Engineering Experiment Station

University of Illinois

August 31, 1955

Technical Report No. 14

PRINCIPLES AND PROCESSES FOR REMOVING

NITROGEN OXIDES FROM GASES

by

M. S. Peters

Contract No. AT(11-1)-276

U. S. Atomic Energy Commission

H. F. Johnstone, Technical Director

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FOREWORD

The work presented here is a part of a program of fundamental research on aerosols related to practical problems in atmospheric pollution and gas-purification operations. The program on the removal of nitrogen oxides from gases was started in June, 1952 as part of Contract Number AT(30-3)-28 with the U. S. Atomic Energy Commission, and was continued on Contract Number AT(11-1)-276 in September, 1953. The original purpose of the work was to develop improved methods for removing nitrogen oxides from gaseous mixtures and to obtain a fundamental understanding of the principles governing the removal operations. This object has been attained during the three years of active research since the start of the program. Progress made during this period has been presented in the regular monthly reports and in Annual Progress Reports and Program Outlines ILU-ES-43, May 31, 1952; ILU-ES-56, April 30, 1953; ILU-ES-70, April 30, 1954; and ILU-ES-82, March 10, 1955. A summary of the research results for the period from June 1, 1952 to August 15, 1953, was presented in Technical Report Number 10 (COO-1011). The following articles have been published or submitted to technical journals for publication: "Controlling Mechanism in the Aqueous Absorption of Nitrogen Oxides" by M. S. Peters, C. P. Ross, and J. E. Klein, A. I. Ch. E. Journal, 1, 105 (1955); "Stop Pollution by Nitrogen Oxides" by M. S. Peters, Chem. Eng., 62, (5), 197 (1955); "Vapor and Liquid Phase Reactions Between Nitrogen Dioxide and Water" by M. S. Peters and J. L. Holman, accepted for publication in Ind. Eng. Chem. (1955).

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The report is divided into sections giving the results of individual phases of the research program. These studies were carried out by Research Assistants under the direction of M. S. Peters and H. F. Johnstone. The work dealing with the multistage bubble-cap column was performed by J. E. Klein. The study on the vapor and liquid phase reactions between nitrogen oxides and water was conducted by J. L. Holman. The work on the absorption of nitrogen oxides in caustic solutions was performed by L. Goldstein. The Venturi atomizer studies and part of the fritted-bubbler work was conducted by L. B. Andersen.

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PRINCIPLES AND PROCESSES FOR REMOVING
NITROGEN OXIDES FROM GASES

by

M. S. Peters

Engineering Experiment Station
University of Illinois
Urbana, Illinois

August 31, 1955

ABSTRACT

A study of the fundamental principles involved in the removal of nitrogen oxides from gases was made, and experimental tests were conducted to develop improved methods for accomplishing the removal operation.

The important factor in determining the rate of removal of nitrogen dioxide and dinitrogen tetroxide from gases was found to be the rate of the chemical reactions involved in the removal process. The roles of gas-phase and liquid-phase reactions, as well as mist formation, were investigated, and the results were interpreted on the basis of chemical reaction rates as the controlling mechanism.

The information from the fundamental studies was applied to a study of improved methods for removing nitrogen oxides from gases. Experimental tests were conducted with bubble-cap towers, packed towers, fritted bubblers, Venturi atomizers, wetted-wall towers, and spray towers. Water, silica gel, and aqueous solutions of sodium hydroxide, sodium chloride, and nitric acid were examined as the removal media. Venturi atomizers were found to be very inefficient for removing nitrogen oxides from gases, while fritted bubblers and silica-gel adsorbers were the most efficient of the various types of equipment tested.

Information was obtained on approach, design data, and operating conditions which can be used for developing new and improved methods for removing nitrogen oxides from gases.

COO-1015

PRINCIPLES AND PROCESSES FOR REMOVING
NITROGEN OXIDES FROM GASES

by 1

M. S. Peters

Engineering Experiment Station
University of Illinois
Urbana, Illinois

August 31, 1955

INTRODUCTION

Many industrial processes evolve gases containing nitrogen oxides, and it is often necessary to effect removal or recovery of these oxides. In some cases, the gases must be cleaned before they can be released to the atmosphere, while, in other cases, efficient recovery of the nitrogen oxides is a direct and essential part of the manufacturing process.

The purpose of the work reported herein was to obtain an understanding of the basic principles governing the removal of nitrogen oxides from gases and to develop improved methods for removing the oxides. Since very little previous work has been done on the fundamental mechanisms and principles involved in the removal of nitrogen oxides from gases, the first investigations in this research program were directed toward a study of the basic factors. The results gave a definite indication of the controlling mechanisms involved in the recovery process and showed the line of approach necessary to develop improved recovery methods. Part of the preliminary work has been described previously by Peters and co-workers (10, 11, 12). A review and extension of this investigation are presented in Parts I and II of this report.

Further work in this research program has dealt with removal of nitrogen oxides from gases using different types of equipment, such as packed towers, bubble-cap towers, spray towers, fritted bubblers, Venturi atomizers, and silica-gel adsorbers. The results of these tests are presented and interpreted in this report.

A. Chemistry of the Aqueous Reactions of Nitrogen Oxides

The important nitrogen oxides in processes involving reactions with aqueous solutions are NO_2 , N_2O_4 , and NO . Small amounts of N_2O_3 and N_2O_5 are also present in the gases, but these compounds rapidly come to equilibrium with NO and NO_2 and represent only a small fraction of the total oxides at room or higher temperatures (11, 12).

The essential chemical reactions occurring in the removal process are

Reaction (D) attains equilibrium rapidly and the equilibrium constant for this reaction is known as a function of temperature between 0°C and 90°C . The oxidation of NO proceeds relatively slowly although the reaction goes essentially to completion.

PART I: CONTROLLING MECHANISM IN THE AQUEOUS

ABSORPTION OF NITROGEN OXIDES

The results of a study on the controlling mechanism in the aqueous absorption of nitrogen oxides have been reported in detail by Peters and co-workers (11, 12). A brief review of this work and an extension of the original data and approach are presented in this section.

The reactions involved in the removal of nitrogen oxides from gases by reaction with water are reversible and proceed at a finite rate. It is possible, therefore, that the rate of aqueous absorption is controlled by the rate of chemical reactions. On this basis, an analysis of the process was developed by the application of chemical kinetics. Simplification and integration of the basic rate equations gave the following results:

$$-\left(\frac{dC_{eNO_2}}{dt}\right)_{\text{net}} = \left(\frac{3 k_1}{2} + \frac{3 k_3}{4 K_C}\right) (C_{N_2O_4})(C_{H_2O}) \quad (1)$$

$$\frac{1}{(P_{f,N_2O_4})^{1/2}} = \frac{1}{(P_{o,N_2O_4})^{1/2}} - 2 \sqrt{K_P} \ln \frac{P_{o,N_2O_4}}{P_{f,N_2O_4}} + Bt \quad (2)$$

where C = concentration, g moles/cc

k_1 = rate constant for the reaction between N_2O_4 and H_2O

k_3 = rate constant for the reaction between NO_2 and H_2O

P_{f,N_2O_4} = final partial pressure of gaseous N_2O_4 , atm

P_{o,N_2O_4} = original partial pressure of gaseous N_2O_4 , atm

K_C = equilibrium constant for the reaction $2 NO_2 = N_2O_4$, (g moles/cc)⁻¹

K_P = equilibrium constant for the reaction $2 NO_2 = N_2O_4$, atm⁻¹

B = a constant at any temperature

t = contact time, seconds

Equations (1) and (2) apply under the following conditions:

1. Rate of eNO_2 removal is controlled by the rate of the chemical reactions.
2. Chemical reactions occur under irreversible conditions.
3. Constant temperature and constant gas rate prevail.
4. Instantaneous equilibrium exists between NO_2 and N_2O_4 .
5. Contact time is sufficiently short so that there is no appreciable oxidation of NO .

Experimental data were obtained with a bubble-cap plate column under conditions of constant temperature, constant gas rate, irreversible reactions, negligible oxidation of NO while gas was in contact with liquid, and essentially instantaneous equilibrium between NO_2 and N_2O_4 . A dense mist was observed in the gas phase in all the runs.

If the rate of eNO_2 absorption is controlled by the rate of the chemical reactions, the experimental data should be correlated by Eq. (2), and a plot of $(1/p_{F_{N_2O_4}})^{1/2}$ versus $\left[(1/p_{O_{N_2O_4}})^{1/2} - 2\sqrt{K_p} \ln (p_{O_{N_2O_4}}/p_{F_{N_2O_4}}) \right]$ should be a straight line with a slope equal to 1.0. Figure 1 shows the excellent correlation obtained between the experimental results and the predicted results. This plot covers a 150-fold change in N_2O_4 concentration in the entering gases and gives strong support to the theory that the rates of the chemical reactions involving N_2O_4 and NO_2 may control the rate of nitrogen oxides removal. The sensitivity of the correlation was checked by making calculations for conversions other than the reported values. It was found that the correlation was sensitive to changes in the experimental results, especially at high eNO_2 concentrations.

Figure 1. Experimental test for validity of integrated rate equation assuming process controlled by chemical reaction rates (Bubble-cap column. Mist present. p = partial pressure. $K_p = 8$)

A plot similar to Figure 1 was presented in Technical Report Number 10 (Serial No. CO-1011) (11). The Figure now contains twice as many experimental points as before, and the range of N_2O_4 concentration covered has been increased by a factor of six.

A. Plate Efficiency

It is of interest to put the theoretical and experimental results on a basis of plate efficiency. With this approach, the practical significance of the results is immediately apparent. Plate efficiency is defined as the amount of nitrogen oxides removed from the gases divided by the amount of oxides which would have been removed if the plate were theoretically perfect.

1. Chemical reaction rates as the controlling factor in the over-all mechanism. By choosing one experimental point as a basis, Eq. 2 can be used to predict the entire curve of plate efficiency versus eNO_2 content of the entering gases. This has been done, and the theoretical curve is presented in Figure 2 for comparison with the experimental data. As shown in Figure 2, the experimental plate efficiencies decrease with reduction in gaseous eNO_2 concentration. This result would be predicted for the case where the controlling mechanism is the rate of the chemical reactions.

2. Gaseous diffusion as the controlling factor in the over-all mechanism. Chambers and Sherwood (4) assumed the controlling factor was the physical diffusion of NO_2 and N_2O_4 through the gas film. If this is the case, the following expression for the absorption rate should apply (4, 9):

$$-\frac{V_g}{A} \left(\frac{dC_{eNO_2}}{dt} \right) = N_{eNO_2} = \frac{2 D_{N_2O_4}}{x_F} \Delta C_{N_2O_4} + \frac{D_{NO_2}}{x_F} \Delta C_{NO_2} \quad (3)$$

where V_g = volume of the bulk of the gas, cc

A = gas-liquid interfacial area, cm^2

Figure 2. Effect of eNO_2 concentration on plate efficiency (One-plate bubble-cap column at one atmosphere total pressure. Gas slot velocity = 1.18 ft/sec. Mist present)

N_{eNO_2} = moles eNO_2 absorbed per unit time per unit area of gas-liquid interfacial area, g moles/(sec)(cm²)

D = gaseous diffusivity, cm²/sec

ΔC = difference in concentration between main body of gas and gas-liquid interface, g moles/cc

x_F = effective film thickness, cm

Equation (3) can be integrated between the limits of zero time (corresponding to an initial N_2O_4 concentration of $C_{oN_2O_4}$) and the time (t) any portion of the gas is in contact with the liquid (corresponding to a final N_2O_4 concentration of $C_{fN_2O_4}$). Using the ratio $D_{NO_2}/D_{N_2O_4}$ as 1.43 (4) and assuming the concentrations of NO_2 and N_2O_4 to be zero at the gas-liquid interfacial region, the following result is obtained from the integration, with the concentration terms expressed in more-convenient units of partial pressure (9):

$$\sqrt{P_{oN_2O_4}} \left(\frac{0.715}{\sqrt{K_p}} + \sqrt{P_{oN_2O_4}} \right)^{1.86} = F \sqrt{P_{fN_2O_4}} \left(\frac{0.715}{\sqrt{K_p}} + \sqrt{P_{fN_2O_4}} \right)^{1.86} \quad (4)$$

where $\ln F = \frac{A}{V_g} \left(\frac{D_{N_2O_4}}{x_F} \right) 1.43 t$.

Equation (4) should apply under the following conditions:

1. Rate of eNO_2 absorption is controlled by gaseous diffusion.
2. Zero oxide concentration exists at gas-liquid interfacial region.

(This would be essentially true if the reactions occurred irreversibly and gaseous diffusion were controlling)

3. Constant temperature and constant gas rate prevail.
4. Instantaneous equilibrium exists between NO_2 and N_2O_4 .
5. Contact time is sufficiently short so that there is no appreciable oxidation of NO .

Equation (4) can be used to predict a theoretical curve of plate efficiency versus $e\text{NO}_2$ concentration in the entering gases if one experimental point is chosen as a basis. The theoretical curve is presented in Figure 2, where it can be seen that the experimental points do not follow the curve predicted for the conditions existing if gaseous diffusion were controlling. Instead, the experimental points follow the curve predicted for the conditions existing if chemical reaction rates were controlling. In general, if operating conditions can be obtained which tend to eliminate chemical reaction rates as the controlling factor, the upper limit on the plate efficiency would be represented by the diffusion-controlling curve in Figure 2.

