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Engineering Experiment Station

University of Illinois

September 30, 1953

Technical Report No. 10

REMOVAL OF NITROGEN OXIDES FROM GASEOUS MIXTURES

by

M. S. Peters

C. P. Ross

L. B. Andersen

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Contract No. AT(30-3)-28

U. S. Atomic Energy Commission

H. F. Johnstone, Technical Director

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3	Knolls Atomic Power Laboratory	58-60
2	Los Alamos Field Office	61-62
6	Los Alamos Scientific Laboratory	63-68
1	Mallinckrodt Chemical Works	69
1	Massachusetts Institute of Technology (Eliassen)	70
1	Massachusetts Institute of Technology (Hood Bldg. Kaufman)	71
2	Mound Laboratory	72-73
1	National Bureau of Standards	74
1	Naval Biological Defense Laboratory	75
1	Naval Research Laboratory	76
1	Ohio State University (Lapple)	77
1	North American Aviation, Inc.	78
2	Savannah River Operations Office (Wilmington)	79-80
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2	Santa Fe Operations Office	84-85
1	Schenectady Operations Office	86
1	Patent Branch, Washington	87
1	Public Health Service (J. G. Terrill)	88
75	Technical Information Service, Oak Ridge	89-163
1	UCIA Medical Research Laboratory (Warren)	164
3	University of California Radiation Laboratory (Thaxter)	165-167
1	University of California Los Angeles (Baurmash)	168
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FOREWORD

The work covered in this report is a part of a research program of fundamental studies on aerosols as they are related to practical problems in atmospheric pollution and gas purification operations. The original program was initiated June 1, 1949 under Contract Number AT(30-3)-28 with the U. S. Atomic Energy Commission.

This report deals with studies on the removal of nitrogen oxides from gaseous mixtures and covers the work done from the inception of the program on nitrogen oxides on June 1, 1952 through August 15, 1953. Progress made during this period has been reported in the regular monthly reports and in Annual Progress Report and Program Outlines, ILLU-ES-43, May 31, 1952 and ILLU-ES-56, April 30, 1953.

The work described herein dealing with the bubble-cap absorption unit was performed by C. P. Ross as the subject of a thesis for the degree of Master of Science in Chemical Engineering under the direction of Professor M. S. Peters. The work on the venturi atomizer was carried out by L. B. Andersen as a part of a Ph.D. thesis in Chemical Engineering under the direction of Professor H. F. Johnstone.

This report presents and interprets the data obtained in careful experimentation and gives a theoretical analysis of the controlling factors in the removal of nitrogen oxides from gaseous mixtures.

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REMOVAL OF NITROGEN OXIDES FROM GASEOUS MIXTURES

by M. S. Peters, C. P. Ross, and L. B. Andersen

Engineering Experiment Station
University of Illinois
Urbana, Illinois

September 30, 1953

ABSTRACT

Nitrogen dioxide and dinitrogen tetroxide may be removed from gaseous mixtures by contact with water. The mechanism of the removal process has been studied in this work using a bubble-cap plate column and a venturi atomizer.

The rates of the chemical reactions involved in the removal process were found to be the controlling factor in the over-all mechanism. The major chemical reactions occur between N_2O_4 and NO_2 , respectively, and water vapor in the gas film. The removal efficiency was greatest at high concentrations of nitrogen oxides (NO_2 and N_2O_4) which correspond to high fractions of N_2O_4 in the equilibrium mixture of NO_2 and N_2O_4 .

The absorption rates obtained with the venturi atomizer were much higher than with conventional absorption equipment due to the large liquid surface available with a venturi atomizer. Tests with steam added to the entering gases indicated that an increase in humidity increases the rate of removal of nitrogen oxides from gaseous mixtures.

TABLE OF CONTENTS

	<u>Page</u>
Distribution List	ii
Foreword	iv
Abstract	v
I. Introduction	1
II. Analysis of the Mechanisms Involved in the Removal of Nitrogen Oxides from Gases	3
A. Gas-Phase Reaction and Liquid-Phase Reaction	4
1. The Gas-Phase Reaction	5
2. The Liquid-Phase Reaction	7
B. Diffusion as the Controlling Mechanism	8
C. Chemical Reaction Rates as the Controlling Factor in the Over-all Mechanism	10
1. Chemical Kinetics of the Nitrogen Oxides Reactions ...	11
2. Simplification and Integration of Rate Equations	17
III. Experimental Equipment and Procedure	20
A. Bubble-Cap Plate Column	20
1. Equipment	20
2. Procedure	22
3. Method of Reporting Absorption Efficiencies	24
B. Venturi Atomizer	25
IV. Discussion of Results	27
A. Bubble-Cap Plate Column	27
1. Efficiency	27
2. Rate of Removal of Oxides from Gases	29

TABLE OF CONTENTS (CONTINUED)

	<u>Page</u>
3. General Observations	29
4. Chemical Reaction Rate as the Controlling Mechanism	30
B. Venturi Atomizer	32
1. Oxygen Absorption	32
2. Simultaneous NO ₂ and O ₂ Absorption	33
3. Steam Injection	35
V. Summary and Conclusions	36
VI. Table of Nomenclature	38
VII. Bibliography	40
Appendix	41
Sample Calculations	41
Bubble-Cap Plate Column	41
Venturi Atomizer	45

LIST OF FIGURES

Figure No.

1. Bubble-Cap Plate Column Experimental Equipment	47
2. Venturi Atomizer Experimental Equipment	49
3. Sample-Collection Tube for Venturi Atomizer	51
4. Effect of eNO ₂ Concentration in Entering Gas on Absorption Efficiency in Bubble-Cap Column	53
5. Effect of eNO ₂ Concentration in Entering Gas on Absorption Efficiency in Bubble-Cap Column	53

TABLE OF CONTENTS (CONTINUED)

<u>Figure No.</u>	<u>Page</u>
6. Effect of eNO_2 Concentration on Fraction of Total Oxides Present as N_2O_4	55
7. Variation of Efficiency with Fraction N_2O_4 and NO_2 in the Oxides in Bubble-Cap Column	57
8. Effect of N_2O_4 Concentration on Rate of Oxides Removal in Bubble-Cap Column	59
9. Experimental Test for Validity of Reaction Rate Equations	61
10. Predicted Curve for Relationship Between Entering and Exit N_2O_4 Concentrations	63
11. Effect of Gas Concentration on Ratio of Original N_2O_4 Partial Pressure to Final N_2O_4 Partial Pressure in Bubble-Cap Column	65
12. Oxygen Absorption in Venturi Atomizer	67
13. Mass Transfer Coefficients in Venturi Atomizer	67
14. Absorption of NO_2 by Water in Venturi Atomizer	69
15. Comparison Between Oxygen Absorption in Pure Water and in a Water Solution Containing HNO_3 and HNO_2 in Venturi Atomizer	73
16. Comparison of Concentration of Acid Formed from Gases Containing NO and from Gases Containing no NO in Venturi Atomizer	75
17. Effect of Steam Injection Rate on Acid Concentration Obtained in Venturi Atomizer	77
18. Equilibrium Constant for NO_2 and NO over Nitric Acid	79
19. Equilibrium Between NO_2 and N_2O_4	81

042-006

TABLE OF CONTENTS (CONTINUED)

LIST OF TABLES

<u>Table No.</u>	<u>Page</u>
I. Tabulated Data and Results for Bubble-Cap Plate -	
Part I	83
II. Tabulated Data and Results for Bubble-Cap Plate -	
Part II	89
III. Data for Oxygen Absorption with Venturi Atomizer	93
IV. Data for $\text{NO}_2\text{-O}_2$ Absorption with Venturi Atomizer	95
V. Data for $\text{NO}_2\text{-NO-O}_2$ Absorption with Venturi Atomizer	97
VI. Data for Steam Injection with Venturi Atomizer	99

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REMOVAL OF NITROGEN OXIDES FROM GASEOUS MIXTURES

by M. S. Peters, C. P. Ross, and L. B. Andersen

Engineering Experiment Station

University of Illinois

Urbana, Illinois

September 30, 1953

I. INTRODUCTION

The removal of nitrogen oxides from gaseous mixtures is an important commercial operation involved in the production of nitric acid and in the cleaning of certain stack gases. The removal may be accomplished by the reaction of nitrogen dioxide (NO_2) or dinitrogen tetroxide (N_2O_4) with water to give nitric acid and nitric oxide (NO). The chemical reactions of the various nitrogen oxides with themselves, with oxygen, and with water have been investigated extensively during the last forty years, and the results of these investigations have been published in the chemical literature. However, very little work has been done on the actual mechanisms involved in the removal of nitrogen oxides from gaseous mixtures.

Industrial nitric acid units use bubble-cap plate towers or packed towers to obtain the necessary contact between water and the gases containing nitrogen oxides. Although these methods have been used for many years, few efforts have been made to determine the efficiency of the units or to devise better methods for removing the oxides.

The purpose of the work presented in this report has been to study the fundamental mechanisms controlling the removal of nitrogen oxides from gaseous mixtures and to develop improved methods for recovering the oxides. Experimental data on the efficiency of nitrogen oxides

removal from gases have been obtained using a conventional bubble-cap plate column. Studies have also been made on the recovery efficiency using a venturi atomizer to obtain the necessary contact between the gases and water.

In order to develop improved methods for recovering the oxides, it is necessary to understand the controlling mechanisms in the oxide recovery process. For example, if the chemical reaction rate in the gas film or the liquid film were the controlling factor in determining the rate of removal of the gaseous oxides, the recovery equipment should provide the largest possible liquid surface area in order to obtain the maximum amount of oxide removal. Under these conditions, the venturi atomizer should be very efficient since the atomized liquid would offer a large area for liquid-gas contact.

The possibility of gas-phase and liquid-phase reactions has been considered in this work. A theoretical analysis of the overall mechanism has been developed and the results have been checked with experimental data.

II. ANALYSIS OF THE MECHANISMS INVOLVED IN THE REMOVAL OF NITROGEN OXIDES FROM GASES

The nitrogen oxides of importance 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, according to Verhoek and Daniels¹⁴ and Smith and Daniels¹¹, these compounds rapidly come to equilibrium with NO and NO_2 and represent only a small fraction of the total oxides at room temperatures or above.

The essential chemical reactions occurring in the removal process may be written as follows:

Reaction (D) reaches equilibrium very rapidly¹³ and the equilibrium constant for this reaction is known as a function of temperature between 0°C . and 90°C .^{10, 14, 15} The oxidation of NO proceeds relatively slowly although the reaction goes essentially to completion. Reaction-rate constants for the oxidation reaction have been determined by Bodenstein.¹

The decomposition of nitrous acid in the liquid phase does not occur rapidly unless the liquid is well agitated. However, under ordinary conditions, this reaction is not the controlling factor in determining the rate of oxides removal since analyses of the liquid product indicate only small amounts of nitrous acid. The NO liberated by the decomposition of nitrous acid may be partially oxidized in the liquid phase by absorbed oxygen. The liquid-phase oxidation reaction could be important only if the rate of oxygen absorption into the liquid were high. The rate of oxygen

absorption into water is very low with most types of absorption equipment; however, the absorption rate can be increased greatly by the use of a venturi atomizer since this type of equipment provides a large interfacial area between the gas and the liquid droplets.⁶

A. Gas-Phase Reaction and Liquid-Phase Reaction

In the past, almost all workers dealing with the reactions between nitrogen oxides and water have assumed that the reactions occur in the liquid phase. They assume the NO_2 and N_2O_4 diffuse into the liquid where the reaction with H_2O occurs. The nitrous acid formed decomposes into NO_2 , H_2O and NO . The NO_2 reacts with more water while the NO is partially oxidized to NO_2 by absorbed oxygen in the liquid phase. Most of the NO is desorbed from the liquid and is oxidized to NO_2 in the gas phase.

The liquid-phase reaction undoubtedly occurs to some extent. However, the results of the present work and those of Chambers and Sherwood³ definitely indicate that a gas-phase reaction does occur, and, under certain conditions, this reaction may be much more important than the liquid-phase reaction.

1. The Gas-Phase Reaction.— There is much evidence to support the occurrence of a gas-phase reaction between water vapor and N_2O_4 or NO_2 . Perhaps the strongest support of the gas-phase reaction lies in the observable formation of a mist when gases containing NO_2 and N_2O_4 are brought into contact with a gas containing appreciable amounts of water vapor. The mist formation has been observed repeatedly in this work and was reported by Chambers and Sherwood³.

In carefully controlled experimental tests carried out in the present work, gaseous N_2O_4 and NO_2 were admitted to a bulb containing nitrogen and water vapor. No droplets of liquid water were present in the bulb

in any form before the admittance of the nitrogen oxides. As soon as the oxides entered the bulb, a mist was formed which quickly spread throughout the entire bulb. The same type of mist was observed when N_2O_4 and NO_2 were brought into contact with liquid water with the mist having the greatest density just above the water surface.

The mist is undoubtedly composed of droplets containing nitric acid and water. The saturation vapor pressure of HNO_3 is very low over dilute liquid mixtures of HNO_3 in water. It is conceivable, therefore, that the vapor-phase reaction could produce enough HNO_3 vapor to cause the formation of droplets of dilute nitric acid.

McHaney⁷, by means of photometric methods, has determined equilibrium constants for the vapor-phase reaction between nitrogen oxides and water. He has compared his experimental results with values calculated from free energy data available in the literature. The following are his results at 45° C.

$$K_I = \frac{P_{HNO_3}^2 P_{NO}}{P_{N_2O_4}^{3/2} P_{H_2O}} \quad \frac{1/2}{\text{atm.}}$$

$$K_{II} = \frac{P_{HNO_3}^2 P_{NO}}{P_{NO_2}^3 P_{H_2O}} \quad \frac{-1}{\text{atm.}}$$

Temperature, 45° C.

	<u>Experimental</u>	<u>Calculated</u>
K_I	0.0036	0.00392
K_{II}	0.0070	0.00973

Although these equilibrium constants are very small, it should be

possible for the vapor-phase reