$

In the reaction, the β-rays (0.018 mev) are produced by the decay of tritium to $_2He^3$.

If an electron-absorbing material is introduced into the gas stream, the flow of current will decrease. The absorption of the electrons is mainly due to the following three reactions:

$$e^- + AB \longrightarrow AB^- + \text{energy} \qquad (2)$$

$$e^- + AB \longrightarrow A + B^- \pm \text{energy} \qquad (3)$$

$$I_g^+ + AB^- \text{ (or } B^-) \longrightarrow I_gAB \text{ (or } I_gB) \qquad (4)$$

In the reaction shown in Equation 2, where the negative molecular ion is formed, the heat of reaction is defined as the electron affinity of the molecule. The energy is released by either radiation, collision with other molecules, or by splitting the negative molecule into a free radical and negative ion. If the exothermic reaction, as shown in Equation 2, were the governing process in electron capture, the sensitivity of the detector would vary inversely with temperature. For the reaction shown in Equation 3, the molecule dissociates after electron absorption to give a free radical and negative ion. This reaction is generally endothermic, and therefore proceeds further to the right with an increase in temperature. Thus, the effect of temperature on electron-capture detection is a function of the heats of the reactions in Equations 2, 3, and 4. If at a given temperature the detector response is calibrated as a function of the concentration of electron-absorbing gas, it can be used for quantitative analysis.

In addition to temperature, the response of an electron-capture detector is a function of the flow rate

of inert gas, cell geometry, and potential, but the absolute sensitivity of this cell is dependent upon the inherent noise from random emission of the β-rays from the tritium source. The magnitude of the noise can be calculated in an approximate manner from the Shot Equation[16]:

$$\overline{i^2} = 2\, e'(a + 1)\, I_o B_w \qquad (5)$$

In Equation 5, e' is the charge of an electron, I_o the quantity of β-rays emitted from the tritium foil per unit time, a the number of electrons formed by ionization per emitted β-ray, B_w the electrometer bandwidth, and $\overline{i^2}$ the mean square fluctuating current due to random arrival of electrons at the anode. Use of this equation gave a noise level of $6(a + 1) \times 10^{-13}$ amperes. Therefore, the theoretical detection limit of this cell could be defined as that quantity of electron-capturing material which would yield a change in current of $6(a + 1) \times 10^{-13}$ amperes.

III. EXPERIMENTAL METHOD

Briefly, the experimental method for the chromatographic analysis of the nitrogen oxides consisted of the following steps:

1. Initial studies were carried out to determine the feasibility of using electron-capture or argon-ionization detection for nitric oxide and nitrogen dioxide in p.p.m. quantities.

2. A number of types of column packings were tested for the separation of nitrogen dioxide from nitrogen, oxygen, and nitric oxide.

3. The response of a commercial electron-capture detector to nitrogen dioxide was studied as a function of the operating parameters.

4. A new electron-capture cell was designed and built.

5. The response of the new cell to nitrogen dioxide was studied as a function of the operating parameters.

6. Calibration data were obtained with the newly designed detector for use in the study of the air oxidation of parts-per-million concentrations of nitric oxide.

With the above outline of the research program in mind, the required equipment was procured and the experimental program begun.

IV. EXPERIMENTAL APPARATUS

The gases and equipment that have been described in Part I of this thesis were used to prepare calibration mixtures for the chromatography unit. A Loenco 15A Chromatograph with a Loenco 15B Electrometer was used in this study. The output of the electrometer was monitored on a Texas Instrument "servo/riter" Recorder. The recorder gave a full-scale deflection for one millivolt, had a 0.5 sec response, and used a 9-3/4 inch chart width. A Hewlett-Packard Model 214A Pulse Generator was used when the plane-parallel detector was operated in the pulse mode for electron-capture. A Type 503 Tektronix Oscilloscope was used to measure the output of the pulse generator. When the detectors were operated in the d.c. mode for electron-capture, Eveready dry cells were used as the voltage source. The high d.c. voltage required for the argon ionization mode was obtained from a Model 218B Alfred Electronics regulated power supply.

Gases

Linde commercial grade argon (purity of 99.996 percent) or hi-purity dry nitrogen from Linde (purity of 99.995 percent) was used as carrier and scavenger gas. Gas regulators recommended by Matheson were used on the outlets of the cylinders. Both the carrier and scavenger

gases were cleaned by passage through a four-foot length of ¼ inch o.d. by 3/16 inch i.d. copper tubing packed with 14/20 mesh 13X Molecular Sieve and mounted in a dry ice-acetone bath. All tubing used in the chromatography equipment, other than that used in the dry ice-acetone traps, was 304 stainless steel and was cleaned before use by passing hi-purity dry nitrogen through it while heating with an oxygen-natural gas torch. One-eighth inch Nupro "very fine metering" needle valves were used to regulate the flow of scavenger and carrier gas. A bubble flow meter was used to measure the flow rates of scavenger and carrier gases.

Chromatography column

The chromatography column that was used for separation of nitrogen dioxide from nitrogen, nitric oxide, and oxygen consisted of a packing of 10 percent by weight of SF-96 (a methyl silicone oil) on 40/80 mesh Fluoropak 80. Both the liquid and solid phase where obtained from Wilkens Instrument and Research, Inc. The packing was placed in a twenty-foot length of 1/8 inch, 304 stainless steel tubing which had a wall thickness of 0.016 inch. The preparation of the column is discussed in Section V. A Loenco 208 stainless steel sampling valve was used to introduce the gas sample into the column. The hold-up time for various components was measured with a Clebar stopwatch.

Detectors

For the early studies, nitric oxide and nitrogen dioxide were detected with a Barber-Colman A-5042 detector. This detector was operated in the d.c. electron-capture mode. Figures 1 and 2 are photographs of this detector, and Figure 3 is a scale drawing of the cross-section. The β-ray source was 220 mc of tritium.

A plane-parallel detector was designed and built, which was similar to that described by Lovelock[10]. A source of approximately 180 mc of tritium was used. It was made by cutting a one-centimeter disk from a sheet of tritiated titanium foil, which had an activity of 1.5 ± 0.3 curies per square inch and was obtained from Radiation Research Corporation. Figure 4 is a photograph of the plane-parallel detector in the oven in which it was used during this study. A Fisher thermoregulator was used to insure that the temperature of the oven never exceeded 220°C. Figure 5 is an enlarged photograph of the detector, and Figure 6 is a photograph of the several parts of the detector. A cross-section drawing is shown in Figure 7. The body of the detector was made from 1-1/4 inch Teflon bar stock and 304 stainless steel. The diffusion screen was 150 mesh with 0.0041 inch openings and was made from 304 stainless steel.

Caution must be used in handling the tritium foil.

The possible radiation hazards which may arise from the use of radiation detectors in gas chromatography have been discussed by Taylor[17].

V. EXPERIMENTAL PROCEDURE

Column preparation

Several columns were tested for their ability to separate oxygen, nitrogen, nitric oxide, and nitrogen dioxide. They were 5 percent by weight of 710 silicone oil on Chromosorb W(HMDS), 5 percent Apiezon L on Chromosorb W(HMDS), 13X Molecular Sieve, an unpacked capillary column with a coating of aluminum oxide, and an uncoated glass capillary column. These columns did not effect a satisfactory separation, and at the suggestion of I. H. Williams of the British Columbia Research Council, 10 percent SF-96 (a methyl silicone oil) on Fluoropak 80 was tried and gave a reasonable separation of nitrogen dioxide from oxygen, nitrogen, and nitric oxide.

Special care was required in the preparation of the column containing 10 percent by weight of SF-96 on Fluoropak 80. Twenty grams of 40/80 mesh Fluoropak 80 were weighed to the nearest 0.1 g and placed into a 1000 ml round-bottomed flask. Two grams of SF-96 were weighed into a 50 ml beaker. Approximately 30 ml of reagent-grade anhydrous diethyl-ether, purchased from the Mallinckrodt Chemical Company, were added to the beaker containing the SF-96. This mixture was stirred with a glass stirring-rod and then poured into the flask containing the Fluoropak 80. The beaker was rinsed several times with the diethyl-ether,

and each rinse mixture was poured into the flask containing the Fluoropak 80 until the solid phase was completely covered with liquid. The mixture of diethyl-ether, SF-96, and Fluoropak 80 was stirred for ten minutes. The flask containing this mixture was next held over a steam bath and stirred until most of the diethyl-ether vaporized. Hi-purity dry nitrogen which had been dried by passage through a 13X Molecular Sieve trap was passed over this mixture for two hours while it remained on the steam bath. The flask was tightly stoppered so that the packing came only in contact with the nitrogen. During this two-hour period the flask was periodically shaken. The packing was then placed into a clean, dry, sample bottle and tightly capped.

The twenty-foot column was packed in two ten-foot lengths. Each ten-foot length was packed by plugging the lower end of the 1/8 inch, 304 stainless steel tubing (wall thickness of 0.016 inch) with a small piece of glass wool and adding the packing to the other end through a funnel. The packing was facilitated by use of a Burgess "vibro tool". When the tubing was completely full of packing, the upper end was closed with a small plug of glass wool. Occasionally large conglomerates of packing would wedge into the tubing. When this happened, the tubing was emptied and packing begun again.

Each of the ten-foot lengths was treated in the same manner. One length was coiled into a diameter of approximately 4 inches and conditioned at 200°C in the chromatograph oven for thirty hours by flowing dry nitrogen through it at a rate of 10 cc per minute as measured at 1 atm and 22°C. Then that length was cooled to 22°C while the nitrogen flow was maintained. Next, twenty 3 cc samples of nitrogen, each containing 300 p.p.m. of nitrogen dioxide were injected into the column at five-minute intervals. This length of column was then put into a desiccator and the second length of column conditioned in exactly the same manner. Then, the two sections of column were connected with a 1/8 inch, 316 stainless steel Swagelock union and put into the chromatograph oven. The complete column was then ready for the calibration runs. The detector was not connected to the column during the above conditioning process. Occasionally a peak emerged after nitrogen dioxide at approximately 340 sec. This was due to water in the samples or column. By evacuating the reactor and making a new dry gas mixture containing 300 p.p.m. of nitrogen, this peak was eliminated after the addition of several 3 cc samples.

Gas analysis

A gas mixture containing nominally 1500 p.p.m. of nitrogen dioxide in nitrogen was furnished by Matheson. It was analyzed for nitrogen dioxide by the phenol-disulfonic acid method (ASTM D 1608-60). The impurities in the gas mixture were no greater than 10 p.p.m. of water, 20 p.p.m. of oxygen, and 20 p.p.m. of hydrogen. The results of this analysis are shown in Table 1. Samples 1 through 3 were taken after the Matheson gas mixture had remained in the reactor for twenty-four hours. Samples 4 through 6 were analyzed after passing the gas mixture straight through the nitrogen dioxide hold tank and reactor, and into the 1000 cc bulbs used for analysis. The results are within the accuracy of the analysis method, i.e., 6 percent. In order to check for adsorption of the nitrogen dioxide on the walls of the reactor or absorption in the Apiezon N stopcock grease, a mixture of approximately 50 p.p.m. of nitrogen dioxide in nitrogen was made in the reactor. This mixture was made by evacuating the reactor below 0.05 mm of mercury and adding approximately one-fifth atmosphere of the Matheson mixture and four-fifths of an atmosphere of nitrogen to the reactor. The resulting gas mixture was diluted two more times by partially evacuating the reactor and adding nitrogen. The result of a chemical analysis of this gas mixture and the calculated concentration is shown in Table 1 as Sample 7. The agreement of the

two values is within the experimental accuracy of the chemical analysis.

A gas mixture containing nominally 1000 p.p.m. of nitric oxide in nitrogen was furnished by Matheson. It was analyzed by the same phenol-disulfonic acid method. The impurities were the same, i.e., less than 10 p.p.m. of water, 20 p.p.m. of oxygen, and 20 p.p.m. of hydrogen. The results of the analysis are shown in Table 2. Samples 1 through 3 were taken after the gas mixture had remained in the reactor for twenty-four hours. Samples 4 through 6 were analyzed after passing the gas mixture straight through the nitric oxide hold tank and reactor, and into the 1000 cc bulbs used for analysis. The results are well within the accuracy of the analysis method. In order to check for wall adsorption or losses in stopcock grease, a mixture of approximately 50 p.p.m. of nitric oxide in nitrogen was made up in the reactor. This was prepared by three successive dilutions. The result of a chemical analysis of this gas mixture and the calculated concentration is shown in Table 2 as Sample 7. The agreement of the two values is again within the accuracy of the chemical analysis.

General

Figure 8 is a complete schematic of the chromatography equipment. Extremely good electrical grounds and insulation were necessary.

Experiments were carried out to determine the optimum operating conditions for the column. In these experiments the A-5042 detector was used. Studies were also carried out with the detectors to determine their sensitivity characteristics. The results of these investigations are discussed in Section VI.

Calibration studies

After the optimum operating conditions for the column and detector were determined, the chromatography unit was calibrated for nitrogen dioxide. The nitrogen dioxide-nitrogen mixture, which has been discussed above, was used in this calibration. The reactor was evacuated below 0.05 mm of mercury. The Matheson mixture, containing 1627 p.p.m. of nitrogen dioxide in nitrogen, was diluted by adding approximately one-fifth atmosphere to the reactor. Next, the purified oxygen and nitrogen were added to the reactor until the pressure was slightly greater than one atmosphere. A cathetometer was used to measure the pressure changes on the mercury manometer. This mixture was diluted approximately one-third, by partial evacuation of the reactor and addition of oxygen and nitrogen.

Several 0.5 cc samples of this mixture were analyzed at five minute intervals until reproducible results were obtained. This required three to ten samples. The samples were taken from the reactor by evacuating the sample loop and then allowing the gas to flow into the 0.5 cc volume. Lower concentrations of nitrogen dioxide were analyzed by subsequent partial evacuation of the reactor and addition of nitrogen and oxygen. Three samples of each gas mixture were analyzed. The samples were introduced at five-minute intervals; otherwise, at concentrations of less than 20 p.p.m. of nitrogen dioxide the nitrogen dioxide peaks were not completely reproducible. A normal calibration run with six to seven different concentrations of nitrogen dioxide required, including evacuation of the reactor, four to five hours. The calculation of the concentrations of the gas samples was done by assuming the gases behaved ideally. Essentially no error was introduced by making this assumption, since the compressibility factors for N_2, O_2, NO, and NO_2 at the conditions used for this work are all greater than 0.995.

VI. DISCUSSION OF RESULTS

Chromatography column

A number of experiments were made to optimize the separability of the SF-96 on Fluoropak 80 column as a function of : (1) carrier flow rate, (2) temperature, (3) packing size, (4) weight fraction of liquid phase and (5) length. The results of these experiments are shown in Table 3.

Previous work has shown that a volume of 0.5 cc is the largest sample which a 1/8 inch column can acceptably separate without excessive overloading and decreased efficiency. Therefore, 0.5 cc samples were used in these optimization studies. The Barber-Colman A-5042 Detector was used for the work.

Low flow rates for the carrier gases tended to give broad tailing of the nitrogen dioxide peaks with large separation times between oxygen and nitrogen dioxide. Higher flow rates gave sharper nitrogen dioxide peaks with smaller separation times. The optimum flow rate value of 10 cc per minute was a compromise which gave only slight tailing of nitrogen dioxide peaks but complete separation between nitrogen dioxide and up to 25 percent oxygen.

The temperature of the column over a range from 0 to 50^{o}C did not measurably affect the separation of

nitrogen dioxide and oxygen. Thus, the column was operated at room temperature, 22 $\pm$ 2°C.

The packing size and weight fraction of liquid phase did not markedly affect the separation. The smaller packing tended to pack more tightly in the column causing a larger pressure drop and decreased column efficiency. The low concentration of liquid phase on Fluoropak 80 was difficult to prepare in the laboratory because the packing would not evenly coat with liquid. The optimum packing thus was 40/80 mesh Fluoropak 80 with 10 percent by weight of SF-96.

With the optimum column parameters it was found that a twenty-foot column was sufficient to separate nitrogen dioxide from nitric oxide, nitrogen, and oxygen. The retention time for oxygen, nitric oxide, and nitrogen was 120 seconds. For nitrogen dioxide the retention time for the optimum column operating conditions was 148 seconds.

Barber-Colman A-5042 Detector

The chromatography column was used at the optimum conditions to study the characteristics of the Barber-Colman A-5042 Detector and to determine the feasibility of its use in the detection of nitrogen dioxide at low concentrations. These experiments were designed so that the optimum operating conditions for the detector would be obtained. Tests were carried out to determine the effect

on the detector of scavenger flow and detector potential. Measurements were also made to determine the noise level of the detector and thus the sensitivity limit for nitrogen dioxide. Preliminary experiments showed that the detector was approximately 100 times more sensitive to nitrogen dioxide than to nitric oxide. Therefore the work reported here is only with regard to the response obtained from nitrogen dioxide.

Figure 9 presents information on the response obtained as the detector potential was varied for constant values of total nitrogen flow. In this study, 0.5 cc samples of nitrogen containing 10 p.p.m. of nitrogen dioxide were used. Within the limits of experimental error for a nitrogen carrier flow of 10 cc per minute, a scavenger flow of 85 cc per minute of nitrogen and a detector potential of 33 volts gave the most sensitive response.

The background current was studied as a function of total nitrogen flow and detector potential for comparison with the results presented in Figure 9. Figure 10 shows the background current as a function of the total flow rate of nitrogen. The data were obtained at a constant potential of 33 volts and a flow of scavenger gas or carrier gas of 10 cc per minute. Figure 11 shows the background current as a function of detector potential for a constant flow rate of 85 cc per

minute of scavenger gas and 10 cc per minute of carrier gas. In Figure 11 the lower curve is the background current as a function of detector potential in the absence of water traps on the nitrogen carrier and scavenger streams. The need for removal of water by the molecular sieves is shown to be very important. It is interesting to note that the optimum conditions for the operation of the electron capture cell, i.e., 33 volts, 10 cc per minute of nitrogen carrier gas, 85 cc per minute of scavenger gas, and a background current of 8.6×10^{-9} amperes, appear in Figures 10 and 11 at the point just before the curve tends to become level. Landowne and Lipsky[7] obtained this same result. The noise level for this detector, operating at the optimum conditions, was 1.6×10^{-11} amperes.

A chromatogram for the optimum conditions of analysis is shown in Figure 12. Nitrogen was the diluent. The concentration of nitrogen dioxide was 18.3 p.p.m. and that of oxygen was 3.9×10^{4} p.p.m. The sample pressure and temperature were 755.4 mm of mercury and 20.7°C, respectively. Oxygen was present just to check separation, and the multiple oxygen peak was developed merely by decreasing the attenuation by factors of two from a value of 128 to 16 during the course of the oxygen peak. The sample volume was 0.5 cc.

Lovelock[10] noted that the electron-capture detector should obey the following equation:

$$I = I_s e^{-BC} \tag{6}$$

in which I is the measured current in the presence of the test substance at a concentration C, I_s is the background current or current measured with no electron-capture material in the detector cell, and B is a constant. Rearrangement of the equation gives

$$C = A - D \ln I \tag{7}$$

in which A and D are constants. I is obtained by use of the following relation:

$$I = I_s - I_p \tag{8}$$

where I_p is a decrease in current effected by the presence of the electron-capture substance and is obtained as the product in appropriate units of the peak height measured for that substance and the prevailing attenuation. A semilog plot of I as a function of the concentration of nitrogen dioxide in parts-per-million in the presence of nitrogen is given in Figure 13. Over the range of 5 to 150 p.p.m. of nitrogen dioxide the experimental data did not exactly follow Lovelock's proposed relationship as expressed

by Equation 7. A least-squares analysis of the data using Equation 7 gave the dashed line with a standard deviation of 7.3 p.p.m. while the best curve through the averaged experimental points was the solid line with a standard deviation of 2 p.p.m. of nitrogen dioxide. The lower limit of concentration of about 5 p.p.m. was set by the noise in the detector circuit. The day-to-day variability for this system was not determined, since a new detector design was to be studied.

Subsequent to the experiments reported above, argon was used as both carrier and scavenger gas. With argon, the sensitivity was increased by a factor or two.

As has been discussed under theory, the noise level of an electron-capture detector should be of the order of 10^{-12} amperes ($a \cong 5$), if the only noise is that due to random emission of the β-rays from the tritium foil. By means of an oscilloscope, measurements were made on the noise under normal operating conditions in the detector circuit. The noise seemed to be somewhat cyclic (10 c.p.s.) and was affected quite markedly by small changes in the flow of scavenger gas. The electrical noise was measured by replacing the detector with a 5×10^{7} ohm resistor and was found to be less than 2×10^{-14} amperes. Therefore the conclusion was that the high noise level was probably due to the flow pattern in the cell. In order to minimize the turbulence

in the cell and hopefully to decrease the noise, a plane-parallel detector was designed and built.

Argon ionization detection

The Barber-Colman A-5042 Detector was also operated in the argon ionization mode[11] but no response to 300 p.p.m. of nitrogen dioxide or nitric oxide was obtained. The sample size was again 0.5 cc at 1 atm and 22°C.

Plane-parallel detector

The purpose of the experiments which are described below was to determine the effect of the geometry of the new detector on electron-capture detection and to compare the d.c. and pulse modes of operation. Only three changes in the chromatography unit were made: (1) a new gas mixture of nitrogen dioxide in nitrogen was prepared for sampling, which had a concentration of 88.3 p.p.m. of nitrogen dioxide at 757.4 mm of mercury and 23.2°C; (2) argon was used as carrier and scavenger gas because of the increased sensitivity which it had given in comparison with nitrogen for the A-5042 detector; and (3) the Barber-Colman A-5042 detector was replaced by the plane-parallel detector[10].

D.c. electron-capture detection.

For the d.c. method of operation with the plane-parallel detector the change in current as a function of detector potential for several argon flow rates is shown in Figure 14. Within the limits of experimental error, a carrier flow of 10 cc per minute of argon, a scavenger flow of 10 cc per minute, and a detector potential of 4.5 volts gave the most sensitive response.

The background current was then studied as a function of total argon flow and detector potential for comparison with the results presented in Figure 14. Figure 15 shows the background current as a function of the total flow rate of argon. The data were obtained at a constant potential of 4.5 volts and a flow of argon carrier gas of 10 cc per minute. Figure 16 shows the background current as a function of detector potential for a constant flow rate of 10 cc per minute of scavenger gas and 10 cc per minute of carrier gas. It is again apparent that the optimum conditions for the operation of the d.c. electron-capture cell, i.e., 4.5 volts, 10 cc per minute of carrier gas, 10 cc per minute of scavenger gas, and a background current of 2.6×10^{-9} amperes, appear in Figures 15 and 16 at the point just before the curve becomes level. The noise level of the cell, operated at these optimum conditions,was 8×10^{-12} amperes.

Pulse electron-capture detection.

The pulse mode of operation with the plane-parallel detector was studied. The only change in the operation of the chromatography unit was the replacement of the d.c. battery with a Hewlett-Packard 214A pulse generator.

Figures 17 and 18 present information on the response obtained when the fraction of on-time for the pulse generator was varied. All other parameters were held constant, i.e., total argon flow rate, detector temperature, and output voltage. For an on-time of less than 2 μ seconds, the background current was not sufficient for the operation of the cell. The response of the detector as a function of the total argon flow is presented in Figure 19. The response was quite markedly affected by the total argon flow below 30 cc per minute, but between 30 and 60 cc per minute the response was nearly independent of flow rate.

In order to determine the optimum operating conditions for the detector, a plot was prepared which included all the data collected during the study of the pulse mode. The data are shown in Figure 20, where the response is plotted as a function of the fraction of on-time for the pulse generator. Between 10 and 50 volts the detector response was relatively independent of voltage. Below 10 volts odd peaks and anamolous results were obtained. The two important variables appear to be

fraction of on-time and total flow rate of argon. For the case of a carrier flow of 10 cc per minute, a scavenger flow of 30 cc per minute of argon and a fraction on-time of 0.027 gave the most sensitive response within the limits of experimental error.

The effect of temperature on the response of the electron-capture detector when operated in the pulse mode was determined. The data are presented in Figure 21. It was found that the sensitivity was increased approximately four-fold in the concentration region from 1 to 10 p.p.m. of nitrogen dioxide when the temperature was decreased from 200 to 25°C, but the effect was not linear with temperature. In fact, nearly all of the increase in sensitivity was obtained in the range from 90 to 25°C. This is the exact opposite effect that has been found by Landowne and Lipsky[7] for sec-butyl bromide. The effect of temperature on the sensitivity of the detector is a characteristic of the substance to be detected and a function of the electron affinity of the molecule and the heat of dissociation for the negatively charged molecule to form a free radical and negative ion.

By using tritium foils with a different activity per unit area, the effect of the size of the tritium-source on the response of the detector was determined. An increase in the strength of the tritium-source did

increase the response for a given quantity of nitrogen dioxide, but the noise level was increased in the same proportion. Thus, the absolute sensitivity was not a function of source strength as long as a reasonable background current could be obtained. The acceptable source size was in the range of 150 to 300 millicurie of tritium. With this quantity of tritium the ratio of the number of electrons collected at the anode per emitted β-ray, a, was five. It should be pointed out that the sensitivity tests on the plane-parallel detector were made using a tritium source of 150 mc. The calibration studies and oxidation tests were carried out using a source of 220 mc.

Therefore, the following detector operating conditions were found to give the optimum sensitivity to nitrogen dioxide: (1) an argon scavenger flow rate of 30 cc per minute, (2) a pulse output of 50 volts with an on-time of 4 μ seconds and a period of 150 μ seconds, and (3) a detector temperature of 200^{o}C. For those conditions the noise level of the detector with a 150 mc tritium source was 4×10^{-12} amperes with a background current of 2.6×10^{-9} amperes. The noise level is a quarter of that obtained with the Barber-Colman A-5042 Detector operated in the d.c. mode. The noise from the plane-parallel detector operated in the pulse mode is shown in comparison

to the noise from the Barber-Colman Detector operated in the d.c. mode in Figure 22. The detector temperature of 200°C was chosen over 25°C for two reasons: (1) the calibration curve at 25°C was much more non-linear than at 200°C and (2) less adsorption of column bleed on the tritium foil was experienced at 200°C.

A chromatogram for the optimum conditions of analysis is shown in Figure 23. Nitrogen was the diluent. The concentration of nitrogen dioxide was 4.22 p.p.m. and that of oxygen was 18.15×10^4 p.p.m. The sample pressure and temperature were 748.7 mm of mercury and 26.2°C, respectively. Oxygen was present just to check separation, and the multiple oxygen peak was developed merely by decreasing the attenuation by factors of two from a value of 128 to 2 during the course of the oxygen peak. The sample volume was 0.5 cc.

Calibration data were obtained for nitrogen dioxide when the detector was operated at the optimum conditions. The data are tabulated in Table 4 and plotted in Figure 24. For the best curve which could be drawn through the data, the average percent deviation was 3.2 percent from 3 to 25 p.p.m. of nitrogen dioxide and 3.4 percent from 3 to 75 p.p.m. The standard deviation was 0.59 p.p.m. from 3 to 25 p.p.m. and 1.32 p.p.m. from 3 to 75 p.p.m. All nitrogen dioxide concentrations were corrected to 26.46°C

and 760. mm of mercury as shown in Table 4. The reason for the correction was to compensate for slightly different sample pressures and temperatures. The fit of the calibration data to the theoretical equation proposed by Lovelock[10] was again unacceptable for this work.

Presented in Table 4 are the calibration data which were used for the oxidation studies. The data were plotted, as shown in Figure 24, with the fraction decrease in current as a function of the nitrogen dioxide concentration in order to compensate for day-to-day variations in the background current. These data were used for Tests 1 through 21. After Test 21, the equipment was not used for approximately two weeks. When the equipment was operated again, the detector sensitivity had decreased approximately 8 to 10%. Therefore, a different calibration curve was used for Tests 22 through 28. The data for this calibration are given in Table 5. This difficulty could have been circumvented by correcting the response to a given concentration of nitrogen dioxide through use of response factors which have been discussed by Woodward[18]. Since calibration tests were made each week and any one calibration curve was accurate for approximately six weeks, the use of these response factors was not required for this study.

The results presented above compare very favorably with chemical techniques for the analysis of nitrogen

dioxide. The chemical methods that are used for the analysis of nitrogen dioxide in the concentration region from 1 to 75 p.p.m. are the phenol-disulfonic acid technique (ASTM D 1608-60) and the Saltzmann technique[15]. The phenol-disulfonic acid method requires one-liter samples and has given in this laboratory an average absolute deviation of 6 percent and a standard deviation of 3 p.p.m. The Saltzmann procedure required 250 cc samples. An average absolute deviation of 3-4 percent has been reported[15] in the concentration range from 8 to 45 p.p.m. The phenol-disulfonic acid method is used for the determination of the total nitrogen oxides as nitrogen dioxide, whereas the Saltzmann procedure is used for analysis of only nitrogen dioxide in the presence of any other nitrogen oxides. In consideration of the analysis time of five minutes for gas chromatography versus three to four days with the phenol-disulfonic acid method and a sample size of 0.5 cc versus nominally 1 liter, the gas chromatographic analysis shows advantages for the particular conditions studied. Similarly the advantage of sample size would prevail relative to the Saltzmann procedure.

VII. CONCLUSIONS

The results presented in this thesis have shown that gas chromatography can be used for the quantitative analysis of nitrogen dioxide at concentrations from 0.5 to 75 p.p.m., when in the presence of nitrogen, oxygen, and up to 75 p.p.m. of nitric oxide. A chromatography column consisting of an inert solid, Fluoropak 80, which had been coated with a methyl silicone oil, SF-96, was used in this study. A parallel-plane electron-capture detector when operated in the pulse mode was found to be the most sensitive chromatography device yet available for the detection of nitrogen dioxide. This chromatographic analysis was shown to be accurate to an average absolute deviation of 3.4 percent, with a standard deviation of 1.32 p.p.m. in the concentration range from 3 to 75 p.p.m. of nitrogen dioxide when oxygen was present to the extent of 25 percent by volume in nitrogen. The detection limit for nitrogen dioxide was found to be 0.5 p.p.m. The main advantages of gas chromatography in comparison with chemical techniques are the short time for analysis and the small samples (0.5 cc) required.

Chromatography column

It has been found that an inert support with a nonpolar liquid phase is the most appropriate column

packing for the separation of nitrogen dioxide from nitrogen, oxygen, and nitric oxide. The inert support was found to be important for two reasons: (1) high tailing of nitrogen dioxide occurred with active supports such as Chromosorb W and (2) adsorption of water on active supports is more pronounced, which prevents reproducibility in the analysis of the nitrogen oxides.

In regard to the use of methyl silicone oil (SF-96) on Fluoropak 80, the most important factor was the removal of all traces of water from the column, samples, and carrier gases. The optimum conditions for operation of the column were: (1) a carrier flow rate of 10 cc per minute, (2) a temperature of 22°C, (3) a packing of 40/80 mesh Fluoropak 80 with 10 percent by weight of SF-96, (4) a sample size of 0.5 cc, and (5) a 20 foot column of stainless steel with an inside diameter of 0.093 inch. The flow rate and column length had the largest effects on the separation.

Detection

Argon ionization.

The use of an argon ionization detector was found to produce no measurable response to 0.5 cc samples at atmospheric pressure and room temperature containing 300 p.p.m. of nitrogen dioxide in nitrogen or 300 p.p.m. of nitric oxide in nitrogen.

Electron-capture.

Nitrogen dioxide was found to be particularly amenable to detection by electron-capture at concentrations between 0.5 and 75 p.p.m., whereas the detector was approximately 100 times less sensitive to nitric oxide.

The geometry of the detector was shown to be important. The plane-parallel detector was superior to the Barber-Colman A-5042 design, because of decreased noise. The higher noise level in the d.c. mode for the A-5042 design (16×10^{-12} compared to 8×10^{-12} amperes) was attributed to gas turbulence in the detector.

The pulse mode of operation with the plane-parallel detector was found to be slightly superior to d.c. operation. The pulse mode gave a noise level (4×10^{-12} amperes) approximately one-half that found for d.c. electron-capture and was also less sensitive to small changes in total gas flow rate and detector potential.

As has been discussed above, the noise level of the detector determines the absolute sensitivity. Although a decrease in noise was obtained by different cell geometries and modes of operation, a significant further reduction in the noise does not seem possible at the present time. The noise level of 4×10^{-12} amperes was almost completely caused by random emission of the β-rays from the tritium source and thus is a characteristic of the electron-capture detector.

Relative to detector sensitivity in the pulse mode, the fraction on-time, temperature, and total argon flow rate were the most important variables. The optimum fraction on-time and total argon flow rate were found to be 0.027 and 40 cc per minute, respectively. At 25°C the sensitivity was approximately four times that at 200°C. The detector sensitivity was relatively independent of source size, voltage, period, and on-time as long as a background current between 2×10^{-9} and 10×10^{-9} amperes could be obtained.

Detector sensitivity to nitrogen dioxide was increased two-fold by the use of argon rather than nitrogen as a carrier and scavenger gas. Whatever carrier and scavenger gas was used, it was essential to remove all traces of water in order to obtain satisfactory background currents.

In order to compensate for day-to-day variability in detector calibration, it was found necessary to plot the fraction decrease in background current versus nitrogen dioxide concentration. By use of this technique, one calibration curve was accurate for as long as six weeks.

VIII. RECOMMENDATIONS

In the future there should be more thought and consideration given to two general areas in the use of gas chromatography for analysis of the oxides of nitrogen.

The first area is the development of new chromatography columns for the separation of the nitrogen oxides. A column capable of reproducibly separating the nitrogen oxides at concentrations below 10 p.p.m. would be particularly applicable to air pollution studies. A chromatography unit capable of analyzing gas mixtures containing hydrocarbons and water vapor as well as oxides of nitrogen when present at low concentrations in air would also be of major interest. The absence of literature for such work lies in the difficulty in reproducing results because of the high reactivity of the nitrogen oxides and their affinity for water. Probably the most promising columns would be those comprised of inert supports coated with relatively polar liquid phases.

The second general area for more thought and experiment is in the study of the actual theory of electron-capture detection. A complete understanding of the important reactions in the detector would yield information relative to the design of more efficient detector cells and the prediction of the sensitivity of the detector to any given compound.

IX. REFERENCES

1. Condon, R. D., Anal. Chem., 31, 1717 (1959).

2. Goodwin, E. S., Goulden, R., and Reynolds, J. G., Analyst, 86, 697 (1961).

3. Greene, S. A., and Pust, H., Anal. Chem., 30, 1039 (1958).

4. Hollis, O. L., Ibid., 33, 353 (1961).

5. Karmen, A., Ginffrida, L., and Bowman, R. L., Chromatog., 9, 13 (1962).

6. Kirkland, J. J., Anal. Chem., 35, 2003 (1963).

7. Landowne, R. A. and Lipsky, S. R., Ibid., 34, 726 (1962).

8. Lovelock, J. E. and Zlatkis, A., Ibid., 33, 1958 (1961).

9. Lovelock, J. E., Ibid., 33, 162 (1961).

10. Ibid., 35, 474 (1963).

11. Ibid., Nature, 182, 1663 (1958).

12. Lovelock, J. E., Zlatkis, A., and Becker, R. S., Nature, 193, 540 (1962).

13. Lovelock, J. E. and Lipsky, S. R., J. Am. Chem. Soc., 82, 431 (1960).

14. Lovelock, J. E., J. Chromatog., 1, 35 (1958).

15. Saltzmann, B. E., Anal. Chem., 26, 1949 (1954).

16. Spangenberg, K. R., Vacuum Tubes, p. 306, McGraw-Hill Book Company, New York, New York (1948).

17. Taylor, M. P., J. Chromatog., 9, 28 (1962).

18. Woodward, J. W., "A Study of the Effects of Dislocation and Crystal Orientation on the Catalyzed Oxidation of Ethylene over a Single Crystal of Silver", California Institute of Technology (1965).

X. NOMENCLATURE

AB	Any molecule composed of atoms A and B.
a	Stoichiometric coefficient (quantity of electrons produced per β-ray).
B	Constant, liter/ g. mole.
B_w	Electrometer bandwidth, cycles per second.
C	Test substance concentration (e.g., nitrogen dioxide), g. mole/liter.
D	Constant, g. mole/liter.
e'	Electronic charge, 1.602×10^{-19} coulomb.
$\overline{i^2}$	Mean-square fluctuating current due to random arrival of electrons at the anode, amperes.
I_o	Charge quantity of β-rays emitted from the tritium foil per unit time, amperes.
I_g	Gas which does not absorb electrons (argon or nitrogen).
I	Measured current in the presence of the test substance (e.g., nitrogen dioxide), amperes.
I_s	Background current, amperes.
I_p	Decrease in current effected by the presence of the electron-capture substance, amperes.

LIST OF TABLES

Table 1. Results of Phenol-disulfonic Acid Analysis of Matheson Gas Mixture Containing Nominally 1500 p.p.m. of Nitrogen Dioxide in Nitrogen.

Sample	Calculated Concentration of Nitrogen Dioxide in Nitrogen Prepared by Dilution Technique[1], p.p.m.	Measured Nitrogen Dioxide Concentration[2], p.p.m.
1a		1539.
2a		1597.
3a		1581.
4b		1723.
5b		1715.
6b		1606.
7	59.0	57.2

Average of Samples 1 through 6 = 1627. p.p.m.

Standard Deviation of Samples 1 through 6 = 70. p.p.m.

[1] Calculated assuming initial nitrogen dioxide-nitrogen mixture contained 1627. p.p.m. of nitrogen dioxide and ideal gas behavior.

2 Measured by phenol-disulfonic acid technique, ASTM D 1608-60.

Table 2. Results of Phenol-disulfonic Acid Analysis of Matheson Gas Mixture Containing Nominally 1000 p.p.m. of Nitric Oxide in Nitrogen.

Sample	Calculated Concentration of Nitric Oxide in Nitrogen Prepared by Dilution Technique[1], p.p.m.	Measured Nitric Oxide Concentration[2], p.p.m.
1		925.
2		929.
3		864.
4		848.
5		823.
6		838.
7	41.5	40.6

Average of Samples 1 through 6 = 871. p.p.m.

Standard Deviation of Samples 1 through 6 = 41. p.p.m.

[1] Calculated assuming initial nitric oxide-nitrogen mixture contained 871. p.p.m. of nitrogen dioxide and ideal gas behavior.

2 Measured by phenol-disulfonic acid technique, ASTM D 1608-60.

Table 3. Result of Experiments to Determine Optimum Characteristics for SF-96 on Fluoropak 80 Column.

Variable	Limits of Variation	Optimum*
Carrier flow rate	3 to 20 cc per minute	10 cc per minute
Temperature	0 to 50°C	22°C
Packing size	20/80 to 60/80 mesh	40/80 mesh
Weight fraction of SF-96	2% to 20%	10%
Length	5 to 30 feet	20 feet

* With these conditions the retention time for oxygen, nitrogen, and nitric oxide was 120 seconds and for nitrogen dioxide was 148 seconds.

Table 4. Calibration Data for Plane-Parallel Detector Operated in the Pulse Mode from November 2, 1964 to December 18, 1964.

On-time: 4 μ seconds
Period: 150 μ seconds
Argon Carrier: 10 cc per minute
Argon Scavenger: 30 cc per minute
Potential: 50 volts
Detector Temperature: 200°C

Nitrogen Dioxide Concentration (C'_{NO_2}), p.p.m.*	Fraction Decrease in Background Current+	C'_{NO_2}, p.p.m.	Fraction Decrease in Background Current+
66.96	0.5997	20.72	0.2241
65.21	0.5836	17.30	0.2053
60.06	0.5785	15.73	0.1623
57.98	0.5384	14.29	0.1530
54.55	0.5350	11.60	0.1180
47.53	0.5149	9.80	0.08998
40.16	0.4351	9.55	0.07471
36.04	0.4173	9.34	0.07993
35.36	0.4094	9.01	0.06963
30.42	0.3299	6.07	0.03896
29.51	0.3673	6.05	0.04274
25.30	0.2804	5.82	0.03317
23.02	0.2707	5.02	0.02762
21.50	0.2566	3.55	0.01535

*$C'_{NO_2} = C_{NO_2}$ (P/760.) (299.62/T), where C_{NO_2} is the nitrogen dioxide concentration of the sample at the system pressure and temperature as calculated by the ideal gas assumption.

+Background Current: $(5.75 \pm 0.15) \times 10^{-9}$ amperes.

Table 5. Calibration Data for Plane-Parallel Detector Operated in the Pulse Mode from December 31, 1964 to January 14, 1965.

On-time: 4 μ seconds
Period: 150 μ seconds
Argon Carrier: 10 cc per minute
Argon Scavenger: 30 cc per minute
Potential: 50 volts
Detector Temperature: 200°C

Nitrogen Dioxide Concentration (C'_{NO_2}), p.p.m.*	Fraction Decrease in Background Current+
59.96	0.5056
58.28	0.4955
30.30	0.2944
30.18	0.2904
15.62	0.1386
15.62	0.1351
8.30	0.05190
8.06	0.05181

* See Table 4.

\+ Background Current: $(5.20 \pm 0.10) \times 10^{-9}$ amperes

LIST OF FIGURES

LIST OF FIGURES (contd.)

LIST OF FIGURES (contd.)

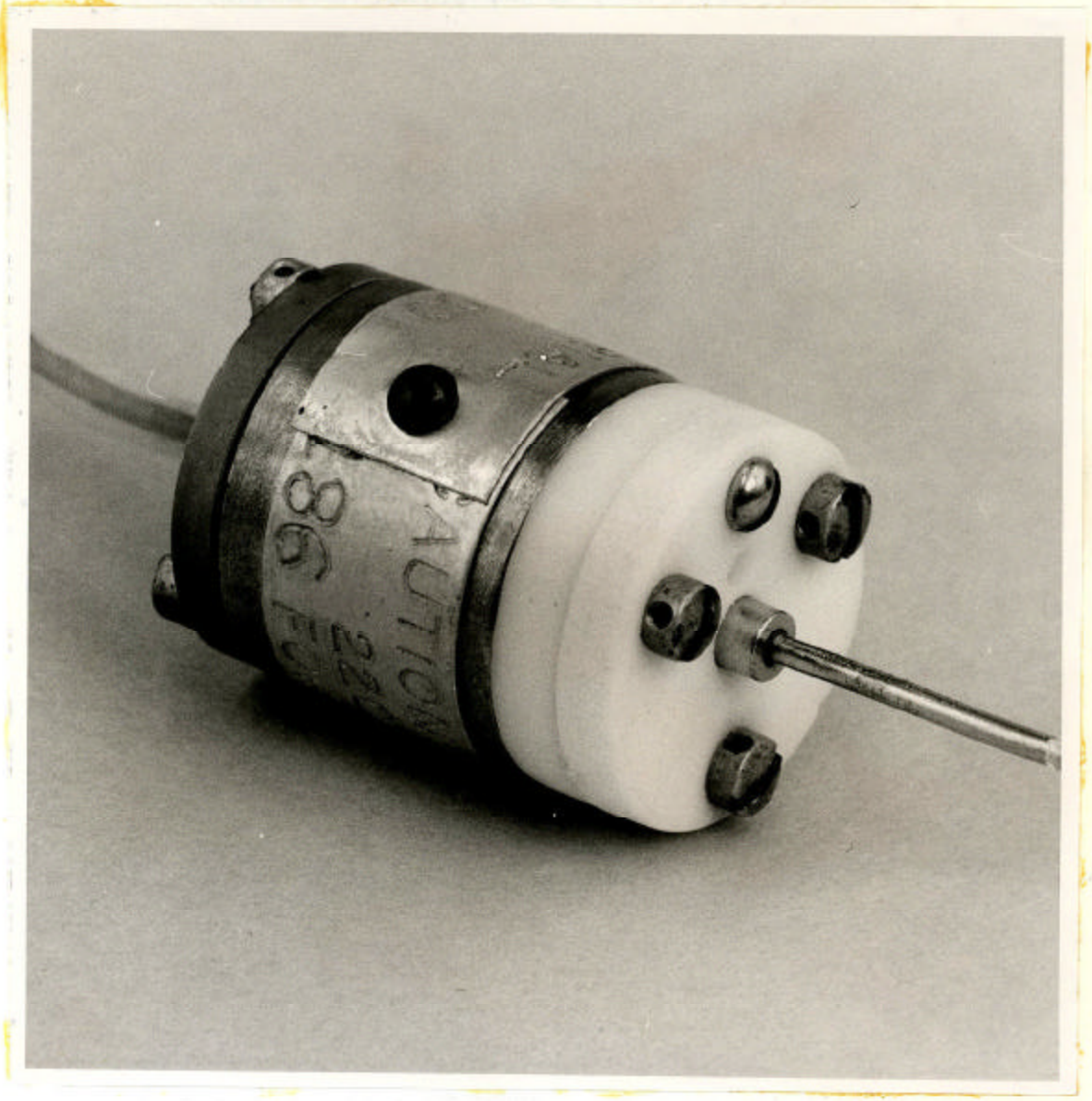


Figure 1. Photograph of Barber-Colman A-5042 Detector.

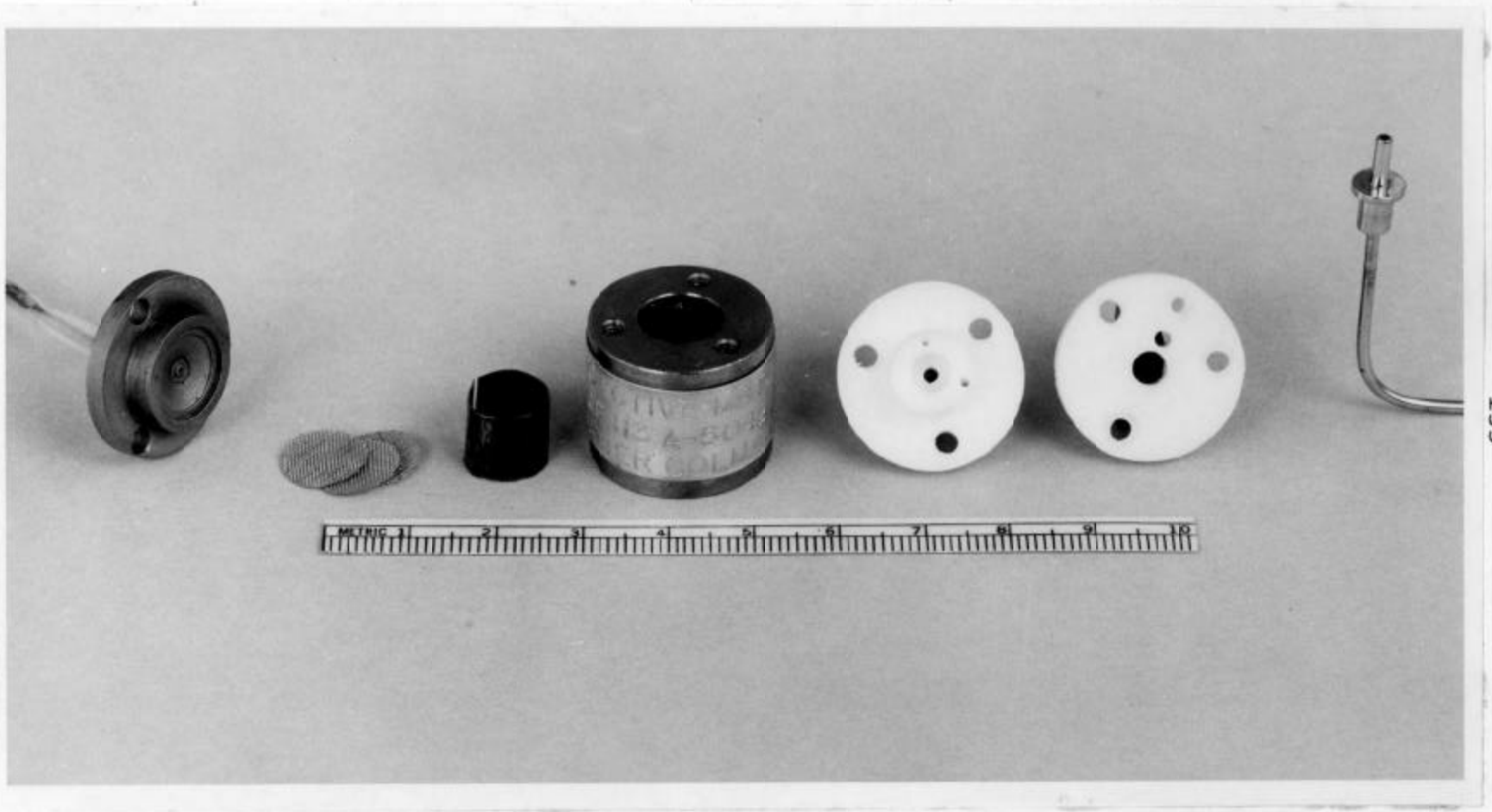
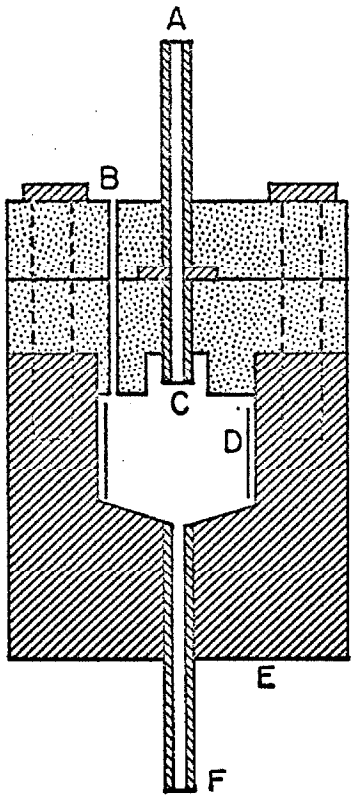


Figure 2. Exploded view of Barber-Colman A-5042 Detector.



A. FROM COLUMN
B. GAS OUTLET
C. ANODE
D. TRITIUM FOIL
E. CATHODE
F. SCAVENGER GAS INLET
STAINLESS STEEL
TEFLON

SCALE-2:1

Figure 3. Cross-sectional drawing of Barber-Colman A-5042 Detector.

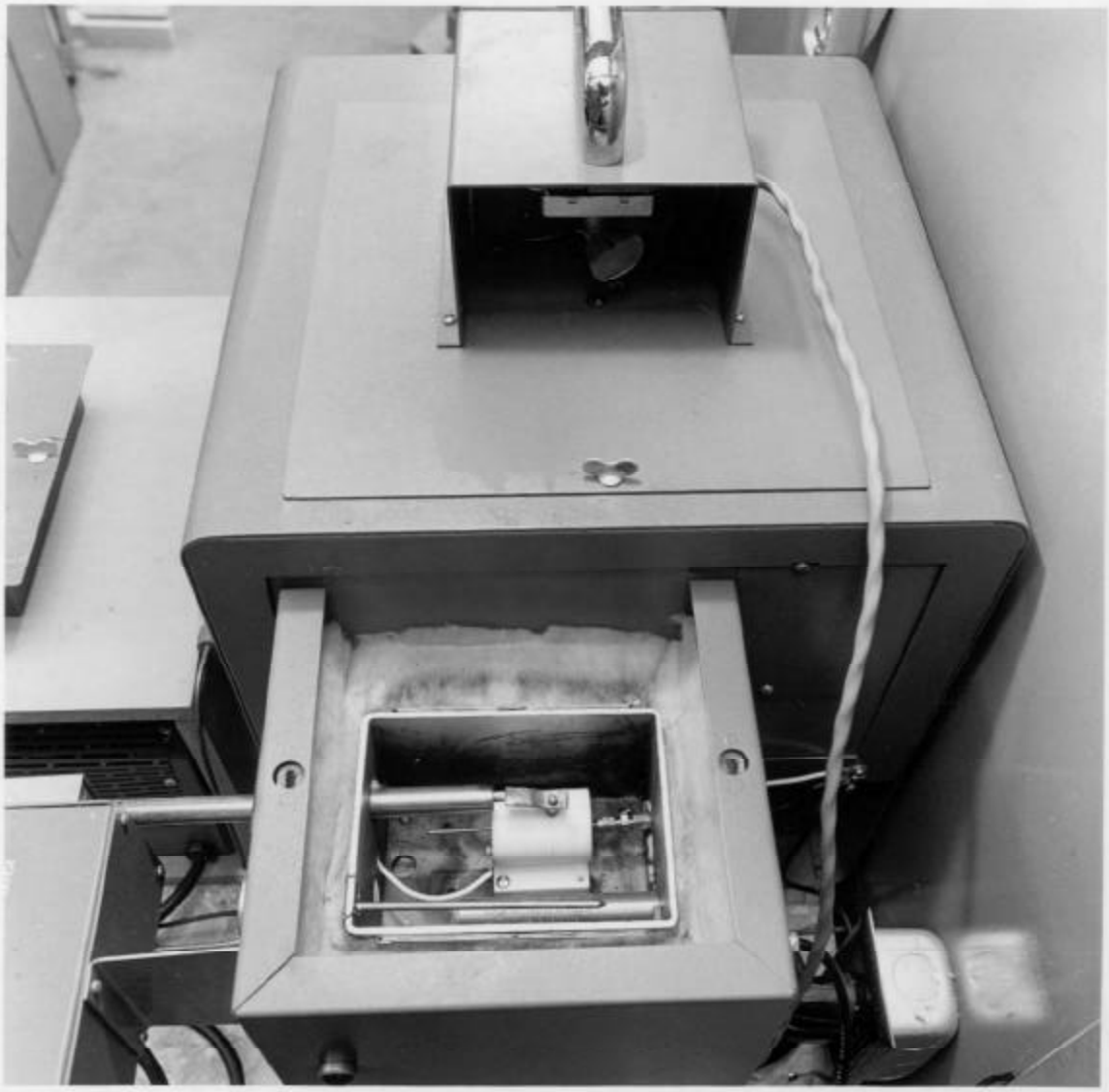


Figure 4. Photograph of oven for Plane-Parallel Detector.

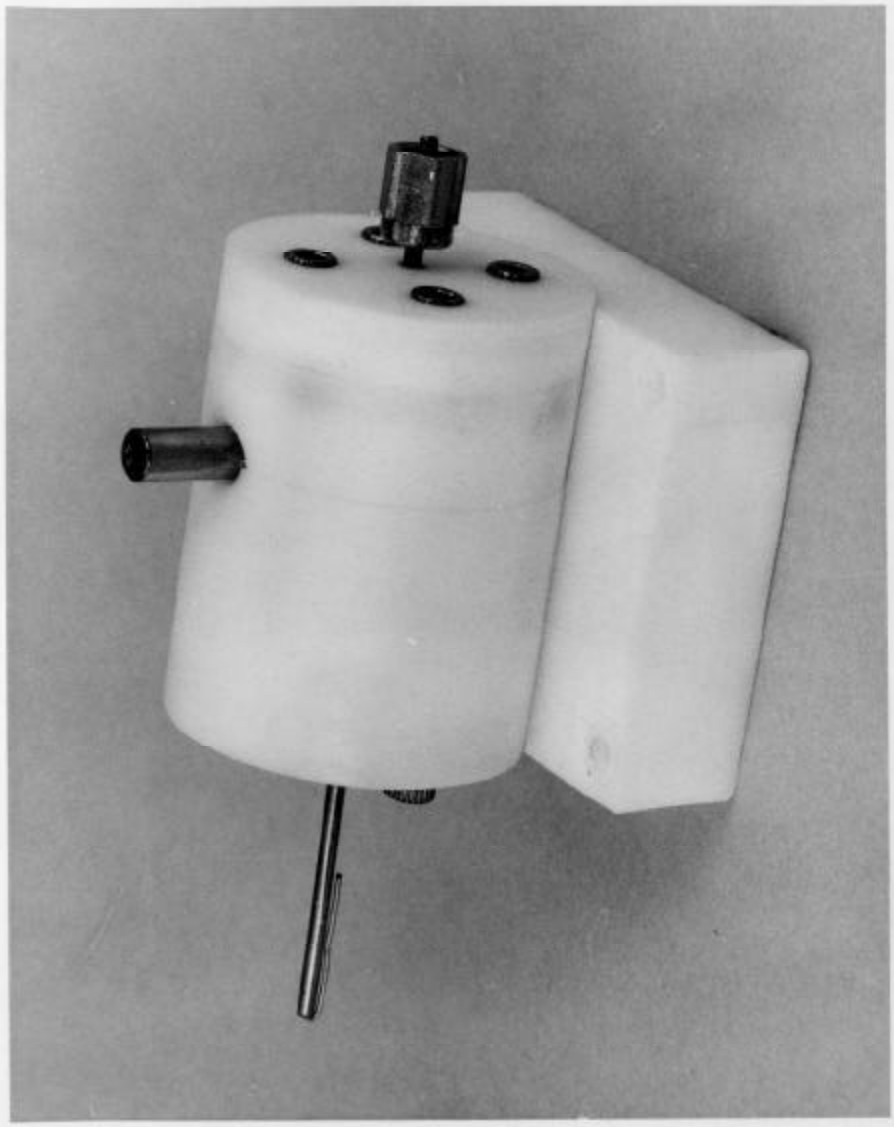


Figure 5. Photograph of Plane-Parallel Detector.

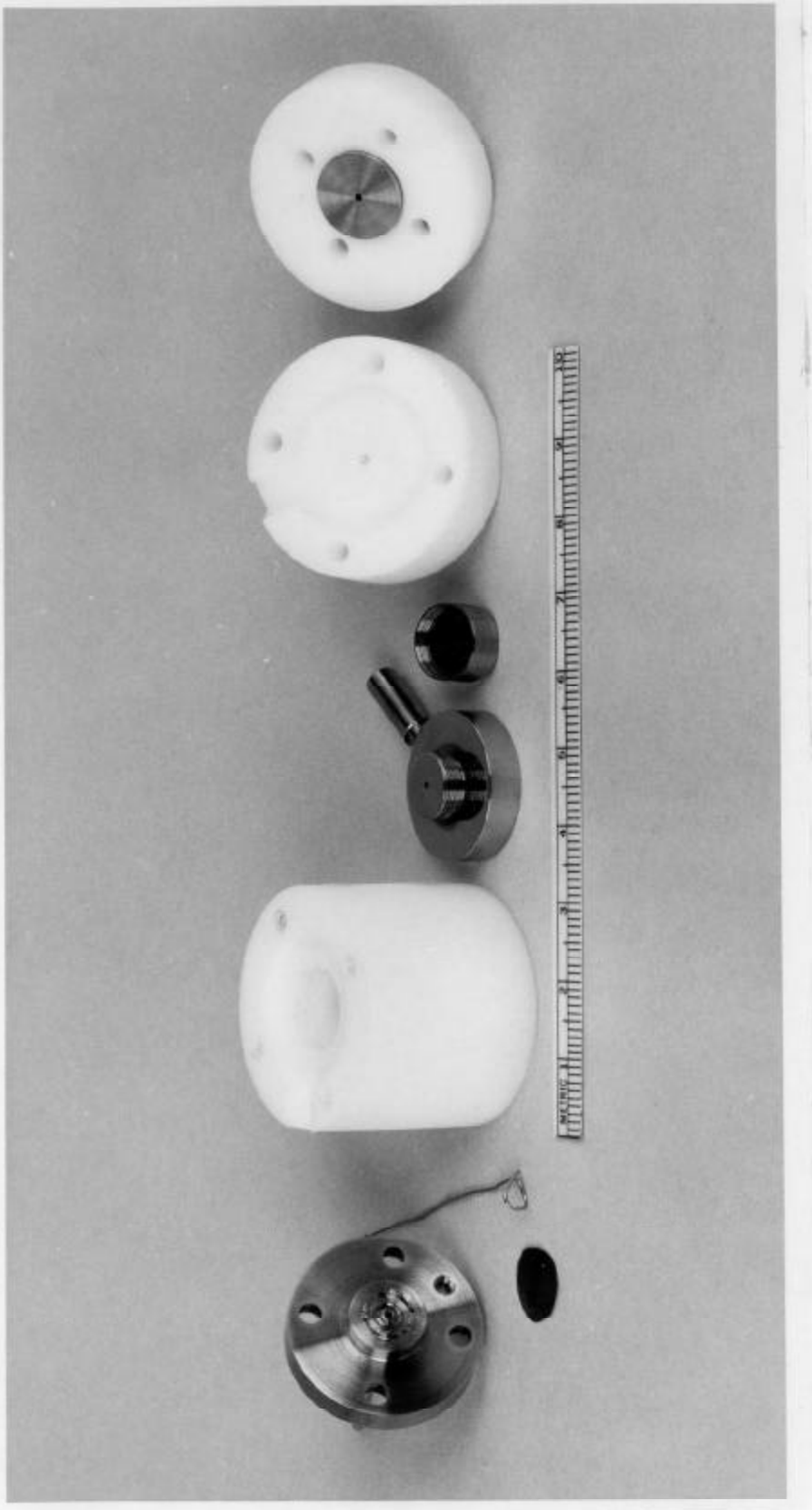


Figure 6. Exploded view of Plane-Parallel Detector.

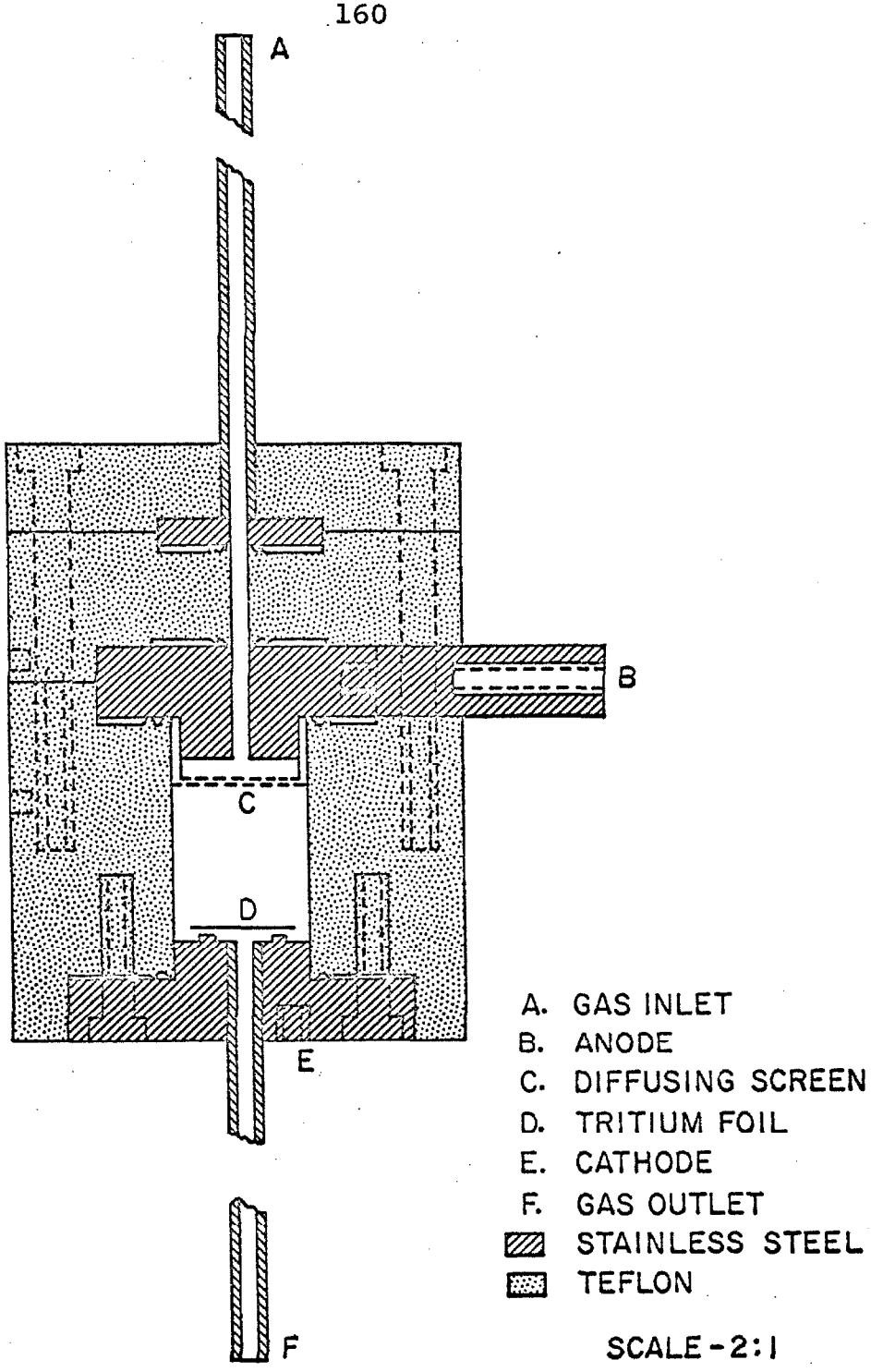


Figure 7. Cross-sectional drawing of Plane-Parallel Detector.

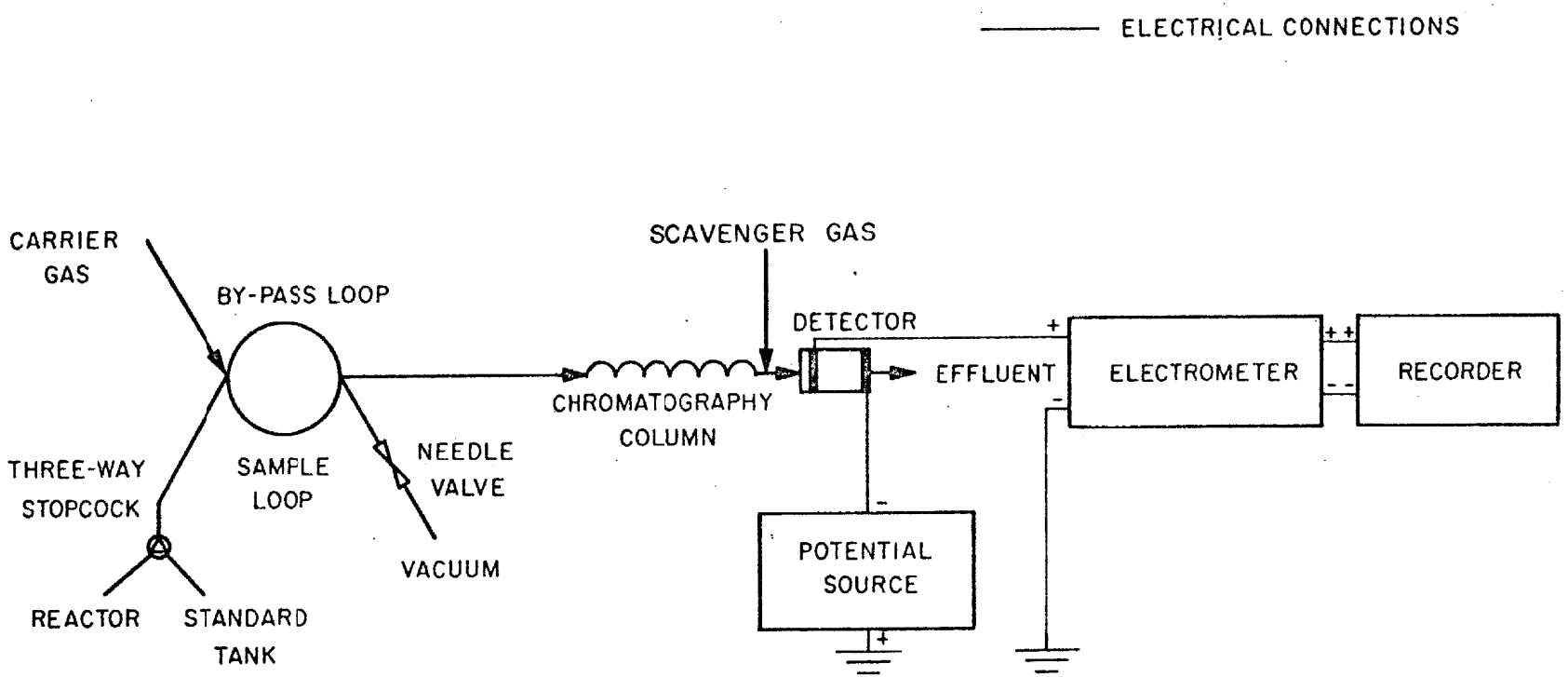


Figure 8. Schematic of the Chromatography Unit.

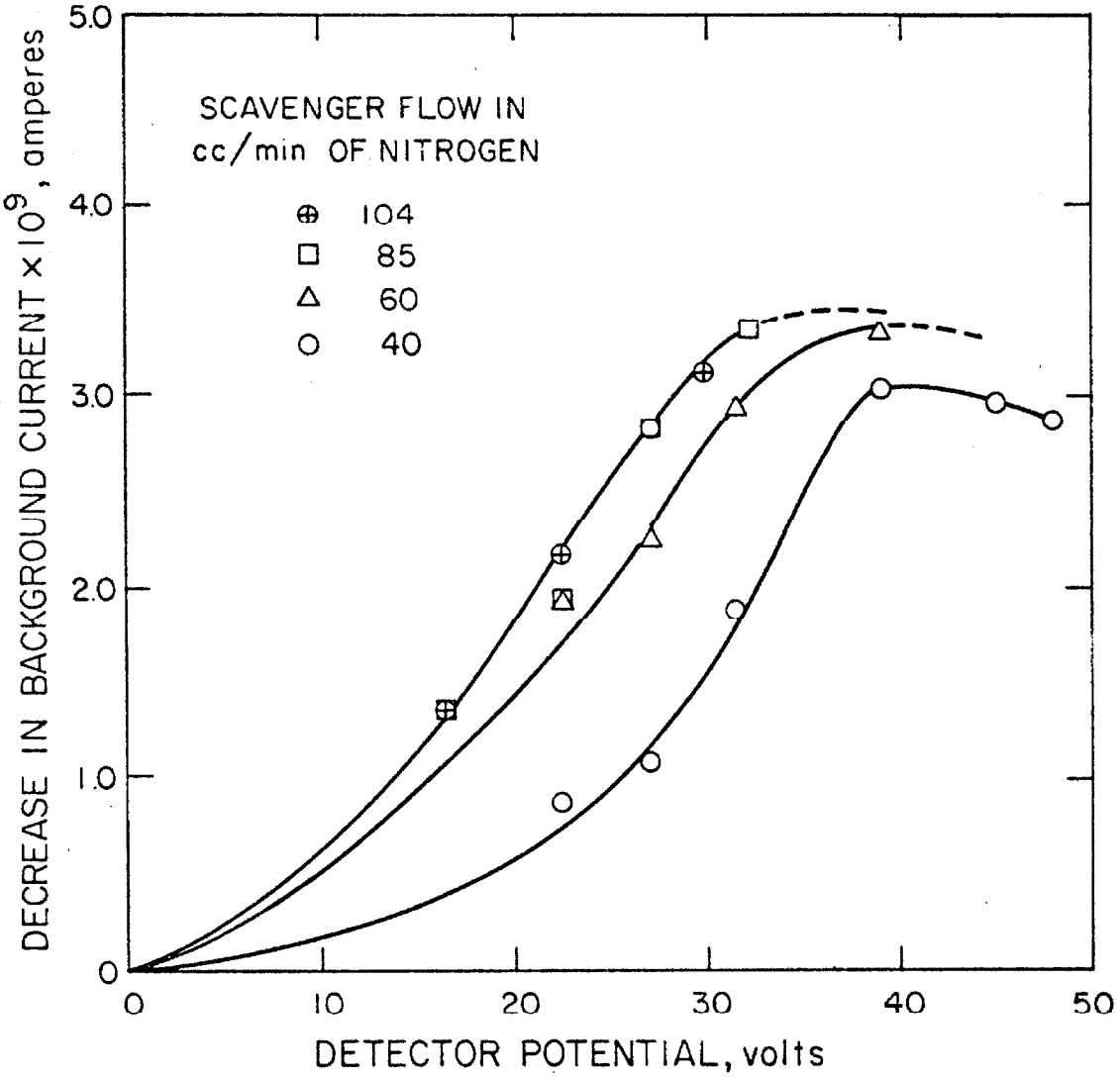


Figure 9. Effect of detector potential on response to 100 p.p.m. of nitrogen dioxide with a carrier flow of 10 cc per minute for the Barber-Colman A-5042 Detector.

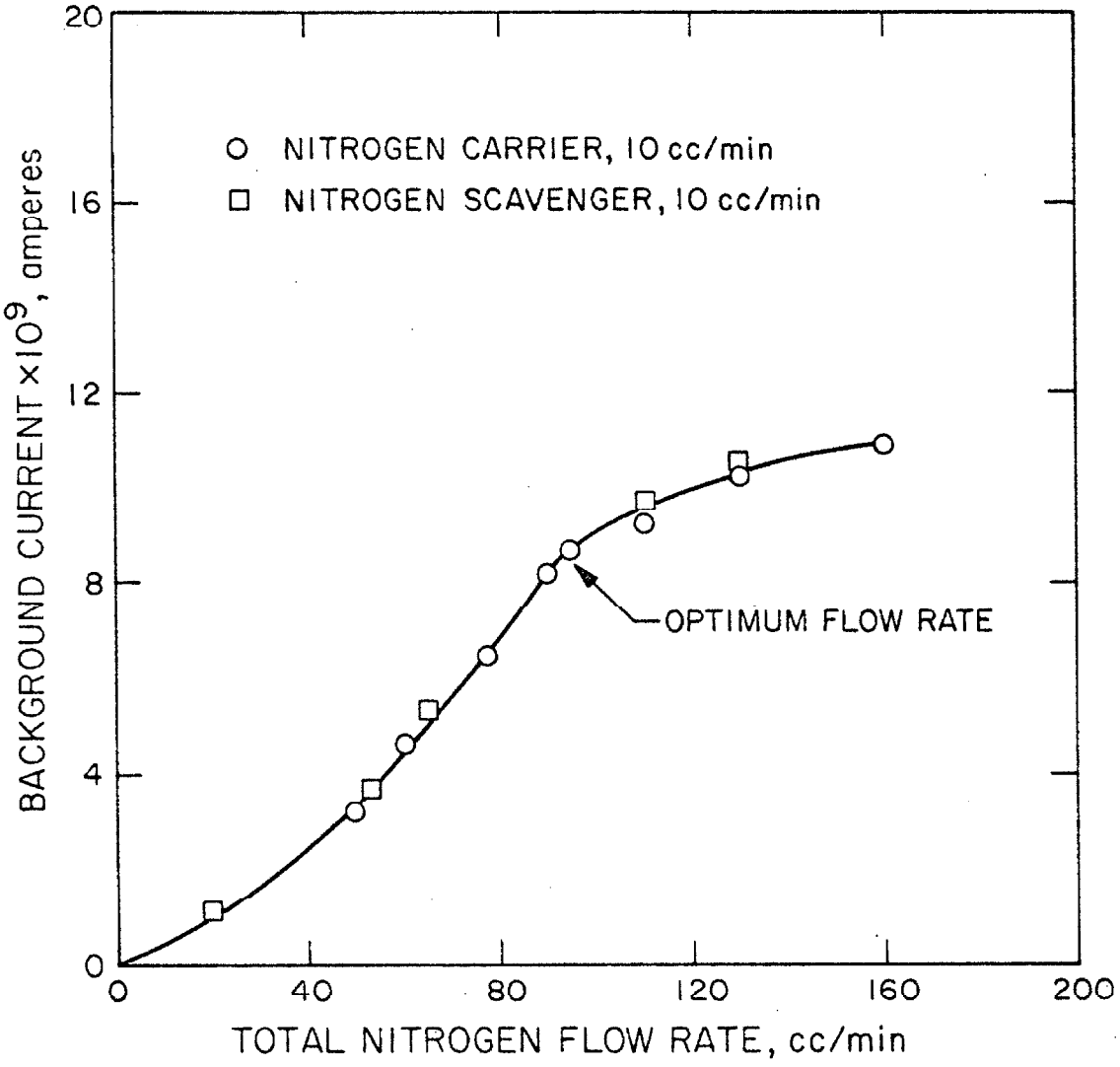


Figure 10. Background current as a function of total nitrogen flow at a detector potential of 33 volts for the Barber-Colman A-5042 Detector.

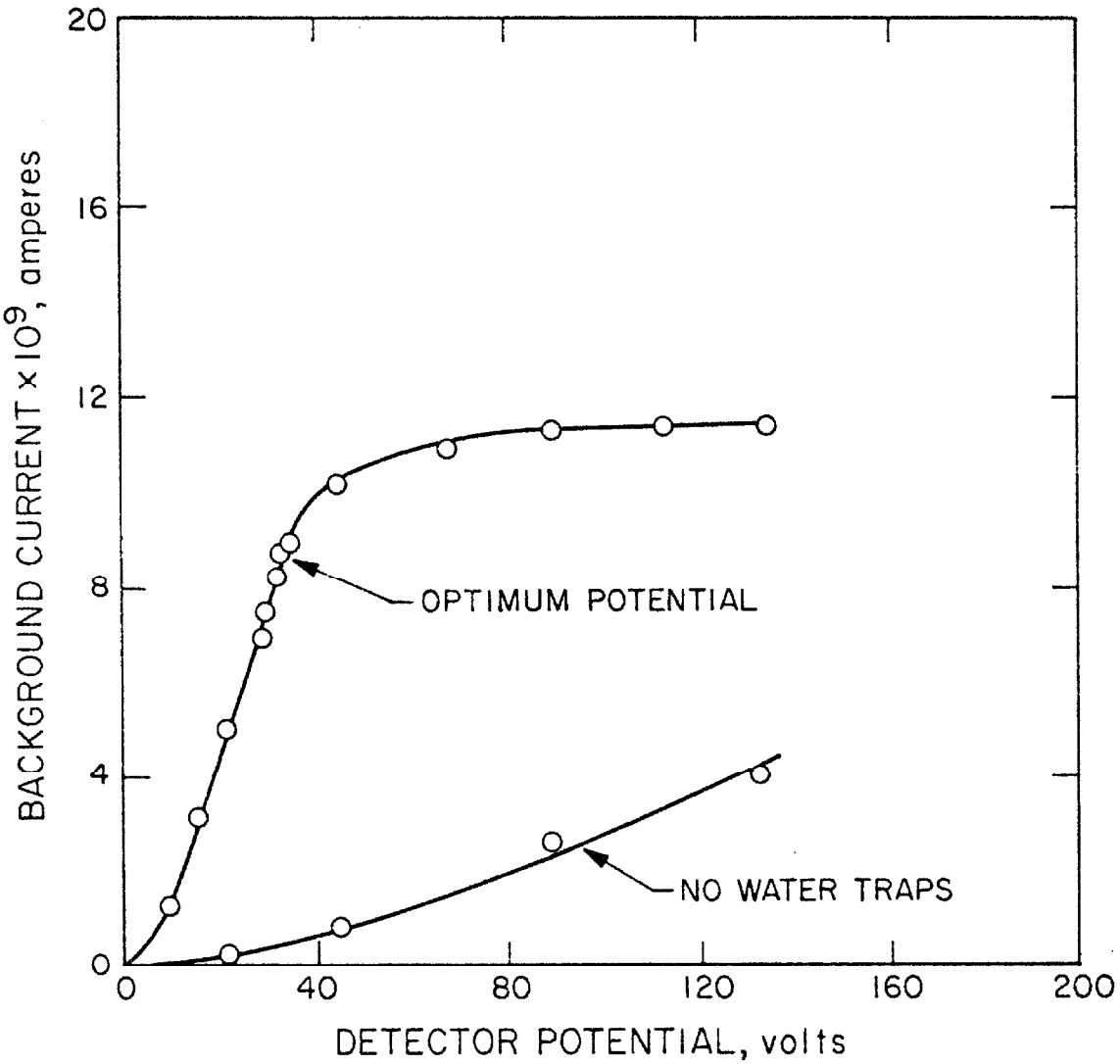


Figure 11. Background current as a function of detector potential for a total nitrogen flow of 95 cc per minute for the Barber-Colman A-5042 Detector.

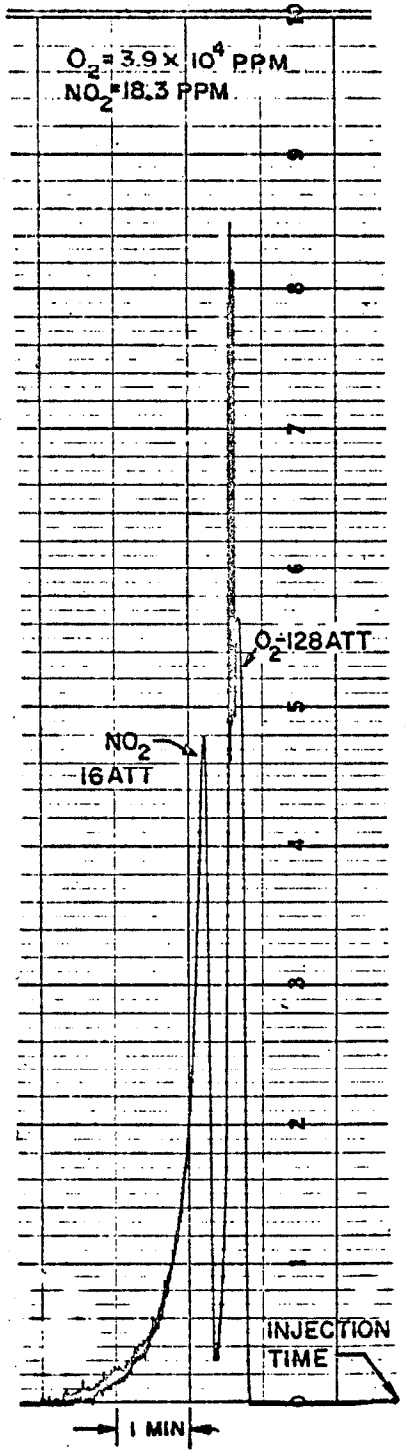


Figure 12. Typical chromatogram of nitrogen dioxide in nitrogen with added oxygen for the Barber-Colman A-5042 Detector.

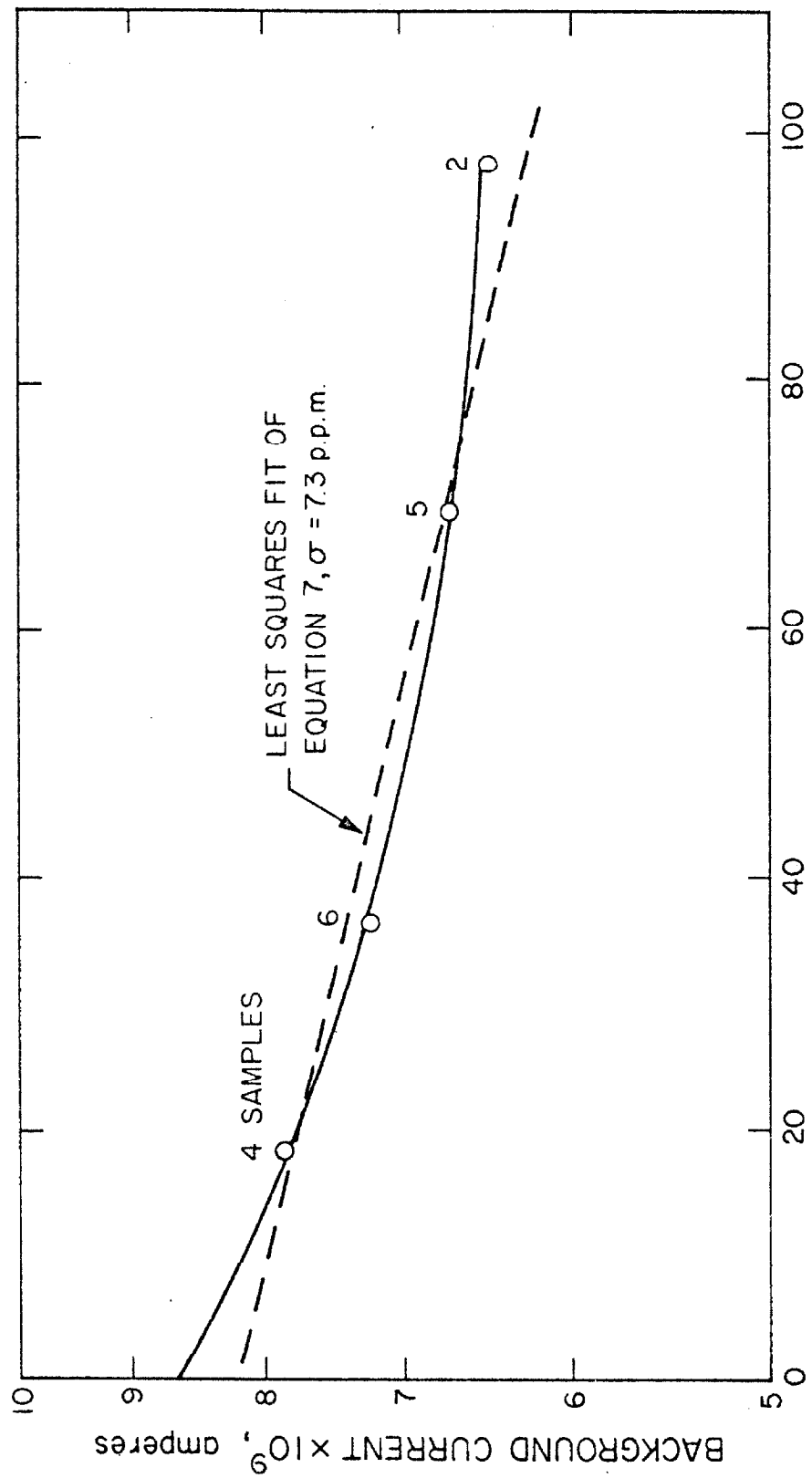


Figure 13. Concentration of nitrogen dioxide as related to current in Barber-Colman A-5042 Detector for 0.5 cc samples containing nitrogen and up to 9 percent oxygen.

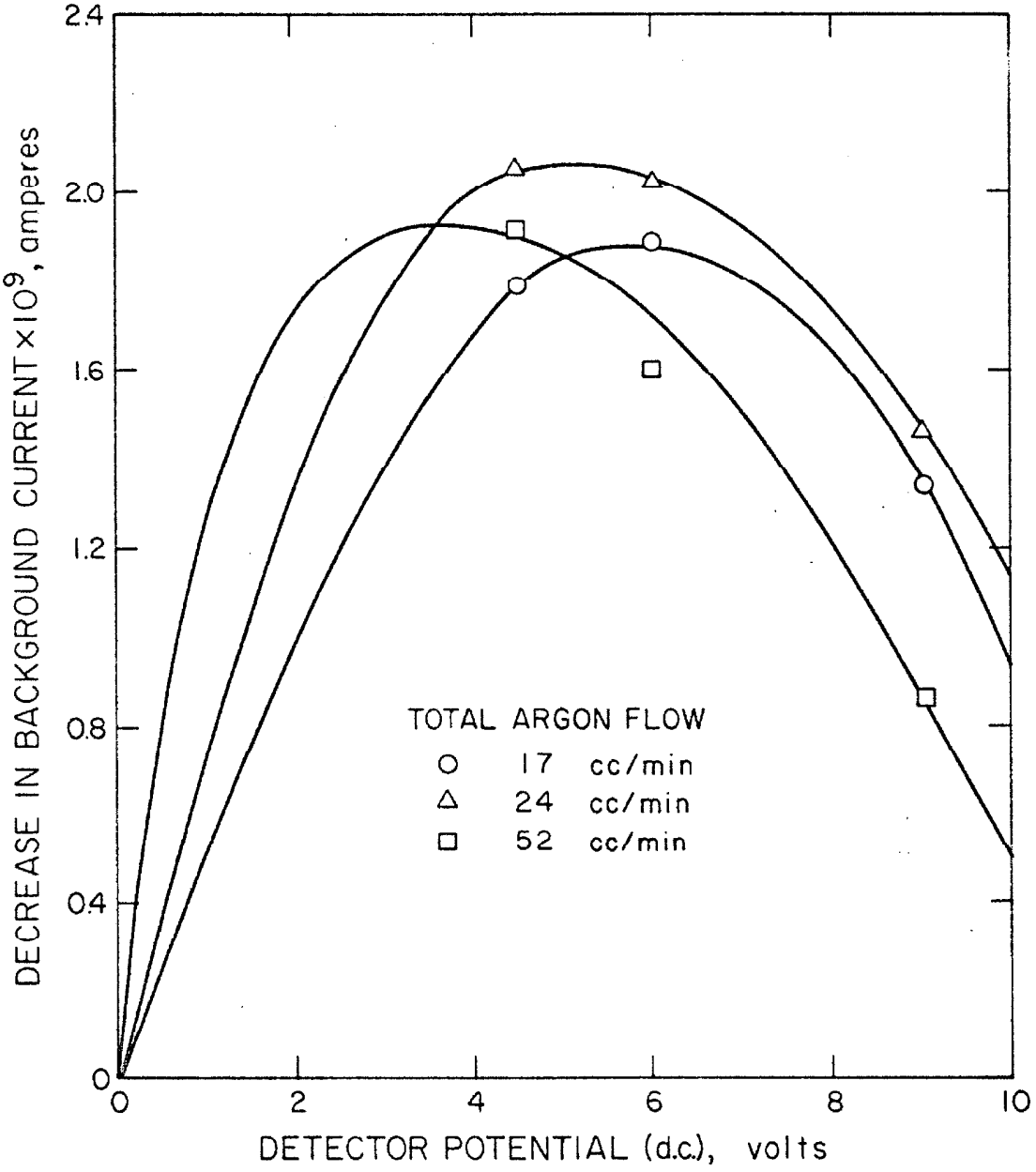


Figure 14. Effect of detector potential on response to 88.3 p.p.m. of nitrogen dioxide with a carrier flow of 10 cc per minute of argon for the Plane-Parallel Detector.

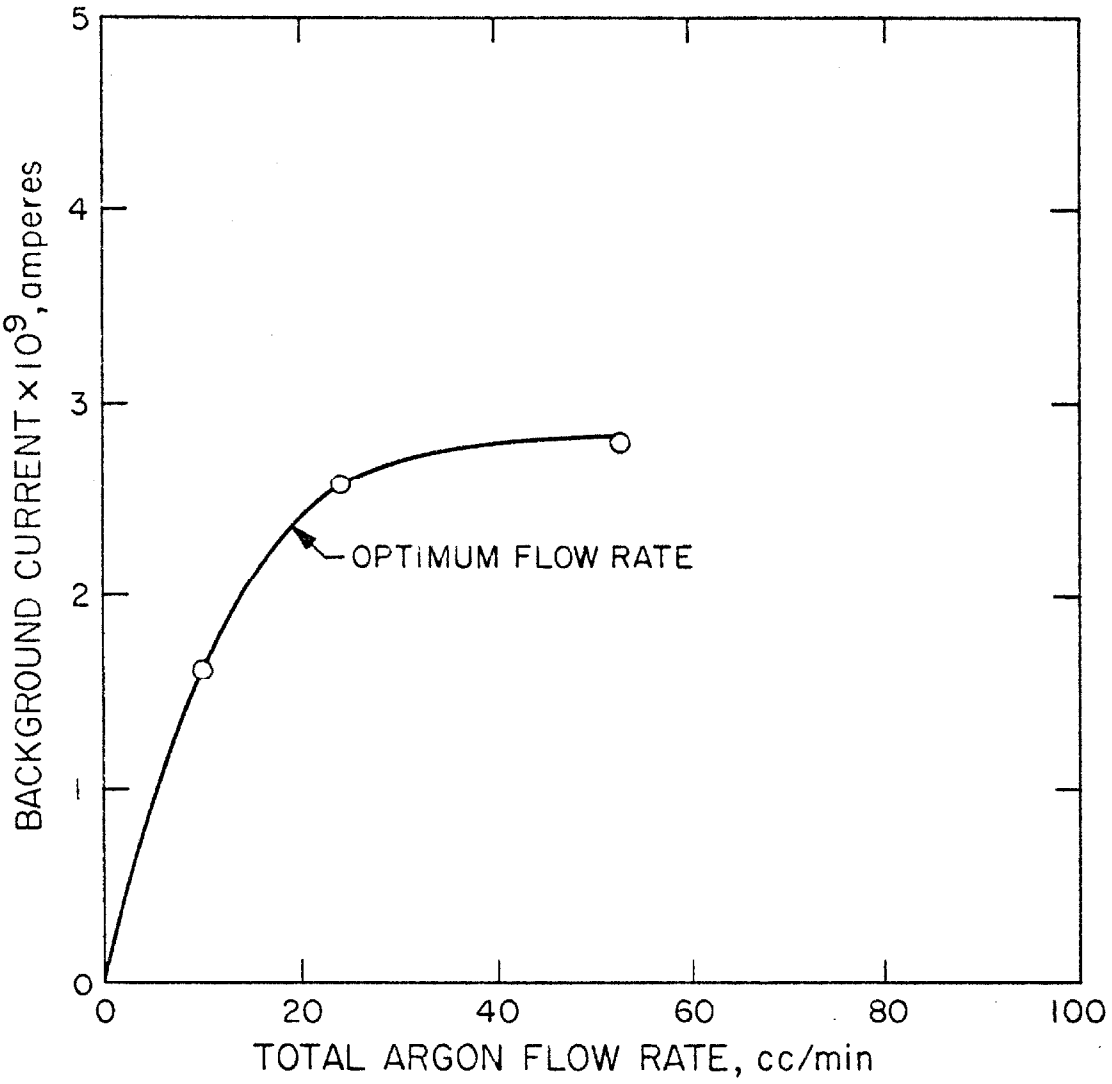


Figure 15. Background current as a function of total argon flow at a detector potential of 4.5 volts with the Plane-Parallel Detector.

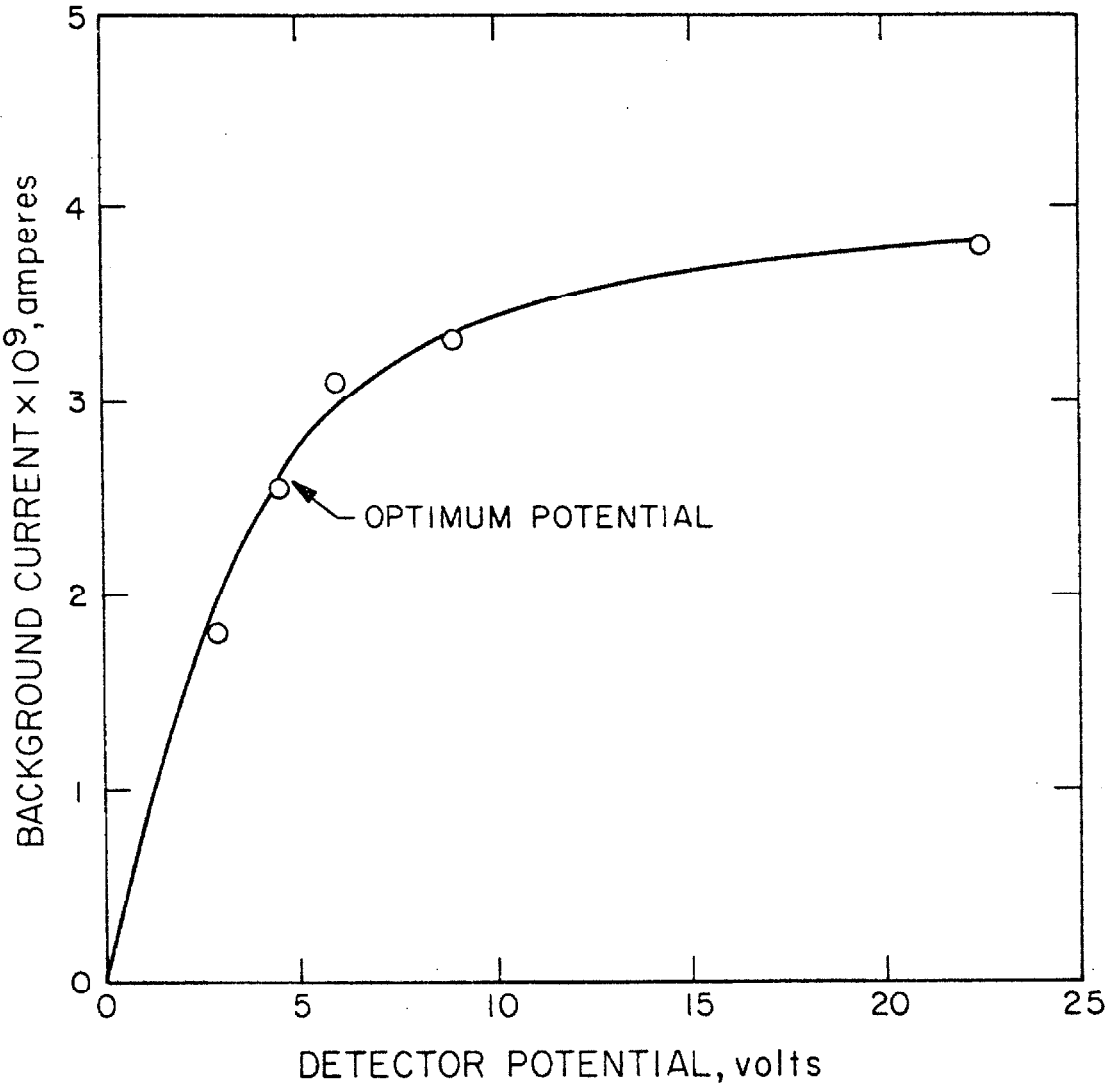


Figure 1[illegible] Background current as a function of detector potential at a total argon flow rate of 20 cc per minute with [illegible]e Plane-Parallel Detector.

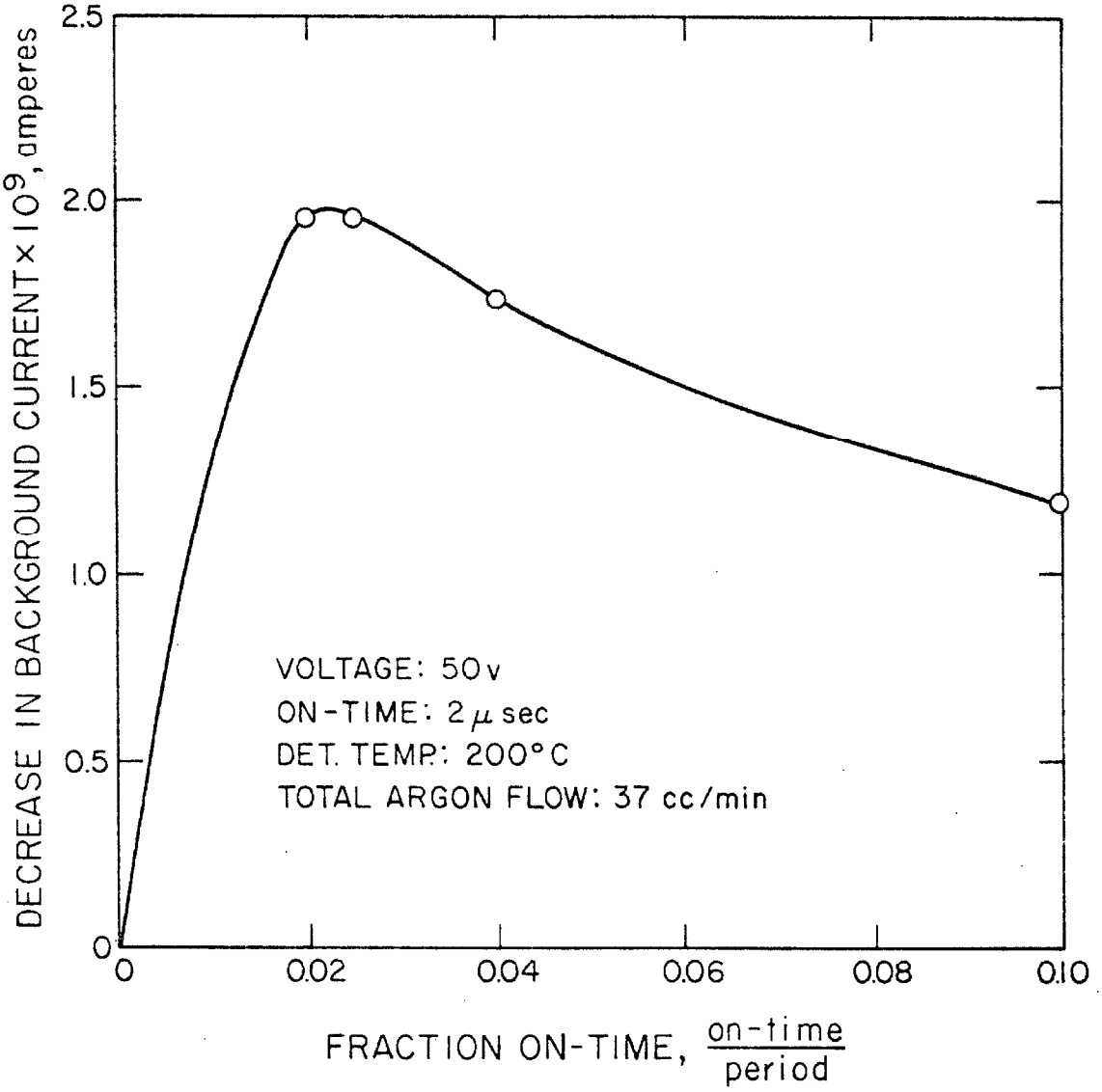


Figure 17. Response of Plane-Parallel Detector to 88.3 p.p.m. of nitrogen dioxide as a function of the fraction on-time when operated in the pulse mode with an on-time of 2 μ sec.

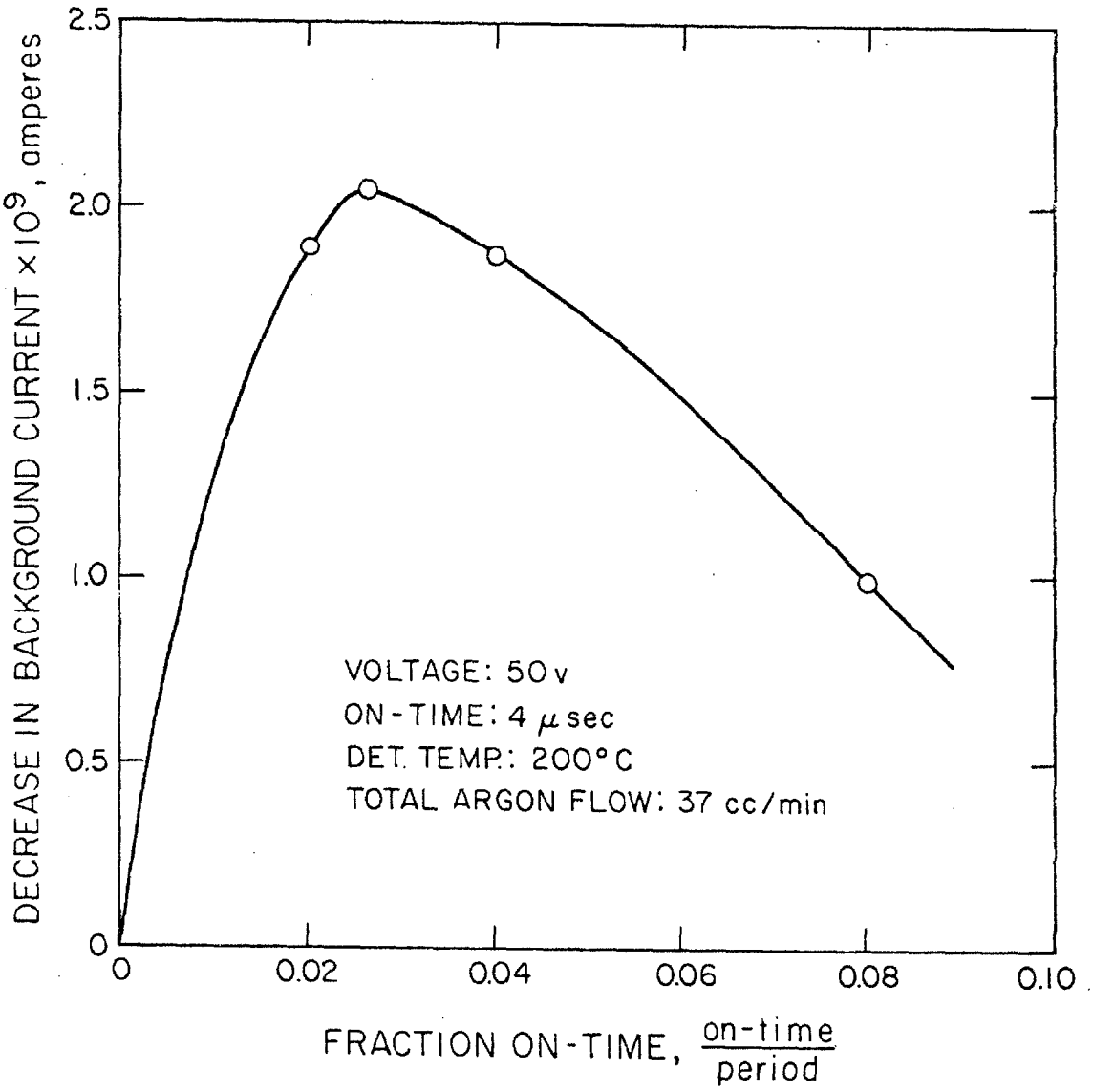


Figure 18. Response of Plane-Parallel Detector to 88.3 p.p.m. of nitrogen dioxide as a function of the fraction on-time when operated in the pulse mode with an on-time of 4 μ sec.

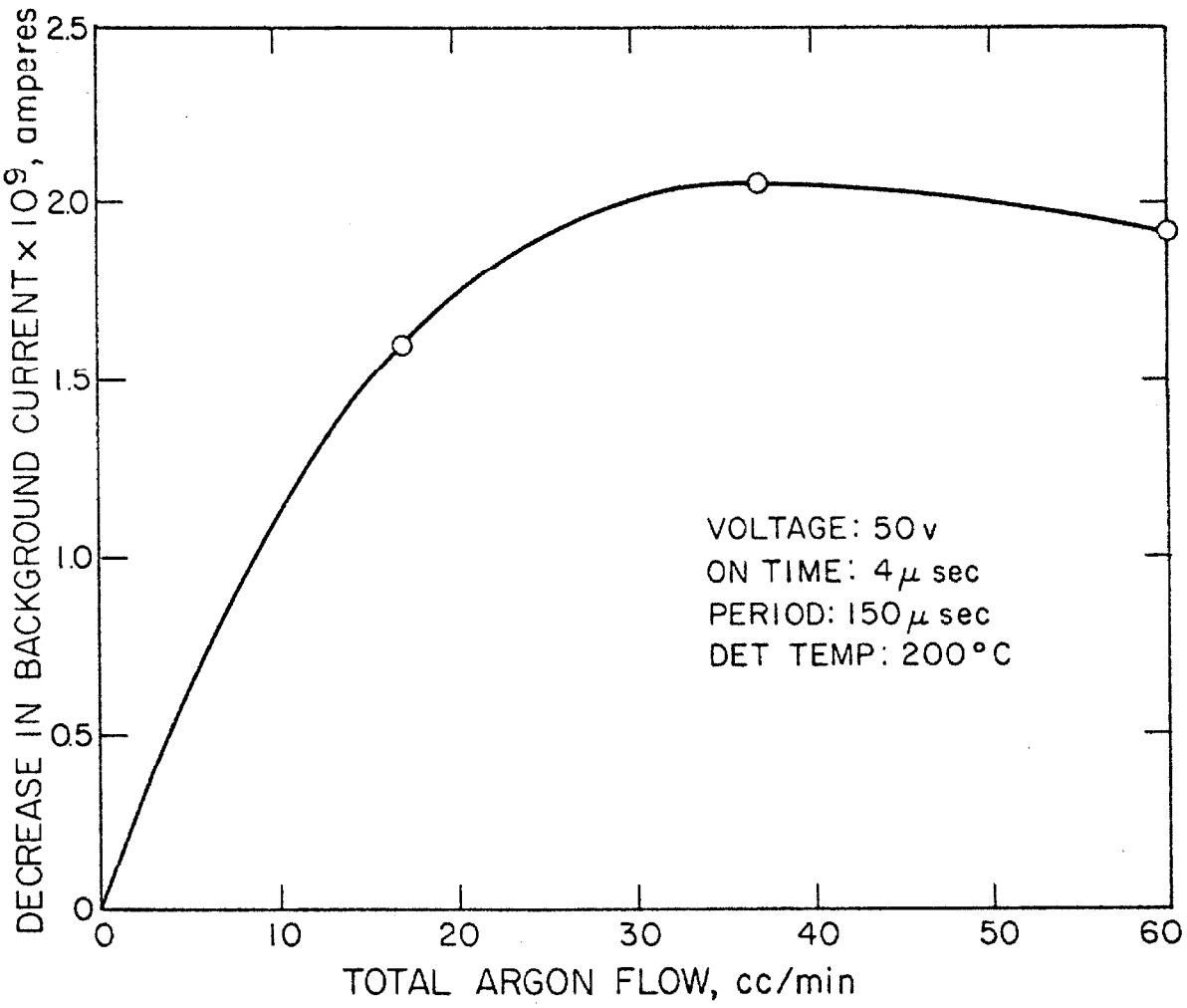


Figure 19. Response of Plane-Parallel Detector to 88.3 p.p.m. of nitrogen dioxide as a function of the total argon flow when operated in the pulse mode.

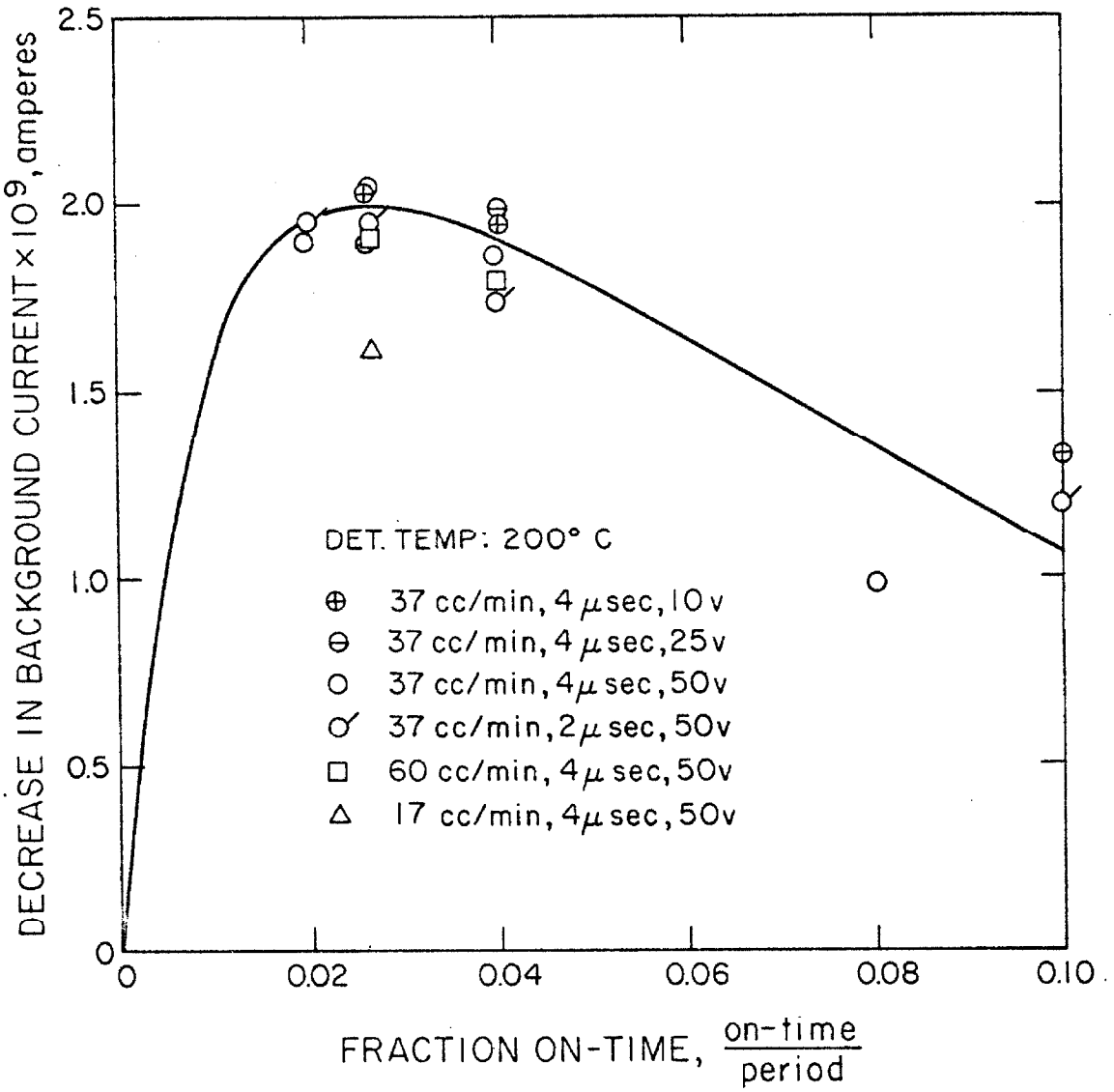


Figure 20. Response of Plane-Parallel Detector to 88.3 p.p.m. of nitrogen dioxide as a function of fraction on-time when used in the pulse mode at different operating conditions.

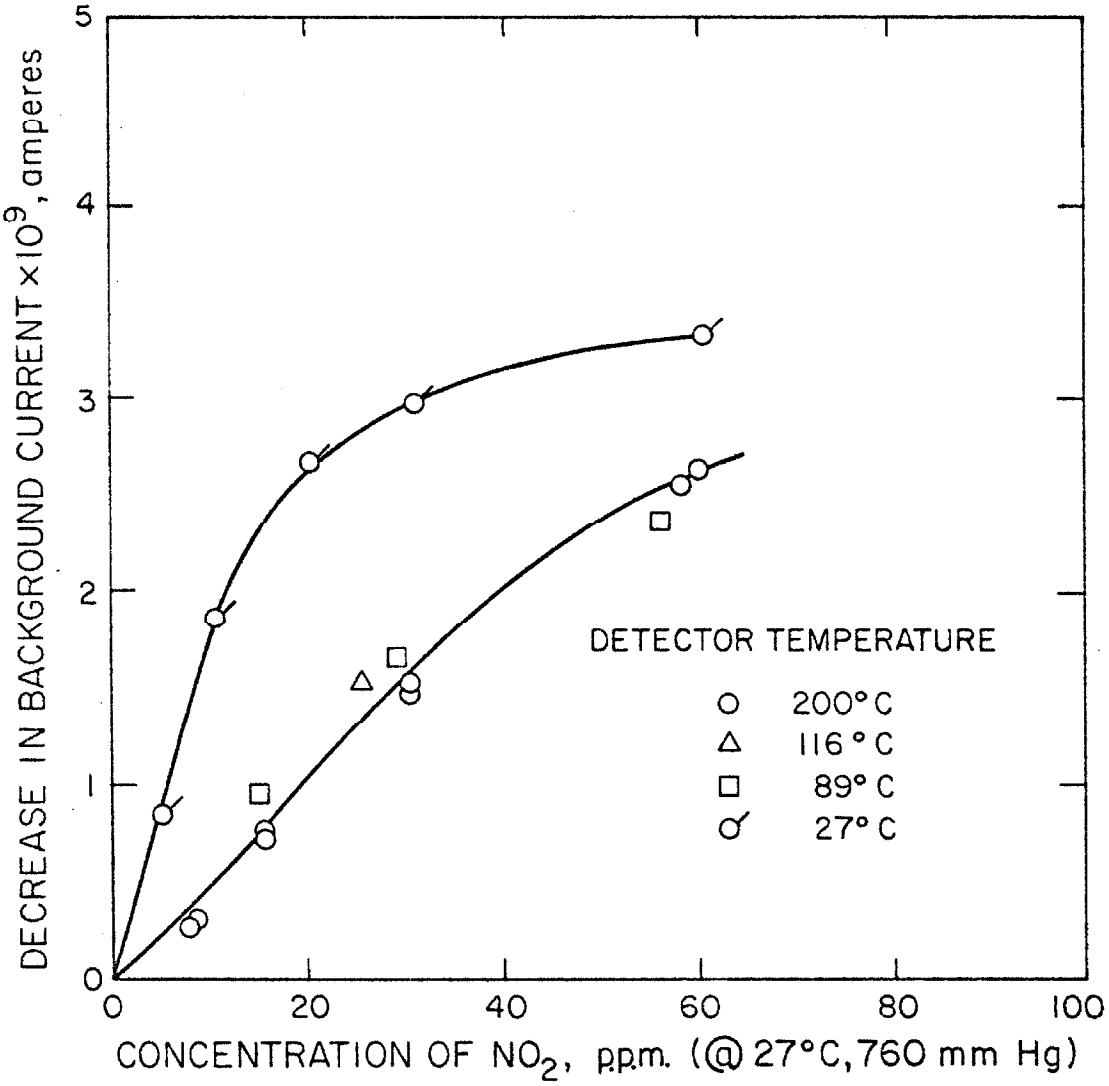
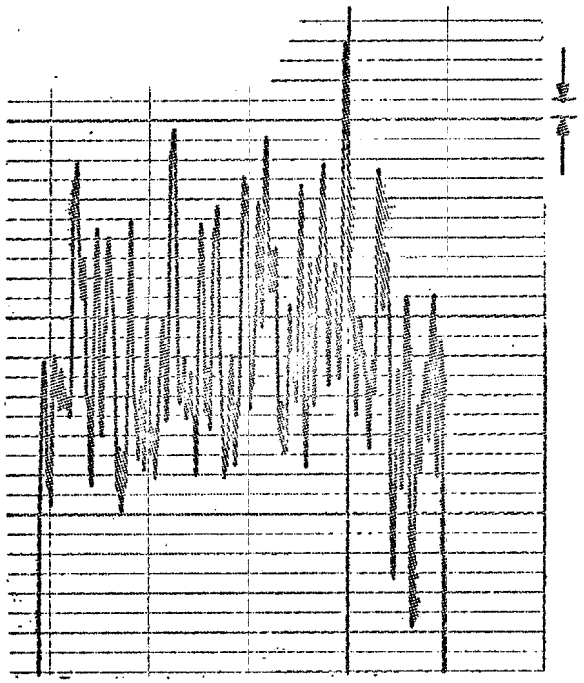
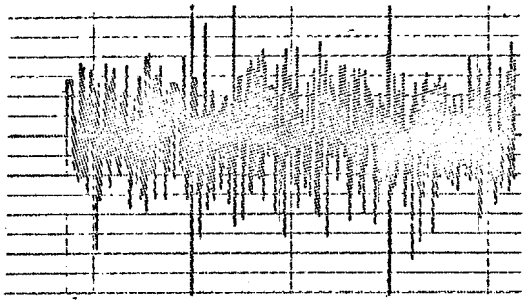


Figure 21. Response of Plane-Parallel Detector as a function of nitrogen dioxide concentration in samples containing nitrogen and up to 25 percent oxygen with temperature as a parameter.



10^{-12} amperes



Barber-Colman A-5042 Detector

Background Current: 7.7×10^{-9} amperes

Carrier Nitrogen: 10 cc/min

Scavenger Nitrogen: 85 cc/min

Potential (d.c.): 33 volts

Detector Temperature: 22° C

Plane-Parallel Detector

Background Current: 6.0×10^{-9} amperes

Carrier Argon: 10 cc/min

Scavenger Argon: 30 cc/min

Potential (pulsed): 50 volts

Period: 150 μ sec

On-time: 4 μ sec

Detector Temperature: 200° C

Figure 22. Comparison of background noise from the Barber-Colman A-5042 and Plane-Parallel Detectors.

$O_2 = 18.15 \times 10^4$ p.p.m.

$N_2 = 81.85 \times 10^4$ p.p.m.

$NO_2 = 4.22$ p.p.m.

NO = 21.35 p.p.m.

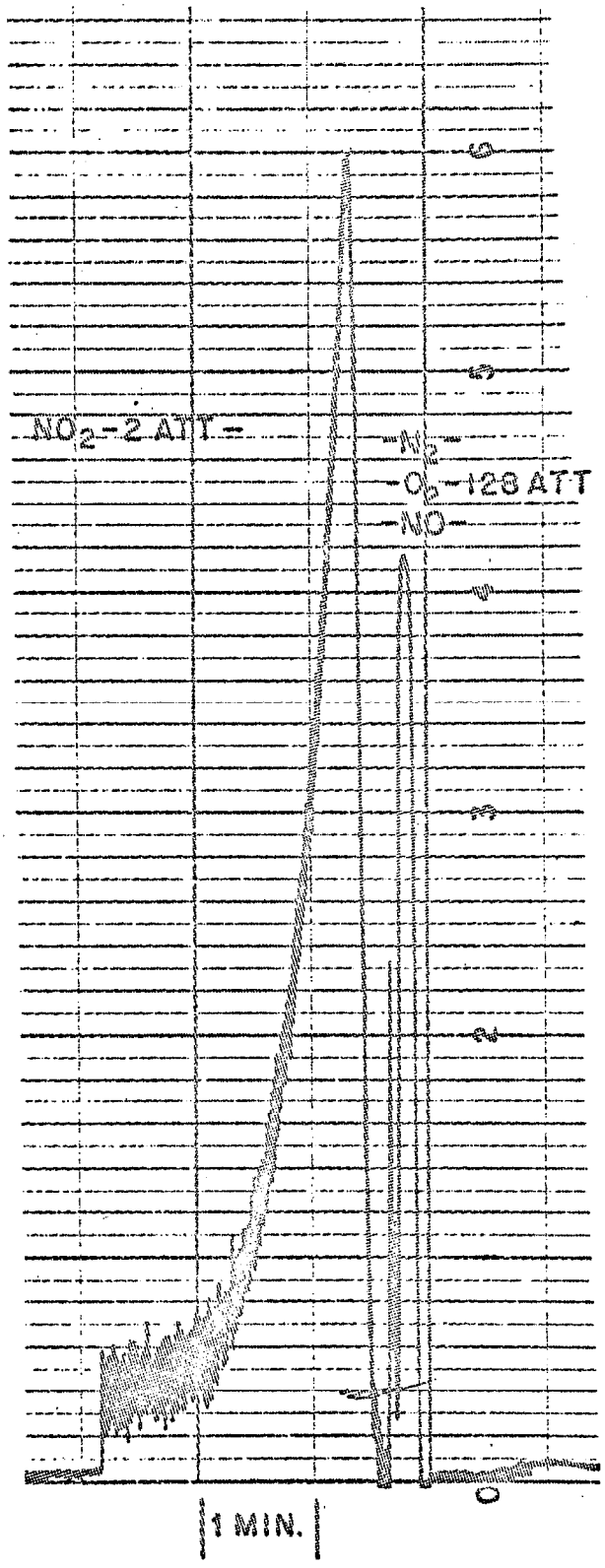


Figure 23. Typical chromatogram for nitrogen dioxide in nitrogen, oxygen, and nitric oxide for the Plane-Parallel Detector.

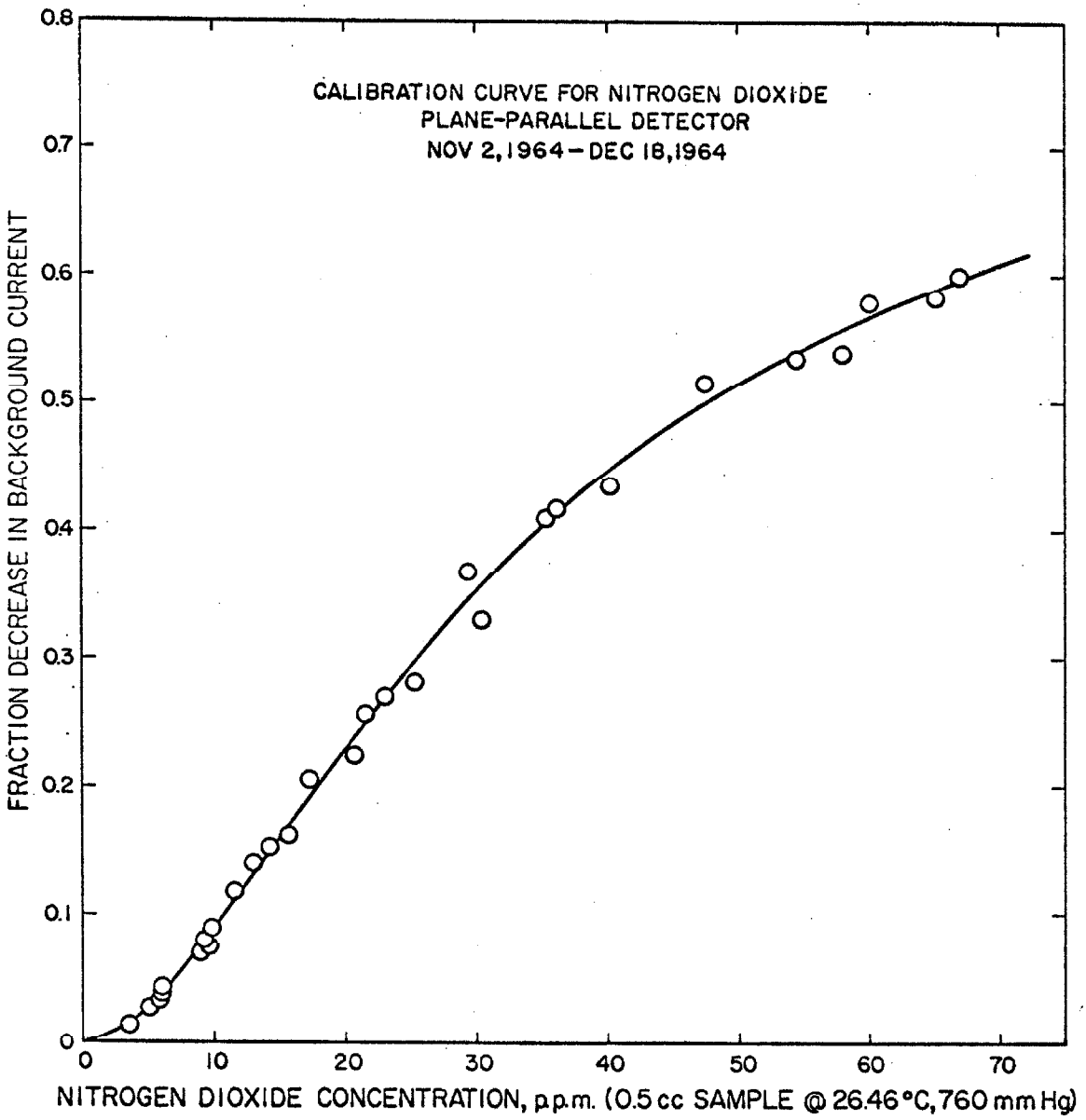


Figure 24. Calibration curve for nitrogen dioxide with the Plane-Parallel Detector when used at the optimum conditions for analysis.

APPENDIX A

A reprint from ANALYTICAL CHEMISTRY Vol. 36, November 1964, Pages 2256-2259

Quantitative Determination of Parts-per-Million Quantities of Nitrogen Dioxide in Nitrogen and Oxygen by Electron-Capture Detection in Gas Chromatography

M. E. MORRISON, R. G. RINKER, and W. H. CORCORAN

Chemical Engineering Laboratory, California Institute of Technology, Pasadena, Calif.

▶ An electron-capture detector was used in a gas chromatograph to measure parts-per-million quantities of nitrogen dioxide in a ternary mixture of nitrogen, oxygen, and nitrogen dioxide. For concentrations of nitrogen dioxide from 5 to 150 p.p.m. and for oxygen present to the extent of 9% by volume in nitrogen, the standard deviation of the best curve through the points showing response vs. concentration was 2 p.p.m. compared to about 3 p.p.m. for chemical techniques. The main advantages of gas chromatography are the short time for analysis and the small samples (1/2 cc.) required.

USE OF GAS CHROMATOGRAPHY for analysis of nitrogen dioxide at concentrations between 10 and 1000 p.p.m. has not been described in the literature. Greene and Pust (*1*) used a wetted molecular sieve column to analyze for nitrogen dioxide at relatively high concentrations. Currently small concentrations of nitrogen dioxide in air are usually measured by means of the Saltzman (*4*) technique which requires much larger samples than gas chromatography.

EXPERIMENTAL

Apparatus. A Loenco 15A gas chromatograph with a Loenco 15B electrometer was used in the study. The electron-capture detector was a Barber-Colman Model A 5042 with a 220-mc. tritium source. High purity dry nitrogen and commercial grade oxygen, both obtained from Linde, were the diluent gases. They were dried by passage through a 4-foot length of 3/16-inch i.d. copper tubing packed with 13-X molecular sieve and mounted in a dry ice–acetone bath.

Several column materials were tested for their ability to separate oxygen and nitrogen dioxide. They were 5% by weight of 710 silicone oil on Chromosorb W (HMDS), 5% Apiezon L on Chromosorb W (HMDS), an unpacked column with a coating of aluminum oxide, and a glass capillary column. These materials did not effect a satisfactory separation, and at the suggestion of

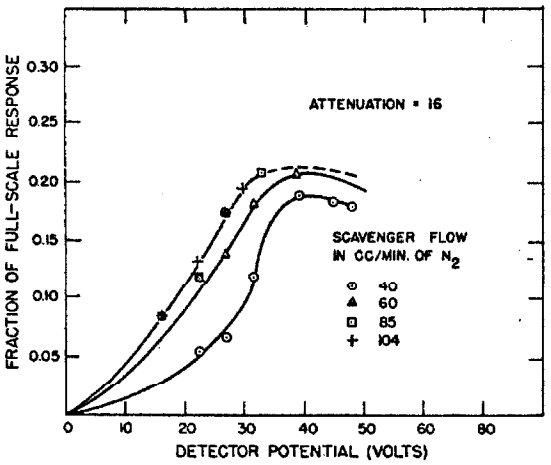


Figure 1. Effect of detector potential on relative response to nitrogen dioxide with a nitrogen carrier flow of 10 cc. per minute

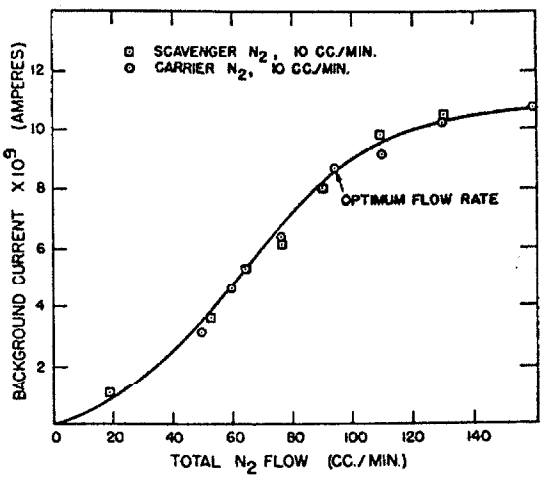


Figure 2. Background current as a function of total nitrogen flow at a detector potential of 33 volts

I. H. Williams of the British Research Council, 10% SF 96 (a methyl silicone oil) on Fluoropak 80 was tried and gave a reasonable separation. It was used in the present study.

Special care was required in the preparation of the column with 10% SF 96 on Fluoropak 80. The SF 96 was placed on the solid phase, which was 20- to 80-mesh, by use of standard evaporation procedures with diethyl ether as the solvent for the methyl silicone oil. The coated packing was then placed into a 15-foot length of a 304 stainless steel tube having an inside diameter of $^3/_{32}$ inch. Three grams of material were used to pack the 15-foot column which was then coiled into a diameter of approximately 4 inches and conditioned at 200° C. for 30 hours by flowing dry nitrogen through it at a rate of 10 cc. per minute as measured at 1 atm. and 22° C. Then the column was cooled to 22° C. while the nitrogen flow was maintained. Next, 20 3-cc. samples of nitrogen, each containing 300 p.p.m. of nitrogen dioxide, were injected into the column at approximately 5-minute intervals. After that treatment, the column quantitatively separated oxygen and nitrogen dioxide. In continuous use, three to four $^1/_2$-cc. samples of nitrogen containing 100 p.p.m. of nitrogen dioxide were injected into the column each day before beginning the quantitative analysis.

Nitrogen Dioxide. Nitrogen dioxide was obtained from a mixture furnished by Matheson containing nominally 1500 p.p.m. of nitrogen dioxide in nitrogen. Analysis of the gas in the cylinder by the phenoldisulfonic acid method (ASTM D 1608-60) showed that the concentration of nitrogen dioxide was 1627 p.p.m., based on moles of nitrogen dioxide per mole of gas, with a standard deviation of 70 p.p.m. Standard mixtures used to calibrate the chromatograph were made by evacuation of a 6000-cc. vessel followed by addition of the appropriate gases. Changes in pressure combined with compressibility factors and the assumption that Dalton's law prevailed were used to calculate the concentrations of the gases in the 6000-cc. vessel. For very low concentrations of nitrogen dioxide, successive dilution procedures were used.

Procedure. The conditioned Fluoropak 80 column was operated at 22° C. (room temperature) to determine the optimum conditions for determination of the nitrogen dioxide. Preliminary work showed that a flow rate of 10 cc. per minute of carrier gas provided the best separation of the nitrogen dioxide. That flow rate then received special interest in studies of detector response as a function of detector potential and flow rate of scavenger gas. In the study of the optimum conditions of operation, $^1/_2$-cc. samples of nitrogen containing 100 p.p.m. of nitrogen dioxide were used.

RESULTS AND DISCUSSION

Figure 1 presents information on the response obtained as the detector potential was varied for constant values of total nitrogen flow. Within the limits of experimental error for the case of a carrier flow of 10 cc. per minute, a scavenger flow of 85 cc. per minute of nitrogen and a detector potential of 33 volts gave the most sensitive response.

The background current was then studied as a function of total nitrogen flow and detector potential for comparison with the results presented in Figure 1. Figure 2 shows the background current as a function of the total flow rate of

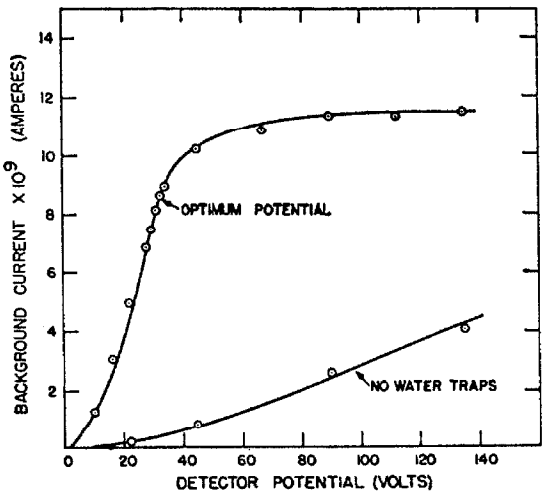


Figure 3. Background current as a function of detector potential for a total nitrogen flow of 95 cc. per minute

nitrogen. The data were obtained at a constant potential of 33 volts and flow of scavenger gas or carrier gas of 10 cc. per minute. Figure 3 shows the background current as a function of detector potential for a constant flow rate of 85 cc. per minute of scavenger gas and 10 cc. per minute of carrier gas. In Figure 3 the lower curve is the background current as a function of detector potential in the absence of water traps on the nitrogen and oxygen streams. The need for removal of water by the molecular sieves is shown to be very important. The optimum conditions for the operation of the electron-capture cell were then selected as 33 volts, 10 cc. per minute of nitrogen as the carrier gas and 85 cc. per minute as scavenger gas, and a background current of 8.6×10^{-9} ampere.

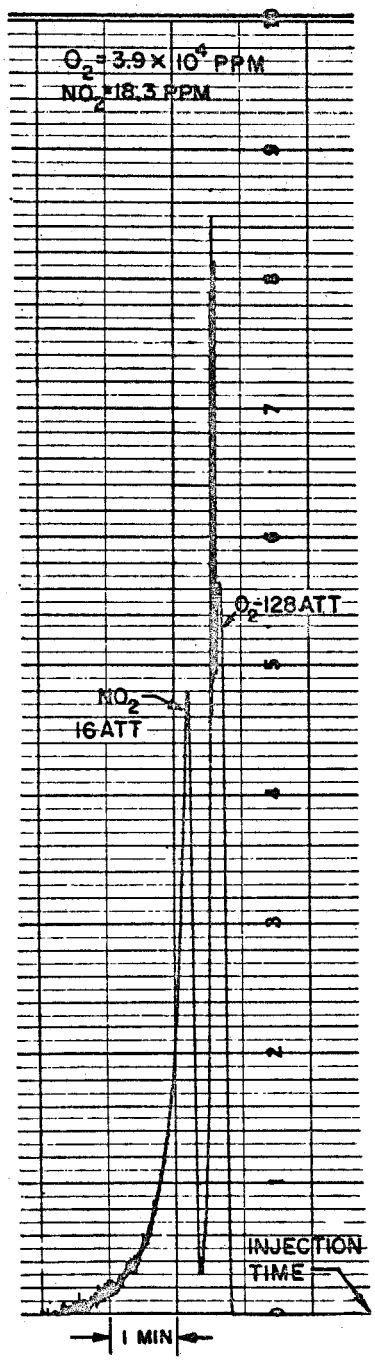


Figure 4. Typical chromatogram of nitrogen dioxide in nitrogen with added oxygen

A chromatogram for the optimum conditions of analysis is shown in Figure 4. Nitrogen was the carrier. The concentration of nitrogen dioxide was 18.3 p.p.m. and that of oxygen was 3.9×10^4 p.p.m. Oxygen was present just to check separation, and the multiple oxygen peak was developed merely by decreasing the attenuation by factors of two from a value of 128 to 16 during the course of the oxygen peak. The sample volume was $^1/_2$ cc.

Lovelock (*2*) noted that the electron capture detector should obey the following equation:

$$I = I_s e^{-BC} \qquad (1)$$

in which I is the measured current in the presence of the test substance at a concentration C, I_s is the background current or current measured with no electron-capturing material in the detector cell, and B is a constant. Rearrangement of the equation gives

$$C = A - D \ln I \qquad (2)$$

in which A and D are constants. I is obtained by use of the following relation:

$$I = I_s - I_p \qquad (3)$$

where I_p is a decrease in current effected by the presence of the electron-capture substance and is obtained as the product in appropriate units of the peak height measured for that substance and the prevailing attenuation. A semilog plot of I as a function of the concentration of nitrogen dioxide in parts per million in the presence of nitrogen is given in Figure 5. Over the range of 5 to 150 p.p.m. of nitrogen dioxide the experimental data do not exactly follow Lovelock's proposed relationship as expressed by Equation 2. A least-squares analysis of the data using Equation 2 gave the dashed line with a standard deviation of 7.3 p.p.m. while the best curve through the averaged experimental points is the solid line with a standard deviation of 2 p.p.m. of nitrogen dioxide. Although no data for day-to-day variability of the standard sample are yet available, it is estimated that the within-day standard deviation would prevail at the level of 2 p.p.m. of nitrogen dioxide. The lower limit of concentration of about 5 p.p.m. was set by the noise in the detector circuit.

Subsequent to the experiments reported in detail here, the noise has been significantly reduced by use of a pulsed voltage (*3*) and a detector with concurrent flow. The change in flow pattern reduced the noise level by a factor of two, and an additional reduction by a factor of two was obtained with the pulsed voltage. In this later work, argon was used as both carrier and scavenger gas for increased sensitivity of signal from the detector. The best performance in the pulsed operation was found for a total flow of argon of 40 cc. per minute, a 50-volt output, an on-time of 4 μseconds, and a period of 150 μseconds. To minimize the effect of

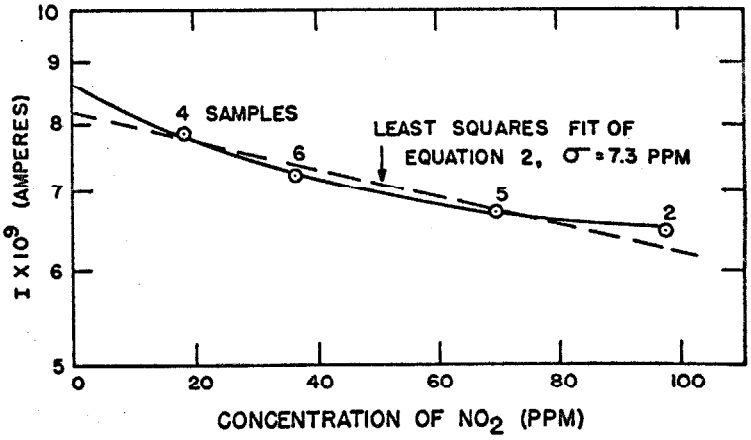


Figure 5. Concentration of nitrogen dioxide as related to detector current for 1/2-cc. samples containing nitrogen and up to 9% oxygen

column bleed on the tritium foil in the detector, the temperature of the detector was held at 200° C. A noise level of 4×10^{-12} ampere was observed with a background current of 2.6×10^{-9} ampere which suggests a limit of detection of 1 p.p.m. of nitrogen dioxide for this particular pulsed system.

In this laboratory, experience with the ASTM D 1608–60 analysis for nitrogen dioxide showed a standard deviation of about 3 p.p.m. at very low concentrations of nitrogen dioxide in comparison with the 2 p.p.m. reported here for the electron-capture unit. In consideration of the analysis time of 5 minutes for the gas chromatography *vs.* 3 to 4 days with the ASTM method and a sample size of $^1/_2$ cc. *vs.* nominally 1 liter, the gas chromatographic analysis shows advantages for the particular conditions studied. Similarly the advantage of sample size would prevail relative to the Saltzman (*4*) procedure. Special care must be exercised to eliminate water or any other impurity that has electron affinity. Where nitrogen is used as a carrier and scavenger gas, water apparently is the main impurity, and it may be relatively easily removed by means of molecular sieves at the temperature of a dry ice–acetone bath.

ACKNOWLEDGMENT

The advice on column packing given by I. H. Williams of the British Research Council is appreciated.

LITERATURE CITED

(1) Greene, S. A., Pust, H., ANAL. CHEM. **30**, 1039 (1958).
(2) Lovelock, J. E., *Ibid.*, **33**, 163 (1961).
(3) *Ibid.*, **35**, 474 (1963).
(4) Saltzman, B. E., *Ibid.*, **26**, 1949 (1954).

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PROPOSITIONS

PROPOSITION I

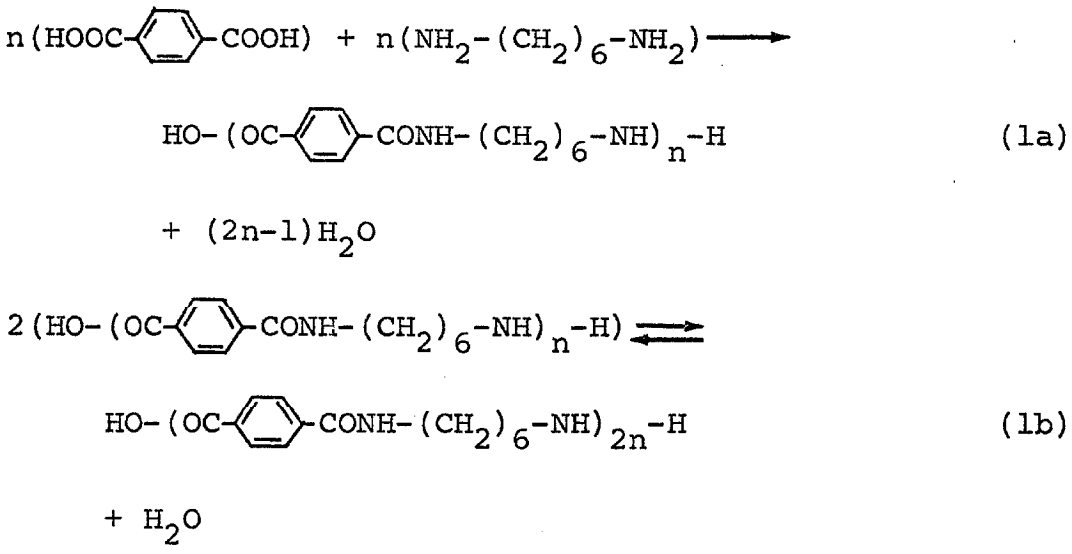
This proposition describes a method for the measurement of the Fick Diffusion Coefficient for water in nylon polymer. The diffusion coefficient can be measured as a function of temperature and the concentration of water.

In the production of nylon, adipic acid and hexamethylenediamine are reacted to form water and the polymer. The water is called a condensation product. In order to increase the molecular weight of the polymer, the water is removed by passing an inert gas over the polymer melt. The rate of polymerization is thus dependent upon the chemical reaction and the diffusion rate of water through the polymer. Therefore, in order to design vessels to contain this reaction, it is desirable to know the diffusion coefficient for water through a nylon melt.

The method described in this proposition for the measurement of the Fick Diffusion Coefficient for the condensation product through the polymer melt can be applied to any condensation reaction. There are many condensation polymers among which urea-formaldehyde resins, phenol-formaldehyde resins, adipic acid-hexamethylenediamine, and dimethylterepthalate-ethylene glycol are the more common. The condensation products in the first three reactions are water. Methanol is the condensation product in the reaction between dimethylterepthalate and ethylene glycol. There

are no published data on the measurement of the diffusion coefficient for the condensation product in these systems, although the chemical industry has done some research on the effect of diffusion during polymerization. The only known research on this problem is being carried out in the Chemical Engineering Department at the University of Delaware.

The reaction of adipic acid and hexamethylenediamine to form nylon will be used to describe the proposed technique. The Fick Diffusion Coefficient for water through a nylon melt will be measured. The production of nylon proceeds by Reaction 1.



$$n(HOOC\text{-}C_6H_4\text{-}COOH) + n(NH_2\text{-}(CH_2)_6\text{-}NH_2) \longrightarrow$$

$$HO\text{-}(OC\text{-}C_6H_4\text{-}CONH\text{-}(CH_2)_6\text{-}NH)_n\text{-}H \qquad (1a)$$

$$+ (2n-1)H_2O$$

$$2(HO\text{-}(OC\text{-}C_6H_4\text{-}CONH\text{-}(CH_2)_6\text{-}NH)_n\text{-}H) \rightleftharpoons$$

$$HO\text{-}(OC\text{-}C_6H_4\text{-}CONH\text{-}(CH_2)_6\text{-}NH)_{2n}\text{-}H \qquad (1b)$$

$$+ H_2O$$

At the conditions of this study there will be no adipic acid or hexamethylenediamine present. Therefore Reaction 1b will be the only reaction proceeding.

Figure 1-P1 is a schematic of the system to be used.

The diffusion cell is cylindrical in shape. A concentration gradient has been imposed on the system in the longitudinal direction (x) by passing an inert gas over the polymer melt. If it is assumed that there are no concentration gradients in the radial and angular directions, the material flux due to diffusion will be entirely in the x direction.

Consider a general material balance on the increment dx.

$$\text{in-out+source-sink} = \text{accumulation} \tag{2}$$

At steady state conditions the concentration at any point will be invariant. If it is assumed that

$$R_{lb} = R'_{lb} \tag{3}$$

at any point in the system under steady state conditions; Equation 2 reduces to

$$\text{in} = \text{out or } \dot{m} = \text{constant} \tag{4}$$

For this system

$$\dot{m} = \dot{m}_i + \dot{m}_j \tag{5}$$

and

$$\dot{m}_j = 0 \tag{6}$$

For unidirectional diffusion

$$\dot{m}_i = u\sigma_i - D_{F_i} \frac{d\sigma_i}{dx} \tag{7}$$

By definition

$$\dot{m} = u\sigma \tag{8}$$

Using Equations 5, 6, 7, and 8

$$\dot{m} = \frac{\dot{m}\sigma_i}{\sigma} - D_{F_i} \frac{d\sigma_i}{dx} \tag{9}$$

or

$$\dot{m} = \frac{-D_{F_i}}{\frac{(1-\sigma_i)}{\sigma}} \frac{d\sigma_i}{dx} \tag{10}$$

Since $$\sigma_i = n_i\sigma \tag{11}$$

$$\dot{m} = \frac{-D_{F_i}}{1-n_i} \frac{d(n_i\sigma)}{dx} \tag{12}$$

or

$$\int_o^h \dot{m}dx = - \int_{n_{i_a}}^{n_{i_b}} \frac{D_{F_i}\, d(n_i\sigma)}{(1-n_i)} \tag{13}$$

From Equations 4 and 13,

$$\dot{m}h = \int_{n_{i_b}}^{n_{i_a}} \frac{D_{F_i}\, d(n_i\sigma)}{1 - n_i} \tag{14}$$

The assumptions inherent in the derivation of Equation 14 were,

1. Steady state conditions
2. $R_{1b} = R'_{1b}$ at any point in the polymer melt.
3. No concentration gradient in the radial or angular directions.
4. $\dot{m}_j = 0$

The boundary conditions on the integral in Equation 14 and the concentration (σ) as a function of n_i can be determined easily in ordinary laboratory glassware and through use of standard analytical techniques.

The Fick Diffusion Coefficient will be a function of the weight fraction of water at equilibrium (degree of polymerization). In order to describe the fact that

$$D_{F_i} = f(n_i) \tag{15}$$

various forms of equations, such as polynomials or exponentials in n_i, can be tested for their applicability. The constants in these expressions can be evaluated and checked by measuring $\dot{m}$ as a function of the polymer layer thickness and the boundary condition n_{i_b} in Equation 14.

In the production of many polymers, including nylon, continuous tank reactors are employed. The residence time for the polymer in the reactor to attain the required degree of polymerization is a function of the reaction rate constant and the diffusion coefficient of the condensation product in the polymer melt. The design of these reactors could be more easily completed, if data were available for

the variance and magnitude of these diffusion coefficients. For this reason it is believed that the work discussed here would be important and useful.

Nomenclature*

σ	Specific weight, lb/ft^3.
D_F	Fick Diffusivity, ft^2/sec.
f(g)	Function of g.
h	Polymer layer thickness, ft.
$\dot{m}$	Material per unit area in the x direction, lb/ft^2sec.
n	Weight fraction, dimensionless.
R_{lb}	Rate of Reaction lb in the forward direction, pound i produced/ft^3sec.
R'_{lb}	Rate of Reaction lb in the reverse direction, pound i produced/ft^3sec.
u	Bulk velocity, ft/sec.
x	Coordinate distance in direction of polymer thickness, ft.

Subscripts

a	Polymer-steam boundary layer.
b	Polymer-inert gas boundary layer.
i	Diffusing component (water).
j	Nylon polymer.

* The F-L-T system of units has been used.

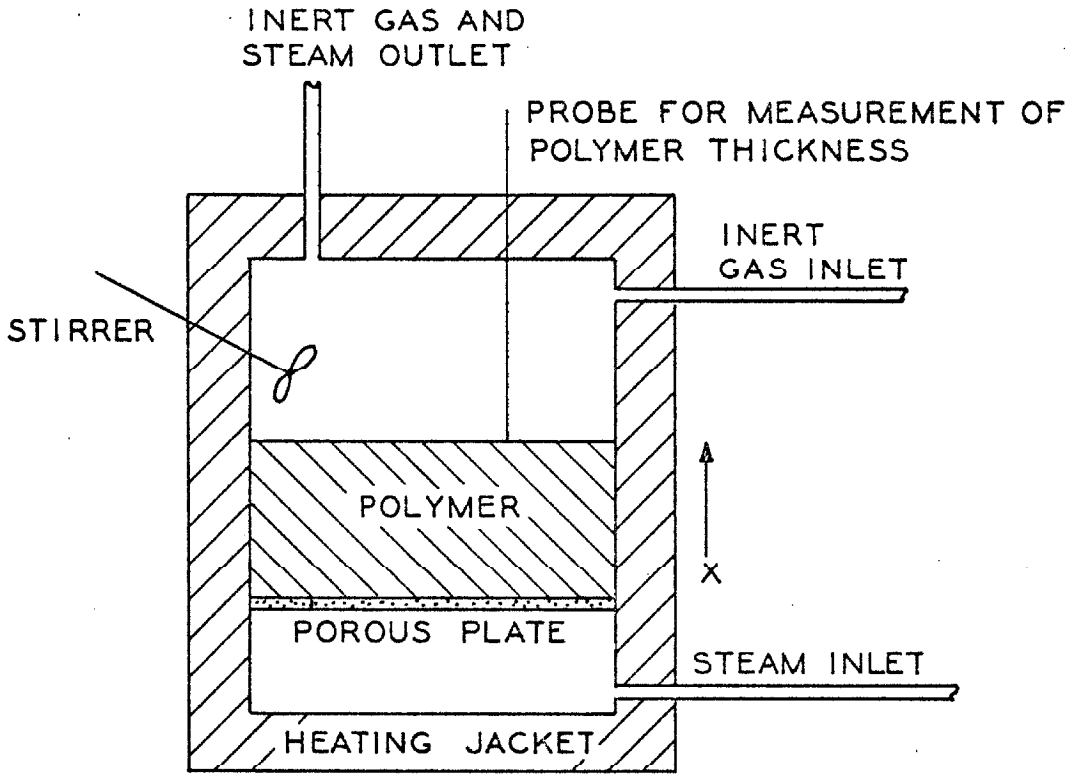


Figure 1-P1. Schematic of cell for diffusion studies of vapors through polymer melts.

PROPOSITION II

This proposition discusses the use of the electron-capture detector and gas chromatography for the measurement of electron affinities. Preliminary studies in the measurement of the electron affinity of nitrogen dioxide are presented and the problems inherent in the method discussed.

Only Wentworth and Becker[1] have used the electron-capture detector for the measurement of the electron affinity of molecules. They made four very basic assumptions.

(1) The main reaction proceeding in the electron-capture detector is the following

$$AB + e^- \rightleftharpoons AB^- \qquad (1)$$

where AB is a neutral molecule.

(2) The reaction is very rapid and is at equilibrium.

$$K = \frac{C_{AB^-}}{(C_{AB})(C_{e^-})} \qquad (2)$$

(3) The statistical thermodynamic equilibrium expression is

$$K = \frac{f_{AB^-}}{f_{AB} f_{e^-}} \; e^{-E_A/RT} \qquad (3)$$

(4) The ratio of the partition functions, f_{AB^-}/f_{AB}, is constant and equal to two for anthracene.

By making these assumptions, Wentworth and Becker were able to experimentally determine, by use of the electron-capture detector and gas chromatography, the electron affinities of phenanthrene, pyrene, and anthracene within 50 percent of the theoretical value.

If assumptions (1) and (2) are made, the data presented in Part II of this thesis can be used to calculate the equilibrium constant, K, for nitrogen dioxide. The following is the result of this calculation.

Temperature, °C	Equilibrium Constant x 10^{-7}, ℓ/g.mole
200.	1.65
116.	1.72
89.	1.69
27.	4.43

Since Wentworth and Becker only carried out the analysis at one temperature, it was difficult to judge whether the assumptions were valid. One check for the validity of assumptions (1) and (2) is to plot ℓn K versus the reciprocal of the absolute temperature. A straight line should result with the slope equal to $-E_A/R$. Such a plot of the above data is truly not a straight line, which indicates the high probability that reactions other

than electron attachment are important in the electron-capture detector. Certainly with the large amount of energy available from the β-rays (0.018 mev), considerable ionization and dissociation reactions may well take place. Among the possible reactions for nitrogen dioxide that should be considered are:

$$I_g + e^- \rightleftharpoons I_g^+ + 2e^- \quad (4)$$

$$NO_2 + e^- \rightleftharpoons NO + O^- \quad (5)$$

$$NO_2 + e^- \rightleftharpoons NO^- + O\cdot \quad (6)$$

$$NO_2 + e^- \rightleftharpoons N^- + 2O\cdot \quad (7)$$

$$NO_2 + e^- \rightleftharpoons N\cdot + O\cdot + O^- \quad (8)$$

$$NO_2 + e^- \rightleftharpoons NO_2^- \quad (9)$$

In addition, any number of the nitrogen oxide compounds could be ionized to yield positive ions or the ions of opposite charge could combine.

Indeed, the number of reactions proceeding in the detector seems quite large. The assumption of the only reaction in the detector as that shown in Equation 1 is rather difficult to believe in light of the data and arguments presented in this proposition. Before accurate values for the electron affinity of molecules can be obtained with the electron-capture detector, the important

reactions that proceed in the cell must be better understood.

References

1. Wentworth, W. E. and Becker, R. S., J. Am Chem. Soc., 84, 4263 (1962).

Nomenclature

AB	Molecule with atoms A and B.
C	Concentration, g.mole/ℓ.
E_A	Electron affinity, cal/g.mole.
e^-	Electron, but not necessarily in thermal equilibrium with the surrounding gas.
f	Molecular partition function.
I_g	Carrier and scavenger gas in electron-capture detector (argon or nitrogen).
K	Equilibrium constant, ℓ/g.mole.
R	Gas constant, 1.987 cal/g.mole ^oK.
T	Absolute temperature, ^oK.

PROPOSITION III

The Fick Diffusion Coefficient, for the diffusion of vapors into polymer films based upon an activity gradient, has been found to be a function of the concentration of the diffusing vapor. The constancy of the Fick Diffusion Coefficient using a concentration gradient as a driving force is compared to the Diffusion Coefficient based upon an activity gradient.

In the diffusion of vapors into polymers, it has been found that the ordinary Fick Diffusion Coefficient ($D_{F,k}$) varies with concentration. This has been attributed to the swelling of the polymer. In particular the diffusion of organic vapors in polyvinyl-acetate has been studied by Kokes and Long[2]. Kokes and Long found experimentally that,

$$D_{F,k} = D_o e^{\delta \sigma_k} \tag{1}$$

where

$$\text{Lim } D_{F,k} = D_o \tag{2}$$
$$\sigma_k \rightarrow 0$$

and

$$\dot{m}_k = -D_{F,k} \nabla \sigma_k \tag{3}$$

Inherent in the derivation of Equation 3 was the fact that the weight fraction of component k was very small.

Kuppers and Reid[3] have developed an expression

for the evaluation of the activity coefficient for vapors in polymer films which involves δ as defined in Equation 1. Inherent in their derivation is the fact that the diffusion coefficient based upon an activity gradient is a constant. This is shown to be untrue in this proposition.

The flux of component k using concentration as a driving force for diffusion can be written as

$$\dot{m}_k = u\sigma_k - D_{F,k}\nabla\sigma_k = \sigma_k u_k \tag{4}$$

If activity is considered the driving force for diffusion, Equation 5 results.

$$\dot{m}_k = u\sigma_k - D_{a,k}\ \nabla a_k = \sigma_k u_k \tag{5}$$

Consideration of Equations 4 and 5 yields

$$D_{a,k}\ \nabla a_k = D_{F,k}\nabla\sigma_k \tag{6}$$

If we consider the fact that the activity is a function of state, then

$$a_k = \Phi(T,\ P,\ \sigma_1, \sigma_2 \ldots\ldots \sigma_{m-1}) \tag{7}$$

So

$$\nabla a_k = \left(\frac{\partial a_k}{\partial T}\right)_{P,n} \nabla T + \left(\frac{\partial a_k}{\partial P}\right)_{T,n} \nabla P + \tag{8}$$

$$+ \sum_{j=1}^{j=m-1} \left(\frac{\partial a_k}{\partial \sigma_j}\right)_{T,P,n_j} \nabla\sigma_j$$

For a binary system at constant temperature and pressure Equation 8 reduces to

$$\nabla a_k = \left(\frac{\partial a_k}{\partial \sigma_k}\right)_{T,P,n_j} \nabla \sigma_k \qquad (9)$$

Comparison of Equations 6 and 9 yields

$$D_{a,k} = \frac{D_{F,k}}{\left(\frac{\partial a_k}{\partial \sigma_k}\right)_{T,P,n_j}} \qquad (10)$$

Values of the Fick Diffusion Coefficient based upon a concentration gradient, for three organic compounds diffusing into polyvinyl acetate, are shown in Figures 1-P3, 2-P3, and 3-P3. The diffusion coefficients are those reported by Kokes and Long (2) at 40°C. The diffusion coefficients are seen to be functions of the concentration of the system.

Using equilibrium absorption techniques, the activity of the organic vapor in the polyvinyl acetate has been reported by Kokes, DiPietro, and Long[1]. These values for the activity were used in conjunction with Equation 10 to evaluate the diffusion coefficient based upon an activity gradient. The results are shown in Figures 1-P3, 2-P3, and 3-P3 for the benzene-polyvinyl acetate, acetone-polyvinyl acetate, and propylamine-polyvinyl acetate systems at 40°C. The Fick Diffusion Coefficient based upon an activity

gradient is seen to be no more constant than the diffusion coefficient based on a concentration gradient for the concentration region studied.

From the results presented in this proposition the Fick Diffusion Coefficient for the diffusion of organic vapors into polyvinyl acetate based upon a concentration or activity gradient is seen to be a function of the concentration of the system.

References

1. Kokes, R.J., DiPietro, A.R., and Long, F.A., J. Am. Chem. Soc., 75, 6319, (1953).

2. Kokes, R.J. and Long, F.A., J. Am. Chem. Soc., 75, 6142, (1953).

3. Kuppers, J.R. and Reid, C.E., J. App. Polymer Sci., 4, 124, (1960).

Nomenclature*

a_k	Activity of component k, dimensionless.
$D_{F,k}$	Fick Diffusion coefficient for component k using concentration as a driving force, ft^2/sec.
$D_{a,k}$	A Diffusion Coefficient for component k using activity as a driving force, lb/ft sec.
D_o	Constant, ft^2/sec.
$\dot{m}$	Material transport per unit area, lb/ft^2 sec.
n_k	Weight fraction component k, lbs k/total lbs.
P	Pressure, lb/ft^2
T	Temperature, ^oK.
u	Bulk velocity, ft/sec.

Greek

δ	Constant characteristic of system, ft^3/lb.
∇	Gradient operator.
σ_k	Concentration of component k, lb/ft^3.

Subscripts

k	Organic vapor
m	Number of components in system (1,2,3,...m).
j	All components other than k and m.

*The F-L-T system of units has been used.

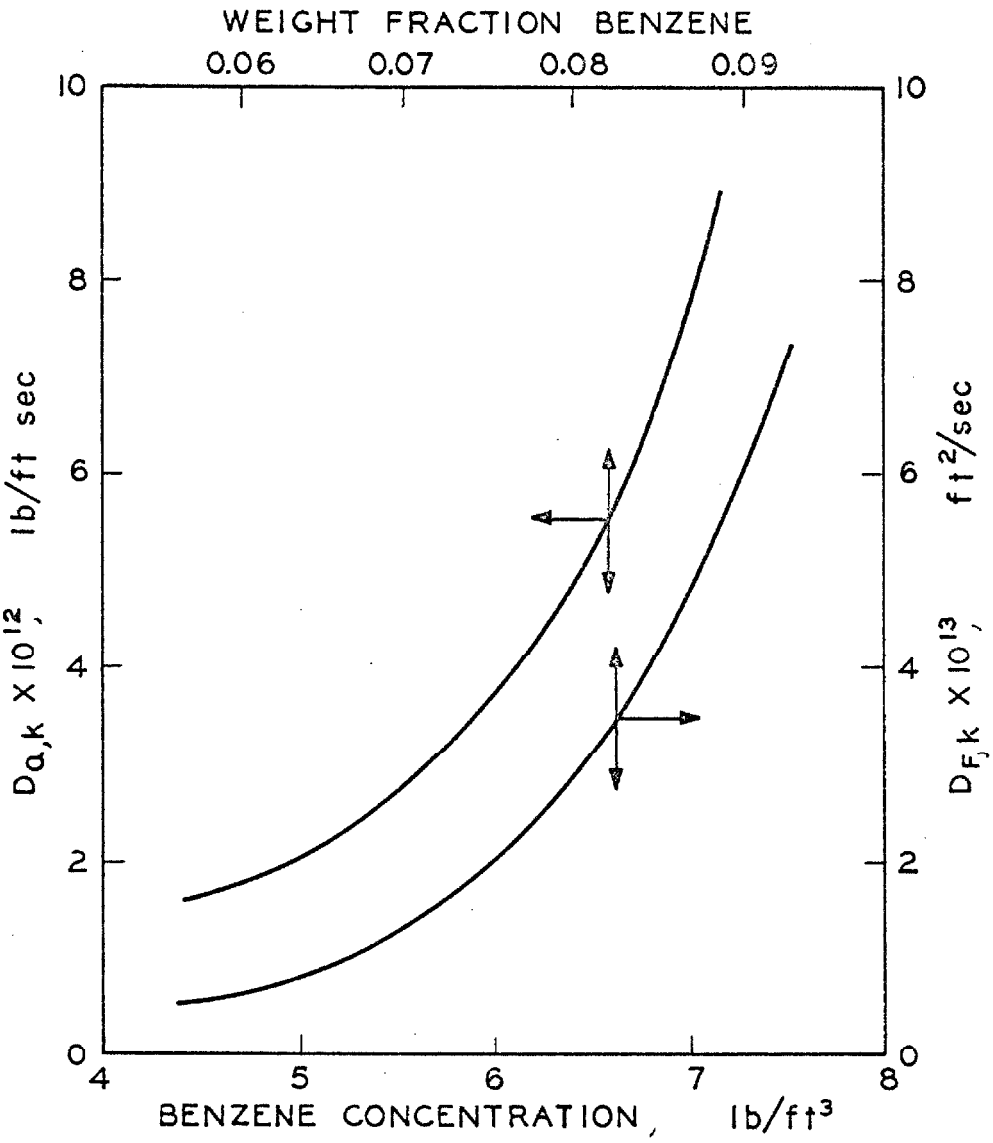


Figure 1-P3. Comparison of $D_{a,k}$ and $D_{F,k}$ for benzene in polyvinyl acetate as a function of the benzene concentration.

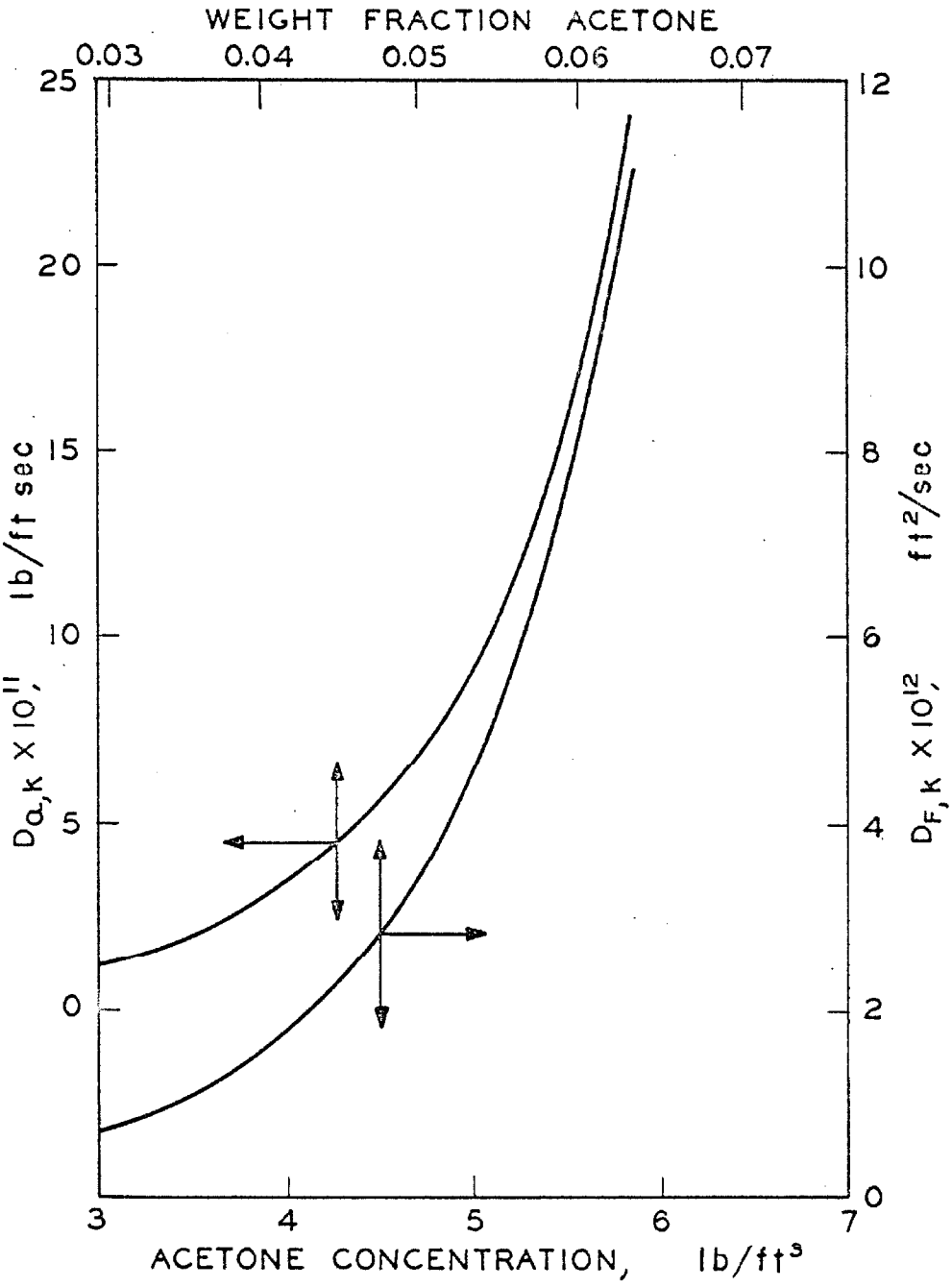


Figure 2-P3. Comparison of $D_{a,k}$ and $D_{F,k}$ for acetone in polyvinyl acetate as a function of the acetone concentration.

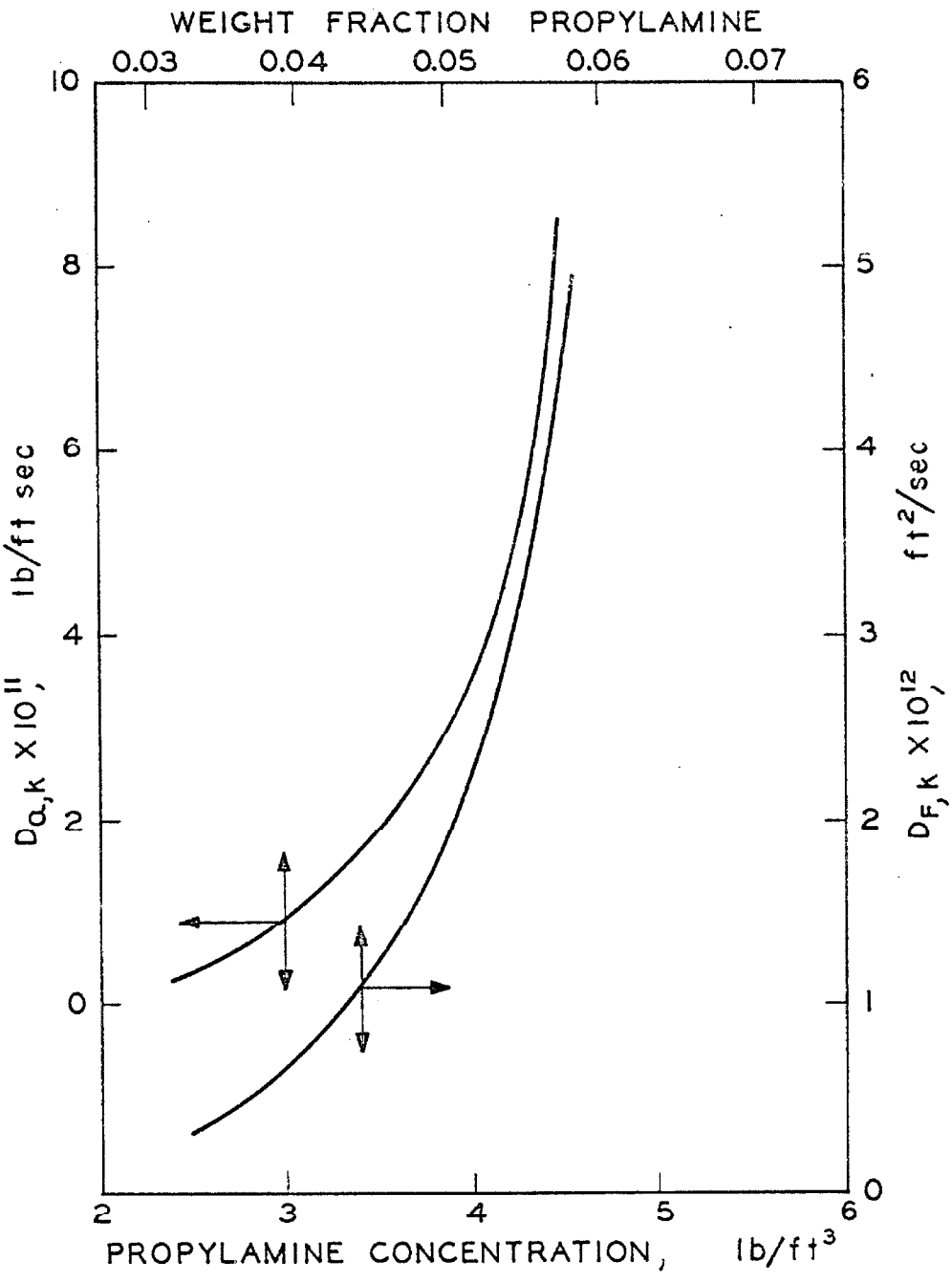


Figure 3-P3. Comparison of $D_{a,k}$ and $D_{F,k}$ for propylamine in polyvinyl acetate as a function of the propylamine concentration.

PROPOSITION IV

The selection of a proper partition liquid for a chromatography column in the separation of a gas sample containing several components is very often a difficult problem. The separation of the nitrogen oxides from nitrogen or other permanent gases is by no means an exception. Therefore, this proposition discusses the physical and chemical properties for partition liquids which are required for the separation of the nitrogen oxides from other permanent gases. Several liquids are proposed for use in the separation.

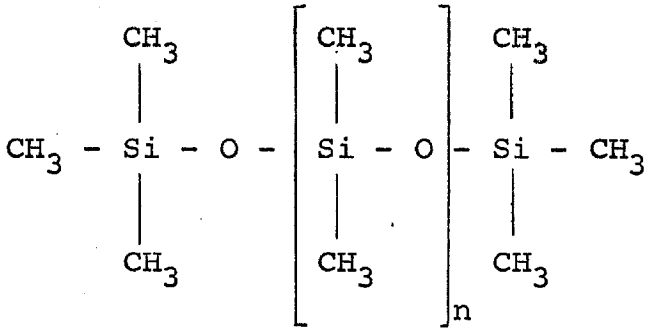
Gas-liquid chromatography is a useful tool for quantitative and qualitative analysis. It is only useful, though, when the correct partition liquid and packing support is used. The separation of several components in a gas sample depends upon the partition coefficient between the gas and liquid phase for each component. When the partition coefficient

$$K_i = \frac{C_{i,g}}{C_{i,\ell}} \qquad (1)$$

is markedly different for each of the components in the gas sample, separation will be obtained. If the separation of nitrogen, nitric oxide, and nitrogen dioxide are desired, a liquid phase which would give relatively high but different partition coefficients for nitric oxide and

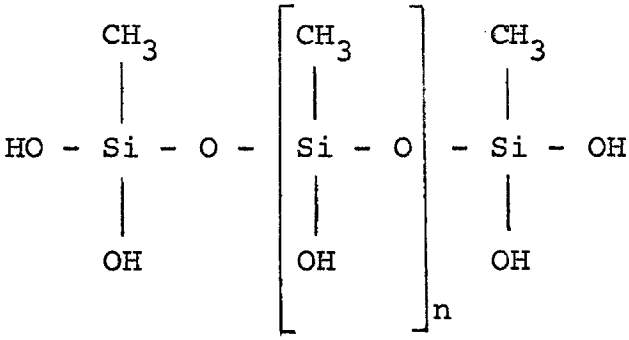
and nitrogen dioxide would be required.

The methyl silicone oil, SF-96 (General Electric Company),



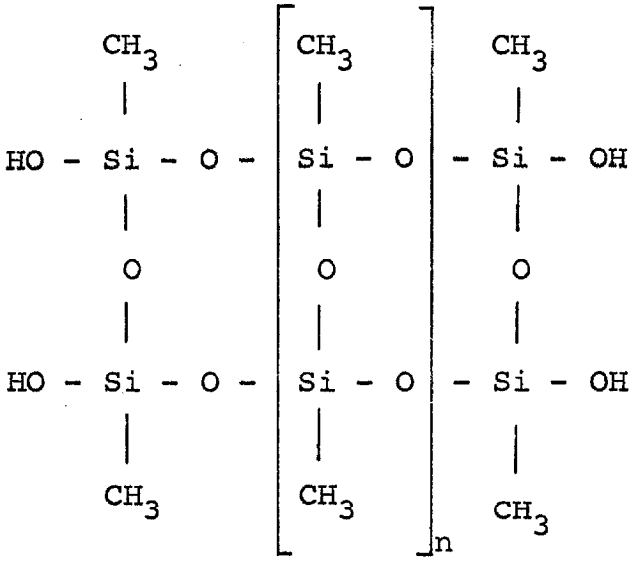
(2)

was found to be applicable for the separation of nitrogen dioxide from nitrogen[2], but no measurable separation was obtained for nitric oxide from nitrogen. The reason for no measurable separation was because of the small partition coefficient for nitric oxide over the silicone oil. In order to separate nitric oxide from nitrogen, a liquid phase more polar than the methyl silicone oil will probably have to be used. One compound that should be tested for the separation of nitric oxide, nitrogen dioxide, and nitrogen is the hydrolyzed trichlorosilane, SF-99,



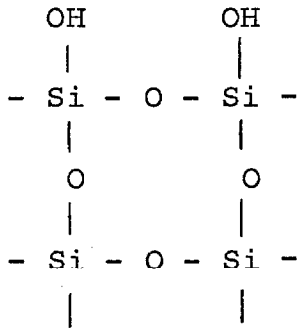
(3)

or the cross-linked polymers



(4)

One striking point is that the structure of the cross-linked silicones is very similar to silica gel[1]

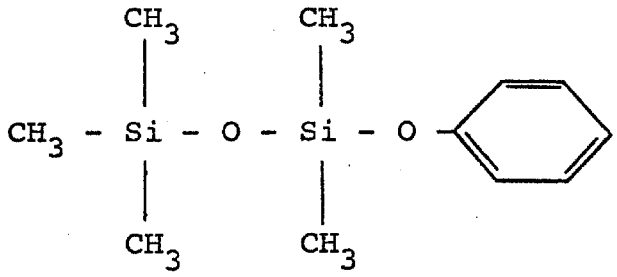


(5)

which has been used for the separation of nitric oxide from nitrogen[3].

Another compound that might prove to be an acceptable partition liquid for the separation of nitric oxide, nitrogen dioxide, and nitrogen is the methyl phenyl

silicone oil, SF-1017,



(6)

Other relatively polar compounds such as aromatic or long chain amines should also be tried as partition liquids in the separation.

In conclusion, relatively polar compounds should be tested for the separation of nitric oxide, nitrogen dioxide, and nitrogen. Materials which possess a large number of free hydroxyl or amide groups should yield a high partition coefficient for nitric oxide and nitrogen dioxide because of the attraction of the negative oxygen atom in the nitrogen oxides for the positively charged portion of the polar partition liquid, thus increasing the probability of the separation.

References

1. Boheman, J., et. al., J. Chem. Soc. (London), 2444, (1960).

2. Morrison, M. E., Ph.D. Thesis, "II. The Quantitative Determination of Parts-Per-Million Quantities of Nitrogen Dioxide in Nitrogen, Oxygen, and up to 75 p.p.m. of Nitric Oxide by Electron-Capture Detection in Gas Chromatography", California Institute of Technology, Pasadena, California (1965).

3. Sakaida, R. R., Ph.D. Thesis, "II. A Chromatographic Apparatus and Technique for the Analysis of Nitric Oxide in Nitrogen", California Institute of Technology, Pasadena, California (1960).

Nomenclature

$C_{i,g}$ Concentration of component i in the gas phase, g.mole/ℓ.

$C_{i,\ell}$ Concentration of component i dissolved in the liquid phase at equilibrium when the concentration of component i in the gas phase is $C_{i,g}$, g.moles/ℓ.

K Partition coefficient.

PROPOSITION V

This proposition describes a technique for determining whether diffusion through a catalyst pore is controlled by wall or molecular collisions. An approximate method is given for the calculation of the effective diffusion coefficient in a catalyst pore when both wall and molecular collisions control the transport process.

In determining the effective activity of the surface inside the pore of a catalyst, Thiele[3] has used an effective diffusion coefficient. When the pore diameter is much smaller than the mean free path in the gas phase, the collisions of the molecules with the walls of the cylinder control the rate of diffusion through the pore. When the pore diameter is much larger than the mean free path, the diffusion will be controlled by molecular collisions. A diffusion coefficient for transport through a pore, when the rate is controlled by wall collisions, has been derived by Knudsen[2]. The Fick Diffusion Coefficient can be used when the transport is due to molecular motion involving only intermolecular collisions. If the transport process involves both wall and intermolecular collisions, the question arises as to what must one use for the effective diffusion coefficient. If it were possible to determine the fraction of collisions which involve the pore wall, this question could be answered more easily.

The calculation of the fraction of collisions, P_w, which involve the pore wall can be carried out in the following manner. Figure 1-P5 shows the path of a molecule leaving the point $(r_1,\theta_1,0)$ and colliding with the wall at (R,θ_2,Z_2). It can be seen that P_w is unity if γ is between 0 and $\cos^{-1}\frac{j}{\ell}$. Therefore, the probability of a wall collision for a molecule with a path length ℓ and which has passed through $(r_1,\theta_1,0)$ is

$$P_{w_{r_1,\theta_1,\theta_2,\ell}} = \frac{\cos^{-1}(\frac{j}{\ell})}{\pi/2} \tag{1}$$

From the geometry of Figure 1-P5, it can be seen that

$$j^2 = r_1^2 + R^2 - 2r_1 R \cos(\theta_2 - \theta_1) \tag{2}$$

Since $P_{w_{r_1,\theta_1,\theta_2,\ell}}$ is for one molecule, the probability of a wall collision must be summed over all possible molecular paths, i.e.,

$$P_w = \int_{r_1}\int_{\theta_1}\int_{\theta_2}\int_{\ell} P_w(r_1,\theta_1,\theta_2,\ell)\, g(r_1,\theta_1,\theta_2,\ell)\, dr_1 d\theta_1 d\theta_2 d\ell \tag{3a}$$

$$P_w = 0 \text{ if } j \geq \ell \tag{3b}$$

If the following assumptions are made,

1. Independent distribution functions for $r_1,\theta_1,\theta_2,\ell$.
2. Rectangular distribution functions for r_1,θ_1,θ_2.

3. Maxwellian distribution for ℓ.

Equations 4, 5, and 6 result.

$$g(\theta) = \frac{1}{2\pi} \tag{4}$$

$$g(r_1) = \frac{1}{R} \tag{5}$$

$$g(\ell) = \frac{1}{\lambda} e^{-\ell/\lambda} \tag{6}$$

Since the distributions are independent, P_w is not a function of θ_1; therefore a new variable, $\theta = \theta_2 - \theta_1$ can be defined. Insertion of Equations 1, 2, 4, 5, and 6 into 3 yields

$$P_w = \frac{1}{\pi^2 R\lambda} \int_0^{\infty} e^{-\ell/\lambda} d\ell \int_0^{2\pi} d\theta \int_0^{R} dr_1 \cos^{-1}\left(\frac{j}{\ell}\right) \tag{8a}$$

$$P_w = 0 \text{ for } j \geq \ell \tag{8b}$$

If the following dimensionless variables are defined as

$$n = \frac{r_1}{R} \tag{9}$$

$$\mu = \ell/\lambda \tag{10}$$

the final equation for P_w results

$$P_w = \frac{1}{\pi^2} \int_0^{\infty} e^{-\mu} d\mu \int_0^{1} dn \int_0^{2\pi} d\theta \cos^{-1}\left(\frac{\sqrt{n^2+1-2n\cos\theta}}{\mu\lambda/R}\right) \tag{11a}$$

$$P_w = 0 \text{ for } j \geq \ell \tag{11b}$$

Equation 11 was solved by numerical techniques on an IBM 7094 computer. The results are presented in Figure 2-P5. It is interesting to note that for 95% of the collisions to involve the wall, the ratio of the mean free path to the pore radius must be at least 50. On the other extreme if the mean free path is $\frac{1}{3}$ the pore radius, less than 5% of the collisions are involved with the wall. This means that at atmospheric pressure the pore radius must be 20 A^{o} or less for Knudsen diffusion to predominate, or must be greater than 3000 A^{o} for the transport process to be controlled by ordinary gas phase diffusion. As the pressure of the system changes, these results will vary in relation to the change in λ.

The results presented above define the limiting conditions for the two transport processes. Although some material[1] has appeared in the literature for the determination of the effective diffusion coefficient when the transport process is controlled by both wall and intermolecular collisions, the calculation is far from finalized or rigorous. If the two transport processes are considered to be linear functions of one another, an approximate effective diffusion coefficient can be calculated from Equation 12.

$$D_{eff} = P_w D_{K,i} + (1 - P_w) D_{B,i} \qquad (12)$$

In conclusion, the results presented in this proposition define the limiting conditions for the two transport processes, i.e., Knudsen flow or molecular diffusion. A method has been proposed for the evaluation of an effective diffusion coefficient in a catalyst pore when transport is controlled by both Knudsen and molecular diffusion. These results are especially useful for determining the effective activity of the surface inside a catalyst pore by the Thiele Method[4] or in designing experiments for the study of diffusion in this transition region.

References

1. Evans, R.B., et. al., J. Chem. Phys. 35, 2076, (1961).

2. Kennard, E.H., "Kinetic Theory of Gases", McGraw-Hill Book Co., New York, N.Y., (1938).

3. Knudsen, M., "Kinetic Theory of Gases", John Wiley & Sons, Inc., New York, N.Y., (1950).

4. Thiele, Ind. Eng. Chem., 31, 916, (1939).

5. Wheeler, A., "Advances in Catalysis", Volume III, Academic Press, Inc., New York, N.Y., (1950).

Nomenclature

λ	Mean free path in the gas, cm.
D_{eff}	Effective diffusion coefficient, $cm^2/sec.$
$D_{B,i}$	Fick (Molecular) diffusion coefficient, $cm^2/sec.$
$D_{K,i}$	Knudsen diffusion coefficient, $cm^2/sec.$
$f(g)$	Function of g.
ℓ	Distance a molecule must travel in the gas phase before colliding with another molecule, cm.
$\dot{m}_{B,i}$	Flux of component i in Z direction due to Fick Diffusion,* $g/cm^2sec.$
P_w	Fraction of collisions which involve the pore wall.
P	System pressure, atmospheres.
R	Radius of pore, cm.
r,θ,Z	Cylindrical coordinates.

Subscripts

1	Point where path of molecule intersects cross section at Z = 0.
2	Point where path length, ℓ, of molecule touches the pore wall.
r_1,θ_1,ℓ	At constant r_1,θ_1, and ℓ.

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* Fick Diffusion

$$\dot{m}_{B,i} = -D_{B,i}\frac{\partial \sigma_i}{\partial Z}$$

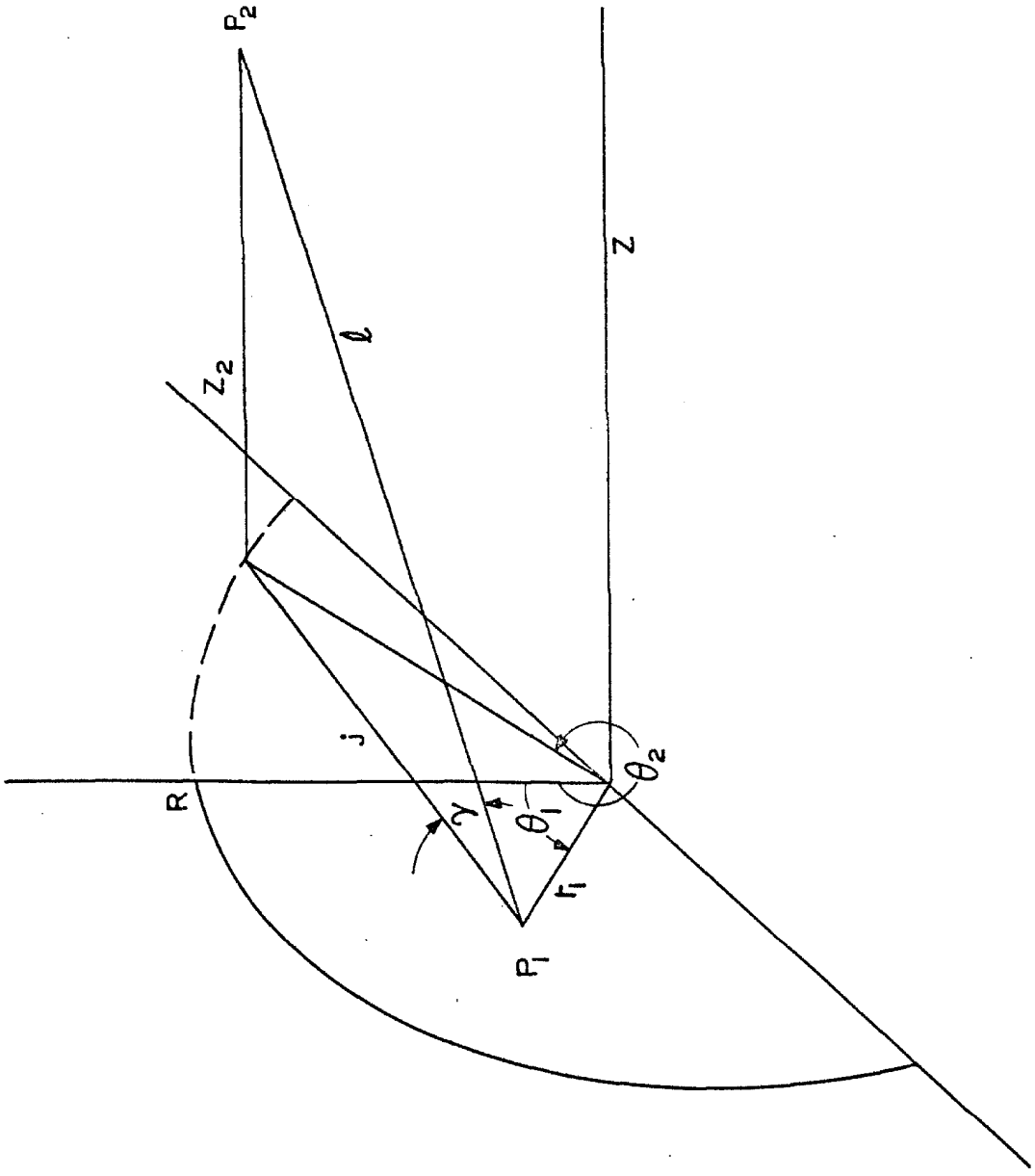

Figure 1-P5. Pictorial definitions required for calculation of P_w.

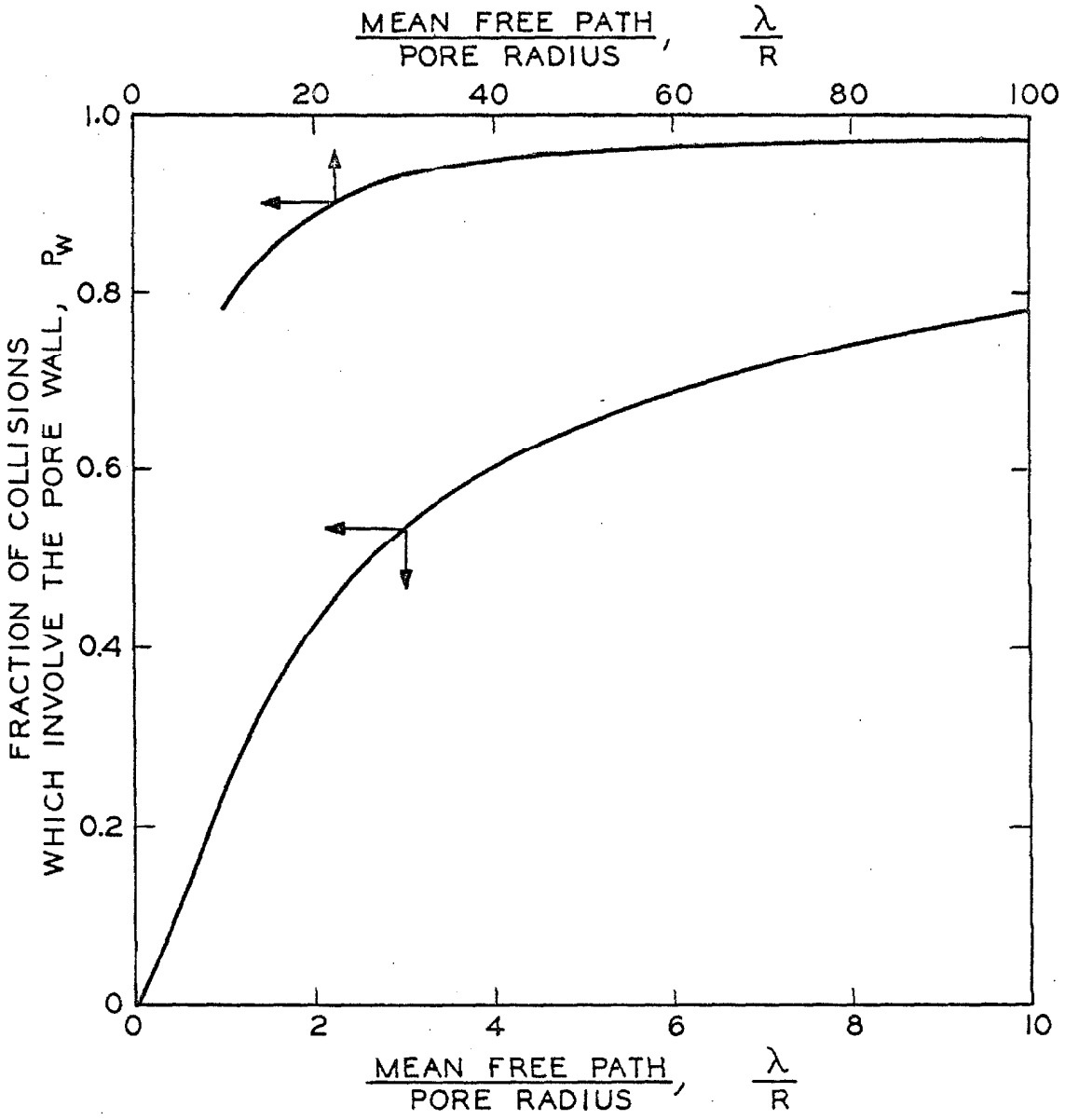

Figure 2-P5. Fraction of collisions which involve the pore wall as a function of λ/R.