PART II. VAPOR AND LIQUID PHASE REACTIONS BETWEEN
NITROGEN DIOXIDE AND WATER

It has generally been assumed in the past that the reactions between nitrogen dioxide and water occur by a mechanism in which gaseous nitrogen dioxide diffuses into the liquid phase where the chemical reactions take place. Chambers and Sherwood (4) have proposed that a gas-phase reaction may occur, and recent investigations (11, 12) indicate the gas-phase reaction may be of considerable importance in the reaction mechanism.

To develop efficient equipment for aqueous absorption of nitrogen dioxide, it is necessary to know if the important reactions occur in the gas phase or in the liquid phase. Therefore, this part of the research program on nitrogen oxides was undertaken to determine in which phase the chemical reactions take place.

A. Theory

The information summarized in Part I indicates that the rate of aqueous absorption of nitrogen dioxide is controlled by the rate of the chemical reactions, rather than by diffusion. By the use of chemical kinetics, therefore, it is possible to predict the manner in which the concentrations of the reactants affect the rate of nitrogen dioxide absorption.

The chemical reactions of importance may be expressed as follows:

The k 's represent the reaction rate constants for the forward and reverse reactions. Reactions (a), (b), and (e) occur simultaneously, while Reactions (c) and (d) are consecutive to reactions (a) and (b). The oxidation of NO to yield NO_2 and N_2O_4 proceeds at a relatively slow rate. This reaction is not included here because experimental tests with the wetted-wall column used in this investigation indicated that the rate of NO oxidation was too slow to have any appreciable effect on the results.

If the absorbing fluid is water or dilute nitric acid, the overall reactions are essentially irreversible and the following relationship, presented in Part I, applies:

$$-\left(\frac{dC_{\text{eNO}_2}}{dt}\right)_{\text{net}} = \left(\frac{3}{2} k_1 + \frac{3}{4} \frac{k_3}{K_G}\right) (C_{\text{N}_2\text{O}_4})(C_{\text{H}_2\text{O}}) \quad (1)$$

At any fixed temperature and liquid composition, the first and last terms on the right-hand side of Eq. (1) are constant, and the absorption rate should be directly proportional to the N_2O_4 concentration. In agreement with Eq. (1), Denbigh and Prince (5), Caudle and Denbigh (3), and Peters, Ross and Andersen (11, 12) found the absorption rate to be directly proportional to the gaseous concentration of N_2O_4 when the absorbing fluid was water or dilute nitric acid and a bubble-cap plate column with mist present or a wetted-wall absorption unit was employed. Caudle and Denbigh have also found that the absorption rate is independent of the bulk liquid

volume or bulk gas volume and is directly proportional to the interfacial area between the gas and the liquid. Therefore, the controlling chemical reactions must take place in the region of contact between the gas and liquid phases. The region in which the major part of the gas-phase reaction occurs may be designated as the gas film while that in which the liquid-phase reaction occurs is designated as the liquid film.

If the reactions occur in the gas film, the water concentration in Eq. (1) is proportional to the water-vapor fugacity and increases with temperature. Therefore, the term involving k_1 , k_3 , and K_G in Eq. (1) can be evaluated as a function of temperature from experimental and physical data giving the variation of absorption rate, N_2O_4 concentration, and water concentration with temperature.

If the rate of equivalent nitrogen dioxide absorption into pure water is determined experimentally, it should be possible to predict the rate of absorption for a different water-vapor fugacity if the other variables, such as temperature and contact time, are held constant. If the major reactions occur in the gas film, the rate predicted with the changed water-vapor fugacity should agree with experimental rates obtained at the new water-vapor fugacity. However, if an appreciable portion of the reaction occurs in the liquid film and a non-ideal solution is used to give the new fugacity, it is very unlikely that the predicted rates will agree with the experimentally observed rates. The reason for the deviation is that the components of the non-ideal liquid solution would probably act as catalysts or inhibitors for the chemical reactions, causing a change in the value of the term involving the reaction rate constants in Eq. (1).

Under conditions in which the partial pressure of equivalent nitrogen dioxide is low, perfect-gas deviations are small, and little error is introduced by assuming the fugacity of the water vapor to be equivalent to the water-vapor pressure. In the experimental work reported here, the maximum partial pressure of equivalent nitrogen oxide is 0.05 atm, and the use of water-vapor partial pressure in place of fugacity is acceptable.

A second experimental test for the occurrence of a gas-phase reaction can be made by including in the liquid phase a material which would react with the nitrous acid formed in Reactions (a) and (b) or with any equivalent nitrogen dioxide that entered the liquid. Under these conditions, no NO would be evolved if all the chemical reactions occur only in the liquid phase, and an analysis of the gases leaving the unit should show an absence of NO.

Sodium hydroxide reacts with equivalent nitrogen dioxide and nitrous acid as follows:

The combined effect of these two reactions should be sufficient to keep any NO from being formed (4). Therefore, if an aqueous solution of sodium hydroxide is used to absorb gaseous nitrogen dioxide, the presence of NO in the exit gases would indicate the occurrence of a gas-phase reaction. Caudle and Denbigh (3) and Chambers and Sherwood (4) have made tests of this type using wetted-wall columns, and their results are directly contradictory. Caudle and Denbigh reported no NO in the exit gases while Chambers and Sherwood found an appreciable amount of this compound in their exit gases.

B. Experimental Equipment

A diagram of the experimental equipment is shown in Figure 3. A wetted-wall Pyrex column having a length of 100 cm and an inside diameter of 2.15 cm was used for the absorption operation. A Pyrex tube 5.0 cm in diameter was placed concentrically around the column and was wrapped with a heating ribbon to permit regulation of the column temperature. A third Pyrex tube 6.0 cm in diameter was placed concentrically around the tubes to insulate the system.

The feed liquid passed from a constant-head tank through a 1/4-inch stainless-steel needle valve and a rotameter to a 500-ml feed bulb at the upper portion of the column. A liquid seal was formed in the bulb by sealing a section of Pyrex tubing to the bulb so that it overlapped and was concentric with the column. A sample tap was located between the feed tank and the rotameter to permit analysis of the feed liquid. A heating element was placed between the rotameter and feed bulb to permit regulation of the feed-liquid temperature. Although the rotameter was calibrated with water, it was used only to give reasonably accurate flow settings, and the exact flow rate was determined by timed volumetric measurements.

Gaseous nitrogen dioxide, obtained from Matheson Company, Inc. of 98 per cent purity, was mixed with filtered and dried air or nitrogen as a diluent. The mixture was sampled and admitted to the bottom of the column through a Pyrex tube of 1.58 cm outside diameter sealed into a 400-ml liquid-exit bulb. The exit bulb was insulated with 85 per cent magnesia to ensure accurate temperature measurement of the exit liquid. A liquid seal was formed by the overlapping of the entering-gas tube with the column. The height of the

Figure 3. Experimental equipment for study on vapor and liquid phase reactions between nitrogen dioxide and water

seal was controlled by a 1/4-inch stainless-steel globe valve which was used to regulate the exit-liquid flow rate. The exit gases passed through an entrainment bulb, past a sample tap, and were exhausted through a hood. The air or nitrogen flow rate was measured by a calibrated Venturi meter, and the approximate flow rate of the nitrogen dioxide was set with the aid of a second, calibrated Venturi meter. The exact amount of nitrogen dioxide entering the unit was determined from the diluent flow rate and an analysis of the entering gas mixture.

Temperatures at the following points were measured by iron-constantan thermocouples: (1) gas leaving the column, (2) liquid entering the column, (3) liquid leaving the column, (4) gas entering the column, (5) gas mixing bulb, and (6) liquid leaving the rotameter.

C. Procedure

All runs were made at a liquid flow rate of approximately 210 cc per minute. The absorbing media used were distilled water, 20 weight per cent aqueous sodium hydroxide solution, and 24 weight per cent aqueous sodium chloride solution. The same flow rate of equivalent nitrogen dioxide ($e\text{NO}_2 = \text{NO}_2 + 2 \text{N}_2\text{O}_4$) was used in all runs. The diluent flow rate was 0.0775 pounds per minute with the entering gas mixture containing 4.8 mole per cent $e\text{NO}_2$. All runs were made at atmospheric pressure and at temperatures ranging from 83°F to 132°F. Since liquid and gas flow rates were maintained constant for all the experimental tests, hydrodynamic effects, such as variation in velocity distribution or liquid-surface rippling, were assumed to be essentially constant for all runs. For normal operation in a wetted-wall column, these effects would be relatively unimportant, and the comparison technique used in

this work would make them even less important.

Nitrogen was used as the diluent in seven of the twenty-two runs in which distilled water was used as the absorbing fluid and in all the runs where sodium hydroxide solution was the absorbing fluid. Air was used as the diluent in the remaining distilled-water runs and in all the runs where sodium chloride solution was the absorbing fluid. If the oxygen in the air diluent had oxidized an appreciable fraction of the NO to NO₂, the fraction of total oxides absorbed with air as the diluent would be greater than when nitrogen was the diluent. However, in the distilled-water runs, no significant difference in results was found between the two diluents, indicating that the gaseous hold-up time in the column was not sufficient to permit any appreciable oxidation of NO.

In the actual operation of the equipment, the diluent flow rate and liquid flow rate were set initially; the column was completely wetted, and the liquid seal in the exit bulb was adjusted by means of the exit-liquid control valve. Blank samples of the entering diluent and leaving liquid were taken. The nitrogen dioxide was then admitted at the desired flow rate, and the temperatures of the entering liquid, leaving liquid, and entering gas mixture were adjusted to the desired value by means of heating elements. These three temperatures were held within a 5°F range for every run. After the desired temperature was reached and equilibrium was attained, the liquid flow rate was determined by measuring the time necessary to collect a known volume of the liquid. All temperatures were recorded and gas samples and product-liquid samples were taken.

The entering-gas samples were taken in evacuated 200-ml glass

bulbs containing hydrogen peroxide. The bulbs were fitted with self-sealing rubber stoppers, and hypodermic needles were used both to evacuate the bulbs and to admit the gas samples. The amount of nitric acid formed by the action of hydrogen peroxide on nitrogen dioxide was determined by titrating the contents of the sample bulb with standard sodium hydroxide. From the weight of the gas sample and the amount of nitric acid formed, it was possible to determine the eNO_2 content of the entering gas.

Samples of the exit gas were taken for all the runs in which sodium hydroxide solution was used as the absorbent and in several check runs when distilled water was the absorbent. Since the exit gases contained NO in addition to NO_2 and N_2O_4 , it was necessary to take two samples of the exit gas to obtain a complete analysis. One sample was taken in a bulb containing hydrogen peroxide, while another sample was taken in a bulb containing potassium permanganate. The amount of potassium permanganate consumed in the reactions with NO and eNO_2 was determined by back titrating with sodium thiosulfate. The results of the two analyses were used to calculate the amounts of NO and eNO_2 in the exit gas.

The exit liquid, with the exception of the runs with sodium hydroxide solution, was analyzed for acid content by titrating a known volume of the liquid with standard sodium hydroxide. The removal efficiency, which is defined as the per cent of the entering oxides removed from the gases, was determined for each run. For the runs with distilled water and sodium chloride solution as the absorbing media, the removal efficiency was determined from the analysis of the entering gas, analysis of the exit liquid, and flow rates of the entering gas and exit liquid. In the runs with aqueous sodium hydroxide

as the absorbent, an accurate analysis of the exit liquid could not be obtained, and the removal efficiency was calculated from the analyses of the entering and leaving gas streams. To check the accuracy of this method for determining removal efficiency, several runs were made with distilled water as the absorbent, and the removal efficiency was calculated on the basis of the exit-liquid analysis and also on the basis of the exit-gas analysis. Good agreement ($\pm 2\%$) was found between the two methods if the unit was operated under conditions in which no mist was formed. It was found that mist formed only if unfiltered air containing oil nuclei was used. Therefore, all tests were carried out using filtered and dried diluent, and no mist was observed in any of the reported runs.

D. Discussion of Results

The important experimental results are presented in Figure 4. The removal efficiency, plotted as the ordinate, is the per cent of the entering eNO_2 removed from the entering gas. The arithmetic mean of the temperatures of the entering liquid, exit liquid, entering gas, and exit gas is plotted as the abscissa.

It can be seen that the removal efficiency decreased significantly over the temperature range investigated ($83\text{--}132^\circ\text{F}$). When distilled water or 24 per cent sodium chloride solution was used as the absorbing liquid, the efficiency at 130°F was approximately 45-50 per cent of that obtained at 85°F , while the rate of decrease was even more rapid when 20 per cent sodium hydroxide solution was the absorbent.

As indicated in the theoretical discussion, the term involving the reaction rate constants in Eq. (1) should be constant at constant

Figure 4. Effect of temperature on removal efficiency with wetted-wall column

temperature if the reactions occur completely in the gas phase. Therefore, the rate of removal and the removal efficiency should be proportional to the water-vapor fugacity at any constant values of temperature, gas rate, and gaseous eNO_2 concentration. If the removal efficiency is known at one temperature and one water-vapor fugacity, it is possible to predict the removal efficiency at a different water-vapor fugacity with all other variables held constant, assuming the reactions occur completely in the gas phase or gas film.

By integrating Eq. (1), the removal efficiencies for 24 per cent sodium chloride absorbent and 20 per cent sodium hydroxide absorbent were predicted at various temperatures on the basis of the experimental results obtained with distilled water as the absorbent. Standard vapor-pressure data for aqueous solutions of sodium chloride and sodium hydroxide were used. In carrying out these calculations, it was necessary to use the equilibrium constant for the dimerization of NO_2 to N_2O_4 (14), and it was found that the ratio of the efficiencies at any given temperature was practically the same as the ratio of the water-vapor pressures.

The predicted efficiency curves are shown in Figure 4, and it can be seen that there are wide deviations between the experimental curves and the theoretical curves. Assuming the rate proportionalities as expressed by Eq. (1) are correct, the deviations between the predicted and experimental curves can only be explained by a change in the rate constants involved. This could be expected to occur if at least part of the reactions occurred in the liquid phase where the reactive ions could serve to catalyze or inhibit the reactions.

In the runs with 20 per cent sodium hydroxide solution as the absorbent, the exit gas was analyzed, and NO was found in every case. The presence of NO in the exit gas indicates the occurrence of a gas-phase reaction, since this compound would not have been formed if the reactions occurred completely in the liquid phase.

Because relatively small amounts of NO were present in the exit gas, it was very difficult to determine the exact amount of NO with high accuracy. On the basis of total material balances, it was possible to calculate the amount of NO which would have been formed if no sodium nitrite was formed in the liquid. For the various runs with sodium hydroxide, it was found that the exit gases contained from 16 to over 100 per cent of the total NO which theoretically could have been formed. These analyses were obviously not precise because of the difficulty of analyzing the small amount of NO present, but they do indicate definitely the presence of NO and give a qualitative indication of the amount of the reaction which occurred in the gas phase.

In all runs, it was found that the temperature of the gas increased as it passed through the tower. The temperatures of the inlet gas, inlet liquid, and exit liquid were all maintained essentially constant at the same temperature throughout each run. However, the exit-gas temperature was always greater than the inlet-gas temperature with the temperature rise varying from 1°F to 11°F for the different runs. The temperature increase was greater in the low-temperature runs than in the high-temperature runs. This increase in gas temperature was probably caused by the occurrence of the exothermic gas-phase reaction between nitrogen dioxide and water.

E. Summary of Study on Vapor and Liquid Phase Reactions

The results of this study indicate that both gas-phase and liquid-phase reactions occur in the removal of nitrogen dioxide from gases by contact with aqueous solutions. The major part of these reactions does not occur in the bulk phases but takes place in the gas film or liquid film at the boundaries between the two phases.

The presence of NO in the exit gases when sodium hydroxide solution is used as the absorbent indicates the existence of a gas-phase reaction, and the observed increase in gas temperature in the absorption column is consistent with a gas-phase reaction. On the basis of chemical kinetics, an equation for the rate of nitrogen dioxide absorption can be developed which has been shown to be applicable when the reactions occur under irreversible conditions. According to this equation, if all variables except the water-vapor fugacity are held constant, the rate of removal of gaseous nitrogen oxides should be directly proportional to the water-vapor fugacity as long as the reactions occur completely in the gas phase. However, if a liquid phase reaction occurs, the proportionality between the oxide removal rate and the water-vapor fugacity would not be expected to apply because the material in the liquid phase causing the change in the water-vapor fugacity would probably inhibit or catalyze the rate of the liquid-phase reactions. The occurrence of a liquid-phase reaction is indicated by the fact that the rate of removal of nitrogen oxides from a dilute gaseous mixture is not directly proportional to the partial pressure (or fugacity) of the water vapor at constant conditions of temperature, gas rate, and gas composition.

PART III. DISPERSION BY VENTURI ATOMIZER AND FRITTED BUBBLER FOR NITROGEN OXIDES ABSORPTION

The results presented in Parts I and II of this report show that two factors are of major importance in the development of improved methods for removing nitrogen oxides from gases: (1) It is desirable to supply the maximum amount of gas-liquid contact area; and (2) Since the rates of the chemical reactions may control the rate of nitrogen oxides removal, a reasonably long time of contact between gas and liquid should be maintained.

A Venturi atomizer can be used to obtain fine dispersion of a liquid in a gas, thereby supplying a large amount of gas-liquid contact area. The same result can be obtained by use of a fritted bubbler giving dispersal of a gas in a liquid. Although the effective gas-liquid contact time in a Venturi atomizer is relatively short, the beneficial effects of the large contact area might be able to overcome the detrimental effects of the short contact time. This study was carried out to determine the characteristics of Venturi atomizers and fritted bubblers for removing nitrogen oxides from gases.

A. Experimental Equipment

1. Venturi atomizer. A Lucite Venturi with a throat diameter of $1/4$ in. and a throat length of $1/2$ in. was used. The gas velocity was 300 ft/sec in the Venturi throat. Gas flow rates were measured upstream from the liquid-injection Venturi by a standard Venturi meter. Nitrogen dioxide was injected sufficiently far upstream to ensure a uniform composition at the gas analysis point. Liquid was injected axially with a single stainless-steel hypodermic needle which had an inside diameter of 0.051 in. Samples of the

spray were collected with an impact tube at 0.25, 0.50, and 1.00 in. from the point of liquid injection.

2. Fritted bubbler. The fritted-glass disperser was a relatively simple apparatus. The contacting element was a standard coarse-porosity Pyrex fritted-glass cylinder. The dimensions of the cylinder were 4 mm I.D., 12 mm O.D., and 19 mm high. The base of the cylinder was sealed and gas passed only through the sides. The cylinder was located at the bottom of a liquid-filled column 43 in. high and 2-3/8 in. in diameter. The gas passed through the interstices in the fritted glass and bubbled up through two liters of liquid. The gas then passed to a column filled with standard sodium hydroxide and hydrogen peroxide for removal of any nitrogen dioxide not absorbed in the first column.

B. Analytical Procedure

The gas phase in the Venturi atomizer was analyzed for nitrogen dioxide by passing a sample through a standard solution of sodium hydroxide containing hydrogen peroxide and measuring the remaining gas in the sample with a wet-test meter. All the nitrogen dioxide was absorbed in the sodium hydroxide, and the excess hydroxide was determined by titration with standard hydrochloric acid. Total acid concentration in the liquid phase was determined by titration with standard sodium hydroxide. Nitrous acid content in the liquid phase was found by addition of an excess of potassium permanganate followed by back titration with standard sodium thiosulfate. Similar procedures were used with the fritted bubbler.

C. Discussion of Results

1. Venturi atomizer. Previous investigations with Venturi atomizers (1, 2, 11) have shown high initial mass-transfer coefficients for oxygen absorption by pure water. These high mass-transfer coefficients can be attributed to the large initial interfacial area, high relative gas-liquid velocity, and great liquid turbulence. The mass-transfer coefficients decrease rapidly with increase in distance from the point of liquid injection. The decrease in mass-transfer coefficients is caused by reduction in interfacial area as the dispersed films and filaments shatter into spherical droplets, by decrease in the relative velocity as the droplets are accelerated to the gas velocity, and by the reduction in liquid turbulence as the droplets pass downstream.

The characteristics of the dispersed liquid in a Venturi atomizer should permit rapid rates of nitrogen dioxide absorption in the atomization zone. Under these conditions, the major chemical reactions could occur in the liquid phase, and the high rate of oxygen absorption could permit rapid oxidation of NO in the liquid phase. Experimental tests indicate that some of the absorbed oxygen does enter into the oxidation reaction, but the oxidation reaction does not control the rate of absorption of nitrogen dioxide.

The removal efficiency for nitrogen dioxide was determined experimentally based on the composition of the effluent from the cyclone following the atomizer. The removal efficiency was low, as shown in Figure 5. The efficiencies decreased from approximately 2.3 per cent for 10 per cent eNO_2 in the gas phase to less than 1 per cent for 1 per cent eNO_2 . This reduction in efficiency would be expected on the assumption that the rate of the chemical reactions controls the rate of absorption. The use of an oxidation catalyst

Figure 5. Effect of gas composition and liquid injection rate on recovery efficiency for nitrogen dioxide in Venturi atomizer

(manganous sulfate) in the liquid gave no improvement in recovery efficiency. From these results, it may be concluded that the short time of contact in the atomization zone overbalances the benefits of increased gas-liquid contact area, and the efficient recovery of nitrogen dioxide from gases by use of a Venturi atomizer does not appear to be feasible.

2. Fritted bubbler. The fine dispersion of the gas phase in a fritted bubbler gives a large gas-liquid contact area, and the time of contact at this large interfacial area is substantially greater than in a Venturi atomizer. Therefore, high rates of removal of nitrogen oxides from gases should be obtained with a fritted bubbler. Experimental tests with this type of equipment were carried out to determine the effects of liquid head, gas rate, and gaseous nitrogen dioxide concentration.

In the absorption of nitrogen dioxide from a gas containing 2.7 mole per cent eNO_2 , an eightfold decrease in liquid volume caused only a 10 per cent reduction in the amount of nitrogen dioxide absorbed. Thus, most of the nitrogen dioxide absorption occurred during the bubble formation in or near the fritted-glass surface.

A fourfold increase in the air rate from 0.05 to 0.2 cu ft/min reduced the recovery efficiency by only 2 per cent. The substitution of pure oxygen for air increased the recovery of nitrogen dioxide by about 6 per cent while substitution of nitrogen for air caused a decrease of about 18 per cent in the rate of absorption of nitrogen dioxide. Thus, oxidation has some influence on the absorption in a fritted-glass disperser, but the oxidation is not the controlling factor.

The recovery efficiencies for nitrogen dioxide in the fritted-glass disperser are shown in Figure 6. These efficiencies are substantially higher

Figure 6. Effect of gas concentration on recovery efficiency for nitrogen dioxide in fritted-glass disperser

than those reported for a bubble-cap column in Part I. The efficiency decreases from 90 per cent at a gas composition of 10 mole per cent eNO_2 in air to 80 per cent at a gas composition of 1 mole per cent eNO_2 in air. This decrease in removal efficiency with reduction in gas concentration agrees with the theory presented in Part I. Tests made with an aqueous sodium hydroxide solution in place of water or nitric acid as the absorbing medium showed increased removal efficiencies.

About 20 per cent of the total acid formed with the fritted-glass disperser was in the form of nitrous acid, while the per cent of total acid as nitrous acid in the liquid product from a bubble-cap column was much less than 20 per cent. The greater percentage of total acid as nitrous acid and the improved removal efficiency with the fritted bubbler as compared with a bubble-cap absorber is due to the combination of increased gas-liquid contact area and contact time obtained with the fritted-glass disperser. These conditions would indicate that a considerable fraction of the total chemical reactions occurs in the liquid film when a fritted-glass disperser is used (2).

The high removal efficiencies obtained in this work with the fritted bubbler show that this type of equipment may be useful for removing nitrogen oxides from gases.

PART IV. REMOVAL OF NITROGEN OXIDES FROM DILUTE GASES

In the removal of nitrogen oxides from gases, it is usually desirable to reduce the oxide content to the lowest possible level. The maximum allowable concentration of nitrogen oxides in stack gases is in the range of 0.05 to 0.2 per cent by volume or 800 to 3200 parts per million. In some processes, essentially all nitrogen oxides must be removed from gaseous products before the gases can be given further recovery treatment.

Nitrogen oxides released to the atmosphere can be a factor in air pollution. Atmospheric concentrations of nitrogen oxides as high as 0.4 parts per million have been reported in the Los Angeles region; however, these oxides are seldom present in sufficient extent to cause noticeable physiological effects. Since nitrogen dioxide can react with the water vapor in air or with rain drops to produce nitric acid, small concentrations in the atmosphere can cause undue corrosion on metal surfaces in the immediate vicinity of the releasing stacks. Plant life may also be damaged if the concentrations become excessive. The oxides of nitrogen can affect atmospheric pollution in an indirect manner by acting as catalysts for certain reactions, such as the oxidation of sulfur dioxide.

This work was undertaken to determine the best methods for removing nitrogen oxides from dilute gases. The investigation has been confined to the removal of NO , NO_2 , and N_2O_4 from gases containing less than 2 volume per cent oxides.

A. Removal Processes

There are two general processes which can be used for removing nitrogen oxides from gases: (1) by absorption combined with chemical reaction, and (2) by adsorption.

1. Absorption combined with chemical reaction. As indicated in Part I, when nitrogen dioxide is removed from a gas by contact with water, the rate of removal is controlled by the rate of the chemical reactions. The removal efficiency, therefore, tends to decrease with reduction in gaseous concentration of nitrogen oxides. At the low concentrations of interest in this work, poor removal efficiencies can be expected unless very effective methods are used for contacting the gas and liquid. Another possible approach for increasing the removal efficiency would be to use a catalyst or other means to speed up the chemical reactions until diffusion becomes controlling; however, no effective catalysts for this purpose have been reported (2).

Experimental data with four types of absorption equipment have been obtained in this work. Tests were conducted using a bubble-cap tower, fritted bubbler, packed tower, and spray tower.

2. Adsorption. The results of Foster and Daniels (1) indicate that adsorption of nitrogen dioxide on silica gel gives good removal efficiencies even at gaseous oxide concentrations as low as 0.1 per cent. Mechanical factors, such as cycle changes and desorption requirements, make the process more complicated than a continuous absorption operation; however, the method is capable of accomplishing essentially complete removal of nitrogen oxides from gases.

B. Experimental Equipment and Procedure

1. Bubble-cap tower. Experimental data were obtained using one bubble-cap plate containing seven bubble caps. One bubble cap was located in the center of the plate and the other six caps were arranged peripherally around the center cap. Eight equally spaced circular slots of 5/16-inch diameter were drilled in the center cap and four slots were drilled in each of the peripheral caps, these slots being directed toward the center to reduce wall effects. The total depth of liquid on the plate was 1 in. and the tops of the slots were 1/2 in. below the liquid surface. The inside diameter of the glass column was 7-1/2 in., and there was a distance of 12 in. between the bubble-cap plate and the top and bottom plates.

2. Packed tower. The packed tower had an inside diameter of 1 in. and was packed to a height of 46 in. with 1/4-in. glass Raschig rings. Liquid was introduced to the top of the column with the flow directed onto the center of the packing. Effective wetting of the packing was obtained and no channeling was observed.

3. Spray tower. The spray tower consisted of one No. T-58 spray nozzle having a nozzle diameter of 1 mm. The nozzle was directed counter-current to a stream of gas rising through a 1-in. inside-diameter tower. The distance from the bottom of the tower to the nozzle was 52 in. A baffled space above the nozzle reduced any liquid carryover to a negligible amount. The nozzle delivered a finely dispersed spray which could be observed throughout the entire length of the column. Liquid product was withdrawn from the base of the tower and analyzed for combined-nitrogen content.

4. Fritted bubbler. Experimental data were obtained using a fritted bubbler consisting of 12 medium-frit glass rods (fritted area =

1.03 sq. in. per rod). These rods were sealed into a Lucite plate contained in a 5-1/2 in. inside-diameter column. The equipment was arranged so that the head of liquid above the frits could be varied from zero head to as much as 15 in. of head.

5. Controls. Water was fed to the units at a constant rate, and the flow rate was measured by a calibrated rotameter and checked by volumetric measurements. Gaseous nitrogen dioxide, obtained from cylinders containing NO_2 and N_2O_4 , was diluted with air and admitted at a steady rate to the lower section of the towers. The gas flow rates were measured by calibrated Venturi meters. Pressures at the top and bottom of the towers were measured by open-tube manometers containing α -bromonaphthalene. The temperatures of the entering liquid, entering gas, and exit liquid were determined by means of iron-constantan thermocouples.

6. Procedure. The towers were operated under steady conditions until equilibrium was attained as indicated by a constant acid concentration in the liquid product. Temperatures, pressures, and flow rates were read, and samples of the inlet gas, inlet liquid, and product liquid were taken. The liquid samples were analyzed by titrating a known volume with standard NaOH solution. The gas samples were taken in evacuated bulbs containing hydrogen peroxide. The amount of gas sample was determined by weighing, and the amount of nitrogen oxides present was determined by titrating the nitric acid formed from the reaction between H_2O_2 and NO_2 and N_2O_4 .

From a knowledge of the flow rates and concentrations, it was possible to calculate the removal efficiency expressed as the per cent of entering oxides removed.

7. Choice of variables. It was necessary to choose the variables, such as gas rate, column height, and liquid rate, of magnitudes which would permit a fair comparison among the removal efficiencies of the various types of equipment. Water was used as the absorbent for all the runs involving absorption with chemical reaction. The removal efficiency was found to be independent of the liquid rate in the bubble-cap tower and the fritted bubbler as long as the concentration of the liquid did not increase above 10 weight per cent nitric acid. The spray tower was operated at a liquid rate which would give a finely dispersed mist, while the packed tower was operated at approximately 90 per cent of the liquid flooding velocity.

The units were all operated at gas rates which would approximate conditions in industrial units. A slot gas velocity of 1.17 ft/sec was used in the bubble-cap tower, while the gas rate used in the fritted bubbler was the rate at which well-dispersed bubbles first appeared. Superficial gas velocities of 1.84 ft/sec were used in both the packed and spray towers.

The efficiencies for the bubble-cap, spray, and fritted-bubbler units are all reported as obtained for a single contact stage. Since one stage of these units requires about one foot of height, the efficiency results for the packed tower are reported on the basis of one foot of packed height.

Air was used as the diluent gas for all the test runs. The gas-liquid contact time in the bubble-cap and fritted-bubbler units was not sufficient for any appreciable oxidation of the NO formed in the chemical reaction. Some of the NO formed was oxidized to NO₂ in the packed and spray towers; however, this difference in the operation is necessary in order to

make a fair comparison among the various types of equipment.

All runs were made at a pressure of one atmosphere and 25°C, and filtered air was used so that no visible mist was formed in any of the runs.

The efficiency results for the silica-gel adsorber are based on the data of Foster and Daniels (7) using a superficial gas velocity of 1.84 ft/sec, packed height of 1.0 ft, gel fraction saturation of 0.90, and cycle time of 30 minutes. Adsorption capacities for gel No. 5 (7) were used, since Foster and Daniels indicate that this gel is one of the most efficient commercial gels for nitrogen dioxide adsorption.

Table 1 gives a summary of the test conditions employed. It is believed that the choice of operating variables as outlined gives a fair basis for comparing the results obtained with the various types of equipment. The values chosen represent as closely as possible those which would be used in corresponding industrial units.

C. Discussion of Results

Figure 7 presents comparative results showing the effect of entering oxide concentration on the removal efficiency for the different types of equipment. A reduction in oxide concentration causes a decrease in removal efficiency for all the types of equipment. Thus, as the gases become more dilute, the removal problem becomes more difficult.

1. Spray tower. The results obtained with the single-nozzle spray tower indicate very poor removal efficiencies at gaseous oxide concentrations less than about 1 per cent. At higher concentrations, the spray-tower efficiencies are comparable to those obtained in the other types of equipment.

Table 1

Test Conditions Used for Determining the Efficiency of Nitrogen Dioxide Removal from Dilute Gases with Different Types of Equipment

Type of Equipment	Gas Rate ft ³ (S.C.) per min	Liquid Rate cc per min	Pressure Drop cm H ₂ O	Remarks
Fritted-Glass Bubbler (one-stage)	0.53	300	59.0	Medium frits. Liquid Head over frits = 3-3/4"
Bubble-Cap Tower (one-stage)	1.06 (slot velocity = 1.17 ft/sec)	300	1.8	Liquid depth = 1"
Packed Tower (1/4" glass Raschig rings)	0.53 (Superficial vapor velocity = 1.84 ft/sec)	150	2.0 per foot of packed height	Packed height = 46". Efficiency as per foot of packed height
Spray Tower (1 No. T58- 1 mm spray nozzle)	0.53 (Superficial vapor velocity = 1.84 ft/sec)	470	1.0	Tower height = 52"
Silica Gel Adsorber (No. 5 com- mercial gel - Ref. 7)	0.53 (Superficial vapor velocity = 1.84 ft/sec)			Packed height = 12". Fraction saturated = 0.90. Time per cycle = 30 min. Effi- ciencies calcu- lated from Ref. (7).

Figure 7. Efficiency of nitrogen dioxide removal from dilute gas with different types of equipment

Absorption units employing multiple spray nozzles are often used in the nitrocellulose industry for removing nitrogen oxides from the fumes leaving the cellulose nitrator. These absorption units consist essentially of a horizontal stainless-steel tube having a diameter of 3 to 6 feet and a length ranging from 30 to 50 feet. Recirculated liquid is sprayed into the tube at various points along the length. A so-called "Piccolo" unit of this type is divided into compartments with a short packed section between each compartment. The liquid flows countercurrent to the gases, and each compartment acts as a separate absorption system, permitting a graduation of acid strength from compartment to compartment. Over-all removal efficiencies as high as 80 per cent are claimed for these types of units with initial gas concentrations of approximately 0.5 per cent by volume nitrogen oxides and superficial gas velocities in the range of 3 ft/sec. Therefore, despite the poor efficiencies obtained with a single spray nozzle, the use of multiple spray nozzles may be feasible for removal of nitrogen oxides from dilute gases.

2. Packed tower. The removal efficiencies with the packed tower are lower than those found with the bubble-cap tower or fritted bubbler. It should be noted, however, that the decrease in efficiency with reduction in oxide content is fairly gradual, and, at nitrogen oxide concentrations less than about 0.2 per cent, the packed tower would be nearly as efficient as the other types of equipment. To permit oxidation of the NO formed in a packed tower, it is best to operate at the lowest practical gas velocity. The superficial gas velocity of 1.84 ft/sec used in the experimental tests is close to the maximum velocity which should be used for nitrogen oxides absorption in packed towers.

3. Bubble-cap tower and fritted bubbler. A fritted bubbler is merely a special type of a bubble-cap unit in which very small and well-dispersed gas bubbles are delivered into the absorbing liquid. A greater head of liquid for the gas bubbles to pass through is ordinarily used in a fritted bubbler. From Figure 7, it can be seen that the fritted bubbler gave much better removal efficiencies than the other types of equipment tested. The pressure drop per stage for the fritted bubbler was approximately 30 times greater than the equivalent pressure drop for the bubble-cap tower. Unless the gases were already under pressure, it would be expensive to add the equipment necessary to force a gas through a number of fritted-bubbler stages.

Since the removal efficiency of the bubble-cap tower approaches that of the fritted bubbler at low gaseous oxide concentrations, the optimum type of absorption equipment should combine the good features of both operations. Figure 8 indicates that the gas rate and liquid head in the fritted bubbler have little effect on the removal efficiency as long as well-dispersed bubbles are formed and the liquid head is greater than about 3 inches.

A bubble-cap unit designed with a number of small gas outlets in the caps should approximate the beneficial effects of the small bubbles and large gas-liquid contact area found in a fritted bubbler. At the same time, this design would reduce the pressure drop per stage to a practical value. The bubble-cap unit should employ a liquid head of at least 3 inches above the caps. This type of design should give efficiencies lying between the values shown in Figure 7 for the fritted bubbler and bubble-cap unit.

The effect of mist formation in a bubble-cap tower was considered in this work. It was possible to cause the formation of mist by using as a diluent air containing dispersed oil nuclei. While it might be expected that the added

Figure 8. Effect of liquid head and gas rate on removal efficiency in fritted-glass disperser

surface area of the mist particles would cause increased removal efficiencies, the experimental data indicated that lower efficiencies were obtained when mist was formed. Consequently, all runs reported here were made under conditions in which no visible mist was formed.

4. Silica-gel adsorber. The results shown in Figure 7 indicate that the silica-gel adsorber gives the best removal efficiency of the units tested at gaseous concentrations less than 0.4 per cent nitrogen oxides. If essentially complete removal of the oxides is necessary, the silica-gel adsorber should be used since the removal efficiency does not fall off rapidly at low gaseous concentrations.

5. Effect of temperature and pressure. The shapes of the efficiency curves for the absorption equipment indicate that the absorption rate is primarily controlled by the rate of the chemical reactions. The reduction in efficiency with decrease in oxide content is caused by lowered fractions of oxides present as N_2O_4 in the more dilute mixtures. An increase in total pressure or a decrease in temperature causes a greater fraction of the oxides to be present as N_2O_4 and would, therefore, tend to improve the removal efficiency (11, 12).

A decrease in temperature or an increase in total pressure also increases the removal efficiency for the silica-gel adsorber. Figure 9 shows the effect of decreasing the temperature from $25^{\circ}C$ to $10^{\circ}C$ and the effect of raising the total pressure from 1 to 2 atmospheres. Figure 9 also indicates the sharp increase in removal efficiency obtained by decreasing the cycle time in the silica-gel adsorber.

Figure 9. Effect of temperature, pressure and cycle time on removal efficiency in silica gel adsorber

D. Summary of Study on Removal of Nitrogen Oxides
from Dilute Gases

Data were obtained on the efficiency of nitrogen oxides removal from dilute gases using bubble-cap, packed, spray, fritted-bubbler, and silica-gel adsorption towers. The efficiencies were determined under conditions which would make possible a fair comparison of the different methods. The tests were limited to dilute gaseous mixtures containing less than 2 volume per cent nitrogen oxides. Water was used as the absorbing medium and air was used as the gaseous diluent.

The results indicate that single-nozzle spray towers are inefficient for removing nitrogen oxides at low gaseous concentrations, although better results would be expected with multiple-spray units. Fritted bubblers give the best removal efficiency among the different types of absorption equipment tested. The high pressure drop with a fritted bubbler causes this type of equipment to be impractical for most industrial operations. Therefore, a special bubble-cap plate design is recommended which would reduce the pressure drop and still include the best features of the fritted bubbler.

Comparison of the various types of equipment indicates that the silica-gel adsorber is superior if it necessary to remove essentially all of the nitrogen oxides from a gas.

PART V. EFFICIENCY OF AQUEOUS ABSORPTION OF NITROGEN
OXIDES WITH MULTISTAGE BUBBLE-CAP COLUMN

The experimental results discussed in Part I were obtained by using a bubble-cap column containing one plate. A subsequent investigation was conducted to determine if the same type of results would be obtained when a multiple-plate bubble-cap column was used in place of the single-plate column. At the same time, a study was made on the effect of mist formation during the aqueous absorption of nitrogen oxides.

The individual plate efficiencies with the multiple-plate column increased significantly for each succeeding contacting stage, and an increase in plate efficiency was observed as the amount of mist formation decreased. These results are presented and interpreted in this section.

A. Experimental Equipment

Experimental data were obtained using a bubble-cap column containing three identical plates, with auxiliary equipment as shown in Figure 10. Each plate was made of 1/2-inch Lucite and was equipped with seven bubble caps and seven gas risers made of polystyrene. Eight equally-spaced circular slots of 5/16-inch diameter were drilled in the center cap, and four slots of the same diameter were drilled in each of the six peripheral caps. The slots in the peripheral caps were directed toward the center to reduce wall effects. The total slot area per plate was 2.46 square inches, which gave a slot velocity, in feet per second, approximately equal to the gas rate in cubic feet per minute. The tops of the slots were 1/2 inch below the liquid surface, and the total depth of liquid on each plate was 1 inch.

Figure 10. Experimental equipment for tests with multistage bubble-cap column

The inside diameter of the glass sidewalls was 7-1/2 inches. The 12-inch high sections set the distance between the bubble-cap plates and the top and bottom stainless-steel plates. Transfer of liquid from one tray to the next lower tray was effected by the use of stainless-steel downcomers which discharged into a well on the delivery plate.

Water was fed to the top tray through a downcomer projecting through the stainless-steel top of the tower. Samples of the liquid leaving the top and middle plates were withdrawn from the well on the next lower plate using the tap provided. The liquid leaving the last tray was sampled, and the flow rate of the discharged liquid was measured.

Gaseous nitrogen dioxide was mixed with air. The mixture was sampled and admitted to the lower section of the tower. The air flow rate was measured by a glass Venturi meter which had been calibrated against a standard rotameter. The nitrogen dioxide flow rate was also measured by a glass Venturi meter. The reading provided by this Venturi meter was helpful in setting the range of gas compositions desired and provided a check on succeeding runs.

The air obtained from the laboratory supply lines passed through a cyclone, a calcium chloride drying tube, a pressure-regulating valve, and a filter before being measured and mixed with the incoming nitrogen dioxide. Provision was made for by-passing both the drier and the filter in order to permit mist formation in the absorption tower.

Pressures at the top and bottom of the column were measured by open-end manometers containing α -bromonaphthalene. The same indicating fluid was used in the Venturi manometers.

Temperatures at the following points were measured by iron-constantan thermocouples: (1) Entering NO_2 gas, (2) gas mixture before heater, (3) gas mixture after heater, (4) gas entering bottom plate, (5) gas entering middle plate, (6) gas entering top plate, (7) exhaust gas, (8) entering water, (9) liquid leaving top plate, (10) liquid leaving middle plate, and (11) liquid leaving bottom plate.

Each plate was fitted with a 3-foot stainless-steel cooling coil made from 1/4-inch tubing. Cooling water was not circulated, however, because preliminary runs indicated that the maximum temperature gradient across the tower was less than two degrees Centigrade.

B. Procedure

All experimental tests were made at a liquid flow rate of 300 cc per minute and a gas slot velocity of 1.2 feet per second. Distilled water was used as the absorbing medium and the gas composition ranged from 0.5 to 8.0 mole per cent eNO_2 . All runs were made at atmospheric pressure and room temperature.

When the tower was to operate without the presence of mist, the supply air was passed through the drier and filter before entering the absorption unit. If mist was desired, the air was passed into the tower without going through the drying and filtering stages.

During the progress of a run, the air rate and liquid rate were set and blank samples of the gas and liquid were taken. The desired gas concentration was then obtained by admitting nitrogen dioxide, and the unit was operated at steady conditions for approximately one hour until equilibrium conditions were obtained. The nitrogen dioxide was supplied from heated

cylinders obtained from Allied Chemical and Dye Corporation (98 per cent purity).

After equilibrium conditions were attained, two samples of the entering gas and the liquid leaving each tray were taken. All rates, temperatures, and other pertinent data were recorded. Gas samples were taken in evacuated 200-ml bulbs fitted with self-sealing rubber stoppers. The bulbs contained hydrogen peroxide and the evacuation and sampling were accomplished by use of 18-gauge hypodermic needles. The bulb containing the gas sample was shaken for one hour to permit complete reaction of the nitrogen dioxide. The bulb contents were then titrated with sodium hydroxide solution using bromcresol green - methyl red mixed indicator. The percentage of nitrogen oxides in the entering gas was determined from the weight of the gas sample and the results of the titration.

The liquid samples were analyzed for combined nitrogen content by titrating with sodium hydroxide solution. Plate efficiencies were calculated as the amount of oxides removed from the entering gas divided by the amount of oxides which theoretically could have been removed if the absorption reaction had gone to completion.

C. Discussion of Results

When runs were made using unfiltered air, a mist invariably appeared over the liquid surface if any nitrogen oxides were present in the gas. However, the mist was not apparent when filtered and dried air was employed. It appears, therefore, that the formation of mist is dependent on the presence of suitable nuclei, such as dispersed oil particles, on which a condensation may take place. The density of the mist was ap-

parently a function of the number of nuclei available, and there was no observable variation in mist density throughout the column. In this work, the impurities present in the laboratory air supply were used as a source of nuclei. The concentration, size, and composition of the aerosol involved was not a controllable factor, and the density of the mist obtained in these tests was less than that in the experimental tests discussed in Part I.

The characteristic efficiency curves for the three plates of the absorption unit, operated with mist, are shown in Figure 11. Figure 12 is a similar plot for the unit operated without mist. In both cases there is a definite trend toward greater plate efficiency as the gas passes up the tower.

The following factors could have an influence on the efficiency of the individual trays: - the concentration of acid on the tray, the temperature of the gas or liquid on the tray, the gas rate, the concentration of NO in the gas phase, and the concentration of water vapor or mist in the gas phase. Previous work (11, 12) has shown that the absorption rate is not noticeably changed when 15 per cent nitric acid is used as the absorbing medium in place of water. In the work reported here, the change in the gas rate and temperature of the gas and liquid phases in the unit was not appreciable. Using the method outlined by Sherwood and Pigford (13), it can be shown that the NO concentration in the gas has no effect on the plate efficiency at the liquid and gas concentrations encountered in this work.

If part of the chemical reaction takes place in the gas phase, a higher concentration of water vapor in this phase would be an advantage, and an increase in plate efficiency might be expected if the water vapor pressure increases. In the present experimental work, the air was brought into the base of the tower essentially dry. As the gas moved up the tower, its water-vapor

Figure 11. Effect of eNO_2 concentration in entering gases on plate efficiency with three-plate bubble-cap column and medium mist

Figure 12. Effect of eNO_2 concentration in entering gases on plate efficiency with three-plate bubble-cap column and no observable mist

content increased. At the gas velocity used, it is believed that saturation could not be attained in one plate contact, but would require several contacts. Therefore, the increase in plate efficiency from the bottom to the top tray may have been caused by the increasing concentration of water vapor in the gas phase.

If the individual plate-efficiency curves for the top, middle, and bottom plates, with and without mist, are compared, the efficiency is lower in each case for the runs in which mist was present. Thus, the presence of mist appears to cause a decrease in the rate at which nitrogen oxides are removed from gases. Comparison of the curves in Figures 11 and 12 gives no indication that the reduction in efficiency with mist present is due to carryover in the mist.

The shapes of all the curves in Figures 11 and 12 approximate the results that would be expected if the chemical reaction rates control the rate of removal of nitrogen oxides. Careful analysis of the results indicate that, when no mist is present, the absorption rate is completely controlled by the rate of the chemical reactions at gaseous concentrations less than about 2 volume per cent eNO_2 . At higher concentrations, diffusional resistances start to become important. The results in the presence of mist come closer to representing conditions which would be predicted if the chemical reaction rates were controlling. Apparently, the mechanism controlling the rate of absorption of nitrogen oxides at gaseous concentrations higher than about 2 volume per cent eNO_2 depends partially on the density of the mist and the type of contacting equipment.

D. Summary of Results Obtained with Multistage

Bubble-Cap Column

When multistage bubble-cap units are employed for aqueous absorption of nitrogen oxides, the individual plate efficiencies increase for any given gas composition as the gas moves up the tower. Higher plate efficiencies are obtained if no mist is present. For the design of a bubble-cap absorption unit, the use of all plate efficiencies based on values applicable at the bottom tray with mist present in the gas would give a good safety factor for the final design.

At low concentrations of nitrogen dioxide in the entering gases, the rate of the chemical reactions controls the rate of removal of nitrogen oxides. At high gaseous concentrations, diffusional resistances as well as chemical reaction rates, may determine the rate of nitrogen oxides removal, especially if there is little mist present in the gas.

PART VI. CAUSTIC ABSORPTION OF NITROGEN OXIDES FROM GASES

The rates of the chemical reactions involved in the aqueous absorption of nitrogen oxides are a major factor in determining the rate of removal of nitrogen oxides from gases. The important chemical reactions occur partially in the gas phase and partially in the liquid phase. One possible way to increase the rate of chemical reaction in the liquid phase would be to employ an aqueous sodium hydroxide solution as the absorbing medium.

Sodium hydroxide reacts with equivalent nitrogen dioxide as follows:

If the reaction rate constant for the preceding equation is sufficiently large, it would be possible for this reaction to proceed so rapidly that the diffusion of gaseous nitrogen dioxide to the liquid surface would ultimately control the rate of oxide absorption. This would result in an increased efficiency for the gaseous-oxide removal. However, if the rate for the sodium hydroxide reaction is not appreciably greater than the rate for the corresponding liquid-phase water reaction, the over-all absorption efficiency could be reduced when caustic solution is used. This reduction in efficiency would be caused by a decrease in the rate of the gas-phase reaction because of the lowering of the water vapor pressure.

Previous studies made with wetted-wall absorption units (4, 6) have indicated that the rate of nitrogen oxides absorption into caustic solutions is less than into water or dilute nitric acid solutions. The same result at temperatures higher than 80°F was indicated in Part II. Andersen

(1, 2) found an increase in removal efficiency for nitrogen oxides when caustic solution was substituted for water as the absorbing medium in a fritted-bubbler absorption unit.

The present study was conducted to determine the role of aqueous solutions of sodium hydroxide in the removal of nitrogen oxides from gases with a hubble-cap absorption unit. The results indicate that dilute sodium hydroxide solutions in bubble-cap columns are no more efficient than water for removal of nitrogen oxides.

A. Experimental Apparatus and Procedure

The experimental equipment used was similar to the three-plate bubble-cap column described in Part V, and the same general procedure was used. Since accurate analyses of the nitrate and nitrite concentrations in the liquid product could not be obtained at high concentrations of sodium hydroxide, an attempt was made to base the results on accurate analyses of the entering and leaving gases. The conventional method of analysis described in Part V gave good results for the entering-gas samples. However, accurate analyses of the exit gas could not be obtained unless mist was absent from the gas.

A large number of experimental tests were conducted with water as the absorbent under conditions of no mist, and the exit gas was analyzed by the procedure given in Part II. Material balances based on rates and analyses of entering gas, leaving liquid, and leaving gas indicated that the exit-gas analyses were essentially correct. A heavy mist was obtained in the gas phase when water was replaced by concentrated sodium hydroxide as the absorbing medium, even though filtered and dried air was used as the gas

diluent. For this reason, all the reported results are for aqueous sodium hydroxide concentrations of 3.6 per cent by weight or less, and all calculations are based on rates and analyses of the entering gas and leaving liquid.

Removal efficiencies are reported as the fraction of entering nitrogen dioxide (including N_2O_4) removed by the three-plate bubble-cap unit. A gas slot velocity of 1.2 ft/sec and a liquid flow rate of approximately 320 cc/min were used in all runs. Entering-gas concentrations varying from 3 to 8 volume per cent eNO_2 were tested, and the sodium hydroxide concentration in the runs was varied from 3.6 to 0.0 weight per cent.

B. Discussion of Results

Within the limits of experimental error, no significant difference in absorption rate was observed when water, 1 per cent, 2 per cent, or 3.6 per cent sodium hydroxide solution was used as the absorbing medium. The over-all removal efficiency for the three-plate bubble-cap column was in the range of 82-92 per cent at a gas composition of 8 volume per cent eNO_2 , and the removal efficiency decreased steadily to 70-80 per cent at a gas composition of 3 volume per cent eNO_2 . (See Appendix for experimental results.)

No definite trend in the removal efficiency was observed with increase in sodium hydroxide concentration. This result would be expected if the reaction with sodium hydroxide does not proceed at a rate considerably faster than the equivalent reaction with water, since the water vapor pressure over 3.6 per cent sodium hydroxide solution is only slightly less than the vapor pressure of pure water.

While only low concentrations of sodium hydroxide were tested in this work, excess sodium hydroxide was present during the runs made at the two highest liquid concentrations. Therefore, a definite increase in removal efficiency should have been observed for these runs if the rate of the reaction with sodium hydroxide reaction is greater than the equivalent reaction with water. Since tripling the concentration of sodium hydroxide had no effect on the removal efficiency, it may be assumed that the contacting mechanism in a bubble-cap column is such that essentially the same results with caustic solutions are obtained in both wetted-wall and bubble-cap absorption units. The use of aqueous sodium hydroxide as the absorbing medium for nitrogen dioxide in a bubble-cap column does not cause an increase in the rate of gaseous-oxide removal and may cause a reduction in the removal efficiency.

PART VII. SUMMARY

This report presents the results of a research program conducted to obtain a fundamental understanding of the principles governing the removal of nitrogen oxides from gaseous mixtures and to develop improved methods for the removal process. A detailed study of the mechanisms controlling the rate of aqueous absorption of gaseous nitrogen oxides was made, and an analysis of the controlling mechanism was developed on the basis of chemical kinetics. The roles of gas-phase and liquid-phase reactions, as well as mist formation, were investigated. Various types of equipment and processes for removing nitrogen oxides from gases were tested. These included bubble-cap columns, wetted-wall columns, Venturi atomizers, fritted bubblers, packed columns, and spray columns. Water, aqueous nitric acid, aqueous sodium hydroxide, aqueous sodium chloride, and silica gel were examined as media for removing nitrogen oxides from gases.

Extensive tests were conducted with a bubble-cap absorption unit to determine the basic mechanisms controlling the rate of nitrogen oxides removal from gases. Pure water and dilute nitric acid were used as the absorbing media, and gaseous concentrations ranging from 0.5 to 10 volume per cent eNO_2 were tested. The individual plate efficiencies decreased with reduction in gaseous-oxide concentration. This indicated that the rates of the chemical reactions involved in the removal process were controlling. An analysis of the results, based on chemical kinetics, permitted an excellent correlation of the experimental data when mist was present in the gases. An equally good correlation on the same basis has been found to apply for wetted-wall absorption units. With other types of contacting equipment, such as fritted dispersers or bubble-cap units with

no mist present, the chemical reaction rates were controlling at gaseous concentrations less than about 2 volume per cent eNO_2 .

A wetted-wall absorption unit was used to examine the roles of gas-phase and liquid-phase reactions. The results indicated that part of the reaction occurs in each phase. Studies were made on the effects of mist formation. The mist formed only when suitable nuclei, such as dispersed oil droplets, were present in the gases. The presence of mist caused a reduction in the rate of removal of gaseous oxides when a bubble-cap contacting system was employed.

Comparative results with various types of equipment showed that Venturi atomizers were very inefficient for removing nitrogen oxides from gases. Fritted dispersers and silica-gel absorbers gave better removal efficiencies than the other types of equipment tested. Packed towers and single-nozzle spray towers were not as effective for removing gaseous nitrogen oxides as bubble-cap towers.

Tests with a multistage bubble-cap tower indicated an increase in plate efficiency as the gases moved up the tower. The use of aqueous caustic solutions as the absorbing media in place of water indicated that sodium hydroxide cannot be used with a bubble-cap or wetted-wall absorption unit to obtain more complete removal of nitrogen oxides from gaseous mixtures.

The basic objects of this research program have been achieved. The careful analyses of the controlling mechanism in the removal operation, combined with the work on gas-phase reactions, liquid-phase reactions, and mist formation, serve to give an understanding of the principles involved in removing nitrogen oxides from gases. The experimental tests show the types of equipment which are most effective and also indicate the approach, operating conditions, and design data which can be used in the development of new and

improved methods for removing nitrogen oxides from gases.

Further work in this field will be conducted. Investigations dealing with agitated absorption units, multiple spray units, quantitative data on the kinetics of the important oxide-removal reactions, and mist formation are planned.

TABLE OF NOMENCLATURE

A = gas-liquid interfacial area, sq cm

B = a constant at any temperature

C = concentration, g moles/cc

D = diffusivity, sq cm/sec

$eNO_2 = NO_2 + 2 N_2O_4$

F = a constant at any temperature and gas rate

k = reaction rate constant

K_C = equilibrium constant for the reaction $2 NO_2 = N_2O_4$, (g moles/cc)⁻¹

K_p = equilibrium constant for the reaction $2 NO_2 = N_2O_4$, (atm)⁻¹

N_{eNO_2} = rate of eNO_2 absorption, g moles/(sec)(sq cm)

$P_{f N_2O_4}$ = final partial pressure of gaseous N_2O_4 , atm

$P_{o N_2O_4}$ = original partial pressure of gaseous N_2O_4 , atm

t = contact time, sec

V_g = volume of bulk of gas, cc

x_F = effective film thickness, cm

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APPENDIX

SAMPLE CALCULATIONS

A. One-Plate Bubble-Cap Plate Column

1. Sample calculations showing the method of determining plate efficiency and the concentration of NO_2 and N_2O_4 are presented in Technical Report No. 10, A.E.C. Serial No. C00-1011 (11).

2. Sample calculation for sensitivity of correlation of data based on integrated rate equation

Run Number 4 - Table 2

	<u>Entering Gas (Mole %)</u>			<u>Exit Gas (Mole %)</u>		
	<u>$\text{NO}_2 + 2\text{N}_2\text{O}_4$</u>	<u>NO_2</u>	<u>N_2O_4</u>	<u>$\text{NO}_2 + 2\text{N}_2\text{O}_4$</u>	<u>NO_2</u>	<u>N_2O_4</u>
Reported	0.685	0.628	0.0286	0.576	0.534	0.0206

Conversion = 50%
of reported value $0.685 - (0.685 - 0.576)(0.5) = 0.631$ 0.582   0.0244

Conversion = 200%
of reported value $0.685 - (0.685 - 0.576)(2.0) = 0.467$ 0.439   0.0139

Reported

$$\text{Abscissa} = \sqrt{\frac{1}{P_{0\text{N}_2\text{O}_4}}} - 2\sqrt{K_p} \ln \frac{P_{0\text{N}_2\text{O}_4}}{P_{f\text{N}_2\text{O}_4}} = \sqrt{\frac{1}{0.000286}} - 2\sqrt{7.24} \ln \frac{0.000286}{0.000206}$$

$$= 57.4$$

$$\text{Ordinate} = \sqrt{\frac{1}{P_{f\text{N}_2\text{O}_4}}} = \sqrt{\frac{1}{0.000206}} = 69.7$$

Value of ordinate from mean line at abscissa of 57.4 = 67.5

Per cent error of reported value = 3.3%

Average deviation of all experimental ordinates from mean = 2.8%

<u>Conversion = 50% of reported value</u>		<u>Conversion = 200% of reported value</u>
Abscissa	58.3	55.2
Ordinate	64.0	84.8
Ordinate from mean line	68.0	65.0
Per cent error	5.9%	30.4%

Run Number 36 - Table 2

	<u>Ordinate</u>	<u>Abscissa</u>	<u>% Error of Ordinate Based on Mean Line</u>
Reported value	12.0	2.1	0
Conversion = 50% of reported value	9.0	5.2	40.0
Conversion = 200% of reported value	158	-26.0	1000 (line extrapolated)

B. Wetted-Wall Absorption Unit

The following calculations show the method used to obtain a material balance and the removal efficiencies: (1) based on the entering gas and exit-liquid analyses, and (2) based on the entering and exit gas analyses.

Run 32 - Table 4

Temperatures: entering liquid - 86°F
 entering gas - 87°F
 exit liquid - 86°F
 exit gas - 92°F

Entering N_2 rate: 0.0775 lb/min

Entering liquid: distilled water

Exit liquid rate: 250 cc/min

Entering gas sample (H_2O_2 in bottle):

Weight = 0.130 g

Base used = 8.94 cc

Leaving gas sample (H_2O_2 in bottle):

Weight = 0.134 g

Base used = 5.76 cc

Leaving gas sample ($KMnO_4$ and H_2SO_4 in bottle):

Weight = 0.150 g

Net $Na_2S_2O_3$ used = 12.05 cc

Exit liquid product:

Base used = 28.47 cc/10 cc sample

Normality of base: 0.0237

Normality of $Na_2S_2O_3$: 0.0148

Entering

$$\text{Wt. fraction } eNO_2 = \frac{8.94 \times 0.0237 \times 46}{1000 \times 0.130} = (0.00163)(46) = 0.0750$$

$$\text{Lb } eNO_2 \text{ entering per minute} = 0.0775 \times 0.075/0.925 = 0.00628$$

$$\text{Mole per cent } eNO_2 = 4.70$$

Leaving

Only $2/3$ of the entering NO_2 reacted is converted into nitric acid:

$$(NO_2 \text{ reacted}) = (3/2) (NO_2 \text{ out in acid})$$

$$\text{Lb } eNO_2 \text{ reacted per minute} = \frac{3 \times 28.47 \times 0.0237 \times 0.250 \times 46}{2 \times 10 \times 454} = 0.002565$$

$$\frac{\text{g eq } (NO + eNO_2) \text{ out}}{\text{g sample}} = \frac{5.76 \times 0.0237}{1000 \times 0.134} = 0.001019$$

$$\frac{\text{g eq } (3 NO + eNO_2) \text{ out}}{\text{g sample}} = \frac{12.05 \times 0.0148}{1000 \times 0.150} = 0.001189$$

$$(\text{NO}) = 0.000085 \text{ g eq NO/g sample} = 0.00255 \text{ g NO/g sample}$$

$$(\text{eNO}_2) = 0.000934 \text{ g eq eNO}_2/\text{g sample} = 0.0430 \text{ g eNO}_2/\text{g sample}$$

$$(\text{N}_2) = 0.954 \text{ g N}_2/\text{g sample} = 0.03405 \text{ g eq N}_2/\text{g sample}$$

$$\text{Mole per cent NO} = 0.24$$

$$\text{Mole per cent eNO}_2 = 2.66$$

$$\text{Total lb combined nitrogen as eNO}_2 \text{ out/min} = \frac{0.0775 \times 0.043}{0.954} + 0.002565 = 0.00606$$

$$\text{Total lb eNO}_2 \text{ in/min} = 0.00628$$

$$\text{Per cent deviation} = 3.5$$

(1) Removal efficiency based on entering gas and leaving liquid:

$$\text{Removal efficiency} = \frac{2 \times 0.002565 \times 100}{3 \times 0.00628} = 27.3\%$$

(2) Removal efficiency based on entering gas and leaving gas:

$$\text{Removal efficiency} = \frac{2 (0.00163 - 0.000934) 100}{3 \times 0.00163} = 28.4\%$$

In the calculation of the efficiency based on the entering and leaving gas, the effect on the nitrogen concentration caused by the small oxide loss incurred while passing through the column has been neglected. The efficiency as calculated in (2) is slightly smaller than that which would have been calculated by not neglecting this effect and thus agrees more closely with the more precise value based on the entering gas and leaving liquid.

C. Three-Plate Bubble-Cap Column

The following calculations show the method used to obtain the efficiencies of each of the trays when all three trays were used for absorption:

Run 98 - Table 7

Over-all equation: $3 \text{ NO}_2 + \text{H}_2\text{O} \longrightarrow 2 \text{ HNO}_3 + \text{NO}$

Pressures: NO_2 cylinder - 2.0 cm Hg
Tower base - 8.0 cm α -bromonaphthalene
Tower top - 4.3 cm α -bromonaphthalene

Temperatures: Entering liquid - 24.9°C
Entering gas - 23.2°C
Exit gas - 26.4°C
Entering air - 25.0°C

Entering air rate: - $1.21 \text{ ft}^3/\text{min}$
- $0.00311 \text{ lb moles/min}$
- 0.0904 lb/min

Exit liquid rate - 296 cc/min

Entering liquid composition - 0 wt per cent HNO_3

Entering gas composition - 2.1 mole per cent eNO_2
- 3.30 wt per cent eNO_2

Total moles gas entering - $0.00318 \text{ lb moles/min}$

Base used to titrate leaving liquid:

Bottom tray - $1.231 \text{ cc base/cc sample}$
Middle tray - $0.589 \text{ cc base/cc sample}$
Top tray - $0.246 \text{ cc base/cc sample}$

Normality of base - 0.0493

Column diameter - 7.5 inches
Column cross-sectional area - 0.307 ft^2
Distance between plates - 12 inches

At all times, the reaction of eNO_2 with water will be considered as going 100 per cent to completion. The small loss of eNO_2 through the column is neglected in making partial pressure calculations, and one mole of gas entering a tray is assumed as equivalent to one mole of gas leaving the tray.

Basis: 1 minute

Bottom Tray

$$\text{Lb eNO}_2 \text{ entering tray} = 0.0904 \times 3.30/96.7 = 0.00308$$

$$\text{Lb eNO}_2 \text{ as acid formed on tray} = \frac{0.642 \times 0.0493 \times 296 \times 46}{1000 \times 454} = 0.000949$$

Since only 2/3 of the entering eNO₂ could have been absorbed and reacted to form HNO₃.

$$\text{Plate efficiency} = \frac{3 \times 0.000949 \times 100}{2 \times 0.00308} = 46.2\%$$

Leaving bottom plate as gas,

$$0.00308 - 0.000949 \times 3/2 = 0.00166 \text{ lb eNO}_2 \text{ unreacted}$$

Since 1/2 mole of NO is formed for every mole of HNO₃ formed,

$$\frac{0.000949}{46 \times 2} = 0.0000103 \text{ lb mole NO formed}$$

$$P_{O_2} = 0.21 \text{ atm}$$

Assuming 1 mole of gas into plate equals 1 mole of gas leaving plate, $P_{NO} = 0.0000103/0.00318 = 0.00324 \text{ atm}$

According to Sherwood and Pigford (13), the amount of NO which is oxidized to NO₂ between plates of a bubble-cap absorber is given by

$$\frac{1}{(P_{NO})_f} = \frac{1}{(P_{NO})_o} + \left[2(P_{O_2})_o - (P_{NO})_o \right] \cdot \frac{k^m t}{2}$$

where $(P_{NO})_f$ = final partial pressure of NO, atm

$(P_{NO})_o$ = original partial pressure of NO, atm

$(P_{O_2})_o$ = original partial pressure of O₂, atm

t = contact time, sec

k^m = a constant = 23.2 (sec)⁻¹ (atm)⁻² at operating temperature

$$t = \frac{0.307 \times 60 \times 1}{1.21} = 15.3 \text{ sec}$$

$$\frac{1}{(p_{NO})_f} = \frac{1}{0.00324} + \left[2(0.21) - 0.00324 \right] \frac{23.2 \times 15.3}{2}$$

$$(p_{NO})_f = 0.00261 \text{ atm}$$

$$(p_{NO}) \text{ converted} = 0.00324 - 0.00261 = 0.00063 \text{ atm}$$

$$0.00063 \times 0.00318 \times 46 = 0.0000921 \text{ lb eNO}_2 \text{ formed}$$

$$\frac{0.001660}{0.001752} \text{ lb eNO}_2 \text{ unreacted}$$

$$\text{0.001752 lb eNO}_2 \text{ entering middle plate}$$

Middle Tray

$$\text{Lb eNO}_2 \text{ entering plate} = 0.001752$$

$$\text{Lb eNO}_2 \text{ as acid formed on plate} = \frac{0.343 \times 0.0493 \times 296 \times 46}{1000 \times 454} = 0.000511$$

$$\text{Plate efficiency} = \frac{0.000511 \times 3 \times 100}{0.001752 \times 2} = 43.6\%$$

$$\frac{0.001752 \times 100}{46 \times 0.00318} = 1.20 \text{ mole per cent eNO}_2 \text{ entering plate}$$

$$\text{Lb eNO}_2 \text{ leaving middle plate as gas,}$$

$$0.001751 - 0.000511 \times 3/2 = 0.00099 \text{ lb eNO}_2 \text{ unreacted}$$

$$\frac{0.000511}{46 \times 2} = 0.00000555 \text{ lb moles NO formed}$$

$$(p_{NO})_o = \frac{0.00000555}{0.00318} + 0.00261 = 0.00436 \text{ atm}$$

Assuming oxygen concentration unchanged,

$$\frac{1}{(p_{NO})_f} = \frac{1}{0.00436} + \left[2(0.21) - 0.00436 \right] \frac{23.2 \times 15.3}{2}$$

$$(p_{NO})_f = 0.00330$$

$$(p_{NO}) \text{ converted} = 0.00106 \text{ atm}$$

$$0.00106 \times 0.00318 \times 46 = 0.000155 \text{ lb eNO}_2 \text{ formed}$$

$$\frac{0.00099}{0.00115} \text{ lb eNO}_2 \text{ unreacted}$$

$$\text{0.00115 lb eNO}_2 \text{ entering top plate}$$

Top Tray

$$\text{Lb eNO}_2 \text{ entering tray} = 0.00115$$

$$\text{Lb eNO}_2 \text{ as acid formed on tray} = \frac{0.246 \times 0.0493 \times 296 \times 46}{1000 \times 454}$$

$$\text{Plate efficiency} = \frac{0.000364 \times 100 \times 3}{0.00115 \times 2} = 47.5\%$$

$$\frac{0.00115 \times 100}{46 \times 0.00318} = 0.79 \text{ mole per cent } \text{eNO}_2 \text{ entering plate}$$

$$0.00115 - 0.000364 \times 3/2 = 0.00060 \text{ lb NO}_2 \text{ unreacted}$$

TABLE 2

EXPERIMENTAL DATA FOR ONE-PLATE BUBBLE-CAP COLUMN (See PART I)

Total Pressure = 1 Atmosphere
Mist Present

Run No.	Plate Temp. °C	Ent. Liq.	Exit Liq.	Exit Liq.	Ent. Gas	Entering Gas			Exit Gas		
		Compn.	Rate	Compn.	Rate	Compn.			Compn.		
		Wt. %	cc	Wt. %	ft ³	Mole %			Mole %		
		HNO ₃	min	HNO ₃	min	NO ₂ + 2N ₂ O ₄	NO ₂	N ₂ O ₄	NO ₂ + 2N ₂ O ₄	NO ₂	N ₂ O ₄
1	19.8	0	292	0.615	1.22	0.454	0.420	0.0171	0.422	0.392	0.0150
2	23.0	0	301	0.845	1.18	0.534	0.497	0.0185	0.491	0.459	0.0159
3	18.2	0	298	0.900	1.21	0.622	0.554	0.0340	0.578	0.518	0.0298
4	23.6	0	302	2.08	1.18	0.685	0.628	0.0286	0.576	0.534	0.0206
5	19.4	0	286	1.84	1.21	0.699	0.622	0.0388	0.611	0.550	0.0306
6	23.0	0	311	1.61	1.18	0.741	0.672	0.0344	0.656	0.602	0.0272
7	21.1	0	304	1.81	1.21	0.794	0.707	0.0435	0.696	0.627	0.0347
8	18.8	0	306	2.23	1.21	0.800	0.697	0.0515	0.686	0.608	0.0393
9	18.4	0	306	2.16	1.21	0.821	0.710	0.0554	0.714	0.628	0.0430
10	24.0	0	288	3.12	1.20	0.831	0.752	0.0394	0.681	0.626	0.0276
11	19.6	0	284	2.78	1.21	0.837	0.731	0.0529	0.706	0.627	0.0394
12	23.6	0	291	3.77	1.20	0.887	0.795	0.0458	0.704	0.644	0.0302
13	20.2	0	292	2.78	1.22	0.900	0.784	0.0580	0.774	0.685	0.0444
14	20.0	0	295	3.91	1.21	0.914	0.793	0.0604	0.720	0.640	0.0400
15	22.2	0	278	2.99	1.18	0.925	0.817	0.0540	0.781	0.702	0.0396
16	21.3	0	307	3.06	1.21	0.965	0.842	0.0615	0.805	0.716	0.0445
17	19.4	0	296	4.71	1.23	1.08	0.912	0.084	0.850	0.740	0.055
18	18.2	0	300	4.52	1.22	1.12	0.928	0.096	0.901	0.769	0.066
19	23.2	0	284	4.75	1.20	1.12	0.978	0.071	0.892	0.798	0.047
20	21.0	0	293	3.62	1.16	1.15	0.970	0.090	0.970	0.840	0.065
21	19.4	0	297	5.90	1.22	1.19	0.992	0.099	0.901	0.779	0.061
22	21.5	0	289	6.11	1.22	1.33	1.118	0.106	1.040	0.904	0.068
23	22.2	0	296	7.00	1.22	1.42	1.192	0.114	1.080	0.938	0.071
24	23.2	0	301	7.20	1.21	1.44	1.222	0.109	1.080	0.948	0.066
25	21.1	0	296	7.25	1.22	1.47	1.212	0.129	1.12	0.958	0.081
26	19.4	0	299	7.95	1.23	1.63	1.292	0.169	1.24	1.026	0.107
27	21.9	0	292	9.10	1.22	1.64	1.34	0.148	1.20	1.026	0.087
28	23.0	0	309	7.00	1.14	1.70	1.40	0.15	1.32	1.12	0.100
29	25.0	0	298	14.4	1.15	2.70	2.10	0.30	1.96	1.62	0.172
30	22.5	0	301	25.8	1.49	3.46	2.50	0.48	2.15	1.70	0.225

TABLE 2 (continued)

Run No.	Plate Temp. °C	Ent. Liq.	Exit Liq.	Exit Liq.	Ent. Gas	Entering Gas			Exit Gas		
		Compn.	Rate	Compn.	Rate	Compn.			Compn.		
		Wt. % HNO ₃	cc min	Wt. % HNO ₃ x 10 ²	ft ³ min	Mole %			Mole %		
						NO ₂ + 2N ₂ O ₄	NO ₂	N ₂ O ₄	NO ₂ + 2N ₂ O ₄	NO ₂	N ₂ O ₄
31	22.5	0	291	33.7	1.19	4.31	2.95	0.68	2.65	2.01	0.32
32	22.0	0	302	39.0	1.22	4.62	3.06	0.78	2.62	1.98	0.32
33	21.5	0	303	59.3	1.24	6.71	4.00	1.36	3.79	2.61	0.59
34	24.0	0	307	73.0	1.21	8.08	4.82	1.63	4.35	3.05	0.65
35	21.5	0	306	75.4	1.21	8.14	4.58	1.78	4.56	3.00	0.78
36	23.0	0	304	84.1	1.20	8.70	5.00	1.85	4.47	3.07	0.70
37	23.0	0	300	87.8	1.20	8.73	5.00	1.85	4.35	3.00	0.68
38	20.0	0	299	105.0	1.23	10.2	5.14	2.53	5.07	3.15	0.96
39	26.0	0	305	116.4	1.24	11.6	6.46	2.57	5.85	3.95	0.95
40	20.5	0	610	4.8	1.18	11.87	1.47	0.20	1.37	1.13	0.12
41	22.0	0	608	25.2	1.23	5.88	3.68	1.10	3.40	2.42	0.49
42	22.5	0	605	47.7	1.22	9.54	5.20	2.17	4.79	3.19	0.80
43	18.0	0	595	54.1	1.23	9.92	4.74	2.59	4.64	2.82	0.91
44	23.0	15	284	18.0*	1.19	2.47	1.91	0.28	1.61	1.34	0.135
45	23.0	15	290	18.8*	1.19	2.70	2.06	0.32	1.78	1.46	0.160
46	23.5	15	288	22.1*	1.19	2.71	2.07	0.32	1.63	1.36	0.135
47	23.5	15	289	53.3*	1.17	5.85	3.75	1.05	3.21	2.40	0.415
48	25.0	15	282	72.7*	1.18	7.41	4.61	1.40	3.90	2.84	0.53
49	25.0	15	292	96.2*	1.22	9.71	5.61	2.05	5.08	3.50	0.79
50	20.0	0	318	3.8	2.26	1.10	0.94	0.08	0.99	0.85	0.07
51	20.0	0	280	6.5	2.11	1.25	1.04	0.106	1.08	0.92	0.08
52	21.0	0	315	18.5	2.26	2.80	2.06	0.37	2.28	1.74	0.27
53	20.0	0	305	29.0	2.30	2.90	2.06	0.42	2.15	1.63	0.26
54	20.5	0	296	30.6	2.37	3.05	2.17	0.44	2.28	1.72	0.28
55	22.0	0	290	57.0	2.45	4.63	3.07	0.78	3.25	2.35	0.45
56	26.5	0	290	60.1	2.43	4.74	3.38	0.68	3.27	2.51	0.38
57	22.5	0	280	91.5	2.46	6.05	3.77	1.14	3.90	2.72	0.59
58	22.0	0	320	108.0	2.36	7.80	4.52	1.64	5.38	3.46	0.96
59	23.0	0	299	157.0	2.43	9.48	5.28	2.10	5.59	3.63	0.98
60	19.0	0	290	123.0	2.44	9.05	4.61	2.22	6.20	3.56	1.32
61	25.0	0	330	128.0	2.61	9.68	5.60	2.04	6.40	4.16	1.12
62	29.0	0	290	160.0	2.60	9.82	6.10	1.86	6.25	4.35	0.95
63	26.0	0	290	173.0	2.68	9.82	5.78	2.02	6.20	4.14	1.03
64	27.5	0	290	170.0	2.67	10.44	6.22	2.11	6.77	4.51	1.13

* Increase over 15 weight per cent.

TABLE 3

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EXPERIMENTAL DATA USING DISTILLED WATER AND
AQUEOUS NaCl AS ABSORBENTS IN WETTED-WALL COLUMN

(Study on Vapor and Liquid Phase Reactions between Nitrogen Dioxide and Water - See Part II)

Total Pressure = 1 Atmosphere

Run No.	Ent. Mole % NO ₂ + 2N ₂ O ₄	NO ₂ Diluent	Diluent Flow Rate (lb/min)	Exit Liq. Flow Rate (cc/min)	Exit Liq. Compn. (Normality)	Exit Gas Temp. (°F)	Ent. Liq. Temp. (°F)	Exit Liq. Temp. (°F)	Ent. Gas Temp. (°F)	Ave. Temp. (°F)	Rem. Efficiency, %
Absorbing Liquid = Distilled Water											
31	4.73	N ₂	0.0775	224	0.0765	89	86	86	86	87	27.4
32	4.70	N ₂	0.0775	250	0.0675	92	86	86	87	88	27.3
5	4.96	Air	0.0775	208	0.0820	91	84	84	82	85	27.0
9	4.80	Air	0.0775	201	0.0760	94	89	85	85	88	25.1
13	4.80	Air	0.0775	210	0.0676	102	95	94	94	96	23.5
16	4.69	N ₂	0.0763	212	0.0657	100	92	91	91	93	22.9
19	4.75	N ₂	0.0763	207	0.0677	105	98	97	94	99	22.7
1	4.81	Air	0.0775	208	0.0653	99	92	91	93	93	22.3
6	4.96	Air	0.0775	206	0.0655	106	100	100	98	101	21.2
10	4.80	Air	0.0775	193	0.0634	108	102	101	101	103	20.0
2	4.81	Air	0.0775	212	0.0551	114	108	107	107	109	19.1
17	4.69	N ₂	0.0763	208	0.0547	112	107	104	104	107	18.7
14	4.80	Air	0.0775	209	0.0484	118	111	111	115	114	16.6
20	4.75	N ₂	0.0763	207	0.0475	122	115	113	115	116	16.0
11	4.80	Air	0.0775	199	0.0478	122	115	115	116	117	15.6
7	4.96	Air	0.0775	205	0.0468	123	116	116	116	117	14.9
3	4.81	Air	0.0775	209	0.0430	124	121	118	124	122	14.7
18	4.69	N ₂	0.0763	206	0.0432	127	122	119	121	122	14.7
15	4.80	Air	0.0775	208	0.0384	129	126	123	128	126	13.1
8	4.86	Air	0.0775	201	0.0371	135	132	128	132	132	12.0
4	4.81	Air	0.0775	212	0.0341	135	132	128	134	132	11.9
12	4.80	Air	0.0775	203	0.0350	137	130	127	132	132	11.7

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TABLE 3 (Continued)

Run No.	Ent. Mole % NO ₂ + 2N ₂ O ₄	NO ₂ Dilu- ent	Dilu- ent Flow Rate (lb/min)	Exit Liq. Flow Rate (cc/min)	Exit Liq. Compn. (Nor- mality)	Exit Gas Temp. (°F)	Ent. Liq. Temp. (°F)	Exit Liq. Temp. (°F)	Ent. Gas Temp. (°F)	Ave. Temp. (°F)	Rem. Effi- ciency, %
Absorbing Liquid = 24 % by Weight NaCl Aqueous Solution											
25	4.62	Air	0.0775	204	0.0326	88	83	83	80	83	11.3
21	4.79	Air	0.0775	222	0.0266	98	93	90	90	93	9.7
26	4.62	Air	0.0775	206	0.0270	102	95	98	94	97	9.5
22	4.84	Air	0.0775	218	0.0254	104	101	94	99	100	9.0
27	4.62	Air	0.0775	204	0.0227	117	110	112	111	112	7.9
23	4.84	Air	0.0775	218	0.0196	123	118	114	122	119	6.9
24	4.84	Air	0.0775	215	0.0167	133	128	123	131	129	5.8

TABLE 4

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EXPERIMENTAL DATA FOR RUNS IN WHICH EXIT GAS FROM WETTED-WALL COLUMN WAS ANALYZED

(Study on Vapor and Liquid Phase Reactions between Nitrogen Dioxide and Water - See Part II)

Total Pressure = 1 Atmosphere

NO₂ Diluent = N₂

Run No.	Diluent Flow Rate (lb/min)	Ent. Mole Per Cent eNO ₂	Exit Mole Per Cent eNO ₂	Exit Mole Per Cent NO	Exit Liq. Flow Rate (cc/min)	Exit Gas Temp. (°F)	Ent. Liq. Temp. (°F)	Exit Liq. Temp. (°F)	Ent. Gas Temp. (°F)	Ave. Temp. (°F)	Rem. Eff. Based on Gas Samples per cent	Removal Eff. Based on Ent. Gas and Lvg. Liq. Samples per cent

Absorbing Liquid = Distilled Water. Diluent = N₂.

31	0.0775	4.73	2.61	0.21	224	89	86	86	86	87	29.4	27.4
32	0.0775	4.70	2.66	0.24	250	92	86	86	87	88	28.4	27.3

Absorbing Liquid = 20 % by Weight NaOH Aqueous Solution. Diluent = N₂.

28	0.0775	4.80	2.90	0.48	205	89	87	87	87	88	25.7	
30	0.0728	4.26	2.90	0.53	200	98	98	98	98	98	20.7	
29	0.0775	4.75	3.98	0.05	199	118	114	114	114	115	11.8	

TABLE 5

EXPERIMENTAL DATA FOR RECOVERY OF NITROGEN DIOXIDE

WITH VENTURI ATOMIZER (See Part III)

Gas Velocity at Venturi Throat = 300 ft/sec

Liquid Rate cc/min	Gas Compn. Mole per cent eNO_2	Total Acid Concn. Moles per Liter	O_2 Deficiency as HNO_2 Moles per Liter	eNO_2 Recovery per cent of Original
50	1.9	0.0056	0.0035	0.21
100	1.7	0.0042	0.0016	0.35
200	1.2	0.0031	0.0005	0.74
300	1.1	0.0022	0.0003	0.86
50	3.4	0.063	0.0138	1.3
100	3.7	0.038	0.0104	1.5
200	2.9	0.021	0.0069	2.1
300	3.7	0.014	0.0051	1.6
50	5.8	0.152	0.033	1.9
100	6.3	0.090	0.026	2.0
200	6.1	0.051	0.018	2.4
300	6.5	0.037	0.015	2.5
50	8.9	0.261	0.051	2.1
100	8.4	0.132	0.040	2.3
200	7.9	0.062	0.022	2.3
300	7.9	0.040	0.014	2.2
50	12.5	0.360	0.075	2.1
100	10.9	0.191	0.054	2.5
200	10.6	0.089	0.033	2.4
300	10.7	0.068	0.025	2.7

TABLE 6

EXPERIMENTAL DATA FOR RECOVERY OF NITROGEN DIOXIDE

WITH FRITTED-GLASS DISPERSER (See Part III)

Gas Rate = 0.05 ft³/min
Two-Hour Run

Initial Gas Composition M. F. eNO ₂	Moles eNO ₂		eNO ₂ Concentration Mole Fraction		eNO ₂ Recovery per cent of Original
	<u>Recovered</u>	<u>Unreacted</u>	<u>Initial</u>	<u>Final</u>	
0.0066	0.038	0.012	0.0063	0.00160	75.6
0.0145	0.090	0.0195	0.0133	0.00248	82.1
0.0170	0.112	0.017	0.0154	0.00217	86.9
0.0260	0.172	0.027	0.0220	0.00356	86.5
0.0310	0.207	0.027	0.0253	0.00356	88.5
0.0370	0.248	0.032	0.0293	0.00415	88.5
0.0520	0.347	0.044	0.0385	0.00576	88.6
0.0555	0.380	0.040	0.0405	0.00530	90.5
0.0720	0.484	0.062	0.0495	0.00826	88.5
0.0870	0.591	0.070	0.0575	0.00942	89.5
0.0995	0.682	0.071	0.0635	0.0096	90.6

TABLE 7

EXPERIMENTAL DATA FOR THREE-PLATE BUBBLE-CAP COLUMN WITH

NO MIST (See Part V)

Total Pressure = 1 Atmosphere

Run No.	Plate Temp. °C	Liq. Compn. Wt. % NO ₂ x 10 ²	Exit Liq. Rate cc/min	Ent. Gas Rate ft ³ /min	Entering Gas Compn. Mole %			Exit Gas Compn. Mole %			Plate Efficiency per cent
					NO ₂ +			NO ₂ +			
					2N ₂ O ₄	NO ₂	N ₂ O ₄	2N ₂ O ₄	NO ₂	N ₂ O ₄	
111 m	27.7	42.5	297	1.284	4.81	3.51	0.646	2.06	1.74	0.1590	57.3
105 m	27.3	40.4	301	1.278	4.30	3.19	0.552	1.67	1.450	0.1140	61.3
107 m	27.2	33.7	302	1.271	3.78	2.87	0.451	1.57	1.351	0.1030	58.5
104 m	26.9	23.0	308	1.251	2.74	2.20	0.271	1.17	1.049	0.0615	57.4
106 m	27.0	22.6	277	1.250	2.62	2.12	0.250	1.23	1.085	0.0655	53.0
103 m	27.6	16.51	296	1.241	2.07	1.75	0.162	0.975	0.895	0.0424	52.9
99 m	25.2	16.51	302	1.240	1.99	1.649	0.173	0.871	0.795	0.0401	56.1
101 m	25.0	11.70	301	1.232	1.52	1.309	0.111	0.720	0.664	0.0286	52.6
98 m	24.9	7.85	296	1.229	1.20	1.071	0.0750	0.698	0.648	0.0220	43.6
110 m	27.6	7.83	304	1.228	1.19	1.071	0.0606	0.646	0.615	0.0195	45.7
102 m	27.6	5.95	296	1.227	1.05	0.956	0.0484	0.653	0.615	0.0200	38.0
113 m	26.5	4.90	299	1.220	0.792	0.730	0.0302	0.454	0.434	0.0108	42.7
112 m	26.9	3.28	293	1.219	0.718	0.670	0.0251	0.496	0.469	0.0123	31.0
100 m	25.0	3.34	304	1.219	0.611	0.564	0.0206	0.378	0.363	0.0086	38.3
111 t	27.7	30.4	297	1.269	2.96	2.38	0.296	0.971	0.886	0.0413	67.0
105 t	27.3	25.0	301	1.260	2.45	2.02	0.221	0.819	0.756	0.0310	66.6
107 t	27.2	30.0	302	1.259	2.29	1.897	0.197	0.540	0.489	0.0143	77.4
104 t	26.9	14.38	308	1.242	1.597	1.383	0.107	0.613	0.576	0.0186	61.7
106 t	27.0	16.99	277	1.242	1.62	1.398	0.108	0.576	0.540	0.0162	64.5
103 t	27.6	10.40	296	1.233	1.223	1.093	0.0631	0.539	0.511	0.0138	56.0
99 t	25.2	11.03	302	1.232	1.133	1.008	0.0649	0.391	0.387	0.0090	65.6
101 t	25.0	7.75	301	1.229	0.910	1.825	0.0441	0.382	0.363	0.0086	58.1
98 t	24.9	5.99	296	1.225	0.790	0.731	0.0310	0.458	0.433	0.0122	47.5
110 t	27.6	5.24	304	1.224	0.840	0.777	0.0319	0.476	0.445	0.0109	43.4

TABLE 7 (Continued)

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Run No.	Plate Temp. °C	Liq. Compn. Wt. % NO ₂ x 10 ²	Exit Liq. Rate cc/min	Ent. gas Rate ft ³ /min	Entering Gas Compn. Mole %			Exit Gas Compn. Mole %			Plate Efficiency per cent
					NO ₂ +			NO ₂ +			
					2N ₂ O ₄	NO ₂	N ₂ O ₄	2N ₂ O ₄	NO ₂	N ₂ O ₄	
102 t	27.6	4.16	296	1.223	0.719	0.673	0.0239	0.439	0.421	0.0094	38.9
113 t	26.5	3.42	299	1.220	0.496	0.464	0.0127	0.262	0.260	0.0037	47.3
112 t	26.9	2.59	293	1.219	0.519	0.491	0.0135	0.342	0.335	0.0063	34.0
100 t	25.0	2.46	304	1.219	0.403	0.382	0.0095	0.232	0.228	0.0034	42.7

m refers to middle tray

t refers to top tray

For additional data see Reference (9)

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TABLE 8

EXPERIMENTAL DATA FOR THREE-PLATE BUBBLE-CAP COLUMN WITH MIST

(See Part V)

Total Pressure = 1 Atmosphere

Run No.	Plate Temp. °C	Liq. Conc'n. Wt. % NO ₂ x 10 ²	Exit Liq. Rate cc/min	Ent. Gas Rate ft ³ /min	Entering Gas Compn. Mole %			Exit Gas Compn. Mole %			Plate Efficiency per cent
					NO ₂ + 2N ₂ O ₄	NO ₂	N ₂ O ₄	NO ₂ + 2N ₂ O ₄	NO ₂	N ₂ O ₄	
121 m	25.3	41.6	301	1.290	5.42	3.69	0.864	2.75	2.16	0.296	49.4
109 m	23.6	35.4	302	1.281	4.75	3.23	0.754	2.42	1.90	0.260	49.0
120 m	25.0	28.9	302	1.270	4.02	2.92	0.552	2.12	1.73	0.194	47.5
108 m	24.0	21.2	304	1.259	3.14	2.36	0.389	1.73	1.44	0.145	45.0
115 m	28.3	16.51	307	1.246	2.42	2.02	0.204	1.23	1.13	0.0639	48.0
114 m	28.4	11.60	291	1.239	1.98	1.700	0.1443	1.20	1.08	0.0584	39.3
117 m	26.0	7.95	306	1.231	1.42	1.232	0.0911	0.871	0.795	0.0379	38.9
119 m	23.5	6.62	302	1.227	1.153	1.010	0.0742	0.707	0.646	0.0304	39.3
116 m	25.8	3.75	308	1.220	0.806	0.740	0.0333	0.540	0.510	0.0158	33.0
118 m	21.8	2.26	302	1.219	0.495	0.462	0.0178	0.338	0.318	0.0084	31.8
121 t	25.3	34.1	301	1.271	3.54	2.64	0.445	1.35	1.181	0.0885	62.1
109 t	23.6	31.0	302	1.265	3.10	2.32	0.389	1.06	0.935	0.0631	65.8
120 t	25.0	24.2	302	1.259	2.64	2.02	0.280	1.03	0.924	0.0553	60.8
108 t	24.0	18.68	304	1.247	2.10	1.697	0.201	0.854	0.770	0.0414	59.1
115 t	28.3	13.08	307	1.239	1.55	1.360	0.0925	0.632	0.600	0.0180	59.2
114 t	28.4	10.55	291	1.235	1.43	1.270	0.0806	0.721	0.675	0.0228	49.5
117 t	26.0	7.11	306	1.226	1.003	0.905	0.0491	0.506	0.484	0.0138	49.5
119 t	23.5	5.80	302	1.222	0.772	0.701	0.0358	0.372	0.347	0.0091	51.8
116 t	25.8	3.24	308	1.220	0.569	0.535	0.0174	0.338	0.325	0.0064	40.6
118 t	21.8	1.92	302	1.218	0.349	0.331	0.0091	0.215	0.210	0.0036	38.6

m refers to middle tray

t refers to top tray

For additional data, see Reference (9)

TABLE 9

EXPERIMENTAL DATA FOR CAUSTIC ABSORPTION OF NITROGEN OXIDES (See Part VI)

Three-Plate Bubble-Cap Tower
Total Pressure = 1 Atmosphere
Mist Present

Run No.	Air Temp. °F	Ent. Liq. Compn. Wt. per cent Caustic	Exit Liquid Rate cc/min	Moles eNO ₂ per Min. Lvg. in Liquid	Gas Rate ft ³ /min	Mole % eNO ₂ Entering	Removal Eff. per cent
90	83	1	320	0.104	1.19	8.00	86.2
100	76	1	319	0.0764	1.19	6.14	84.0
110	76	1	323	0.0597	1.19	5.00	81.8
120	76	1	324	0.0443	1.19	4.02	76.2
130	76	1	318	0.0345	1.19	3.25	74.0
140	82	0	314	0.0942	1.19	7.65	81.9
150	82	0	312	0.0657	1.19	5.72	78.0
160	81	0	308	0.0503	1.19	4.68	73.7
170	81	0	312	0.0397	1.19	3.80	72.2
180	81	0	317	0.0347	1.19	3.10	78.0
190	85	2	315	0.1062	1.19	7.65	92.3
200	85	2	314	0.0770	1.19	5.80	90.0
210	84	2	292	0.0576	1.19	4.78	82.6
220	84	2	294	0.0433	1.19	3.60	83.4
240	84	2	317	0.0565	1.19	4.72	82.0
250	86	3.5	322	0.1020	1.20	7.65	88.6
260	86	3.5	322	0.0702	1.20	5.75	82.8
270	86	3.6	319	0.0545	1.20	4.80	77.8
280	86	3.6	319	0.0440	1.20	3.80	80.2
310	79	2	315	0.0780	1.19	5.78	91.5
320	79	2	319	0.0648	1.19	4.78	92.8
330	79	2	313	0.0474	1.19	3.80	86.4
360	76	0	323	0.0750	1.19	5.78	88.0
370	76	0	325	0.0582	1.19	4.78	83.4
380	76	0	323	0.0432	1.19	3.80	78.7
390	76	0	323	0.0322	1.19	3.10	72.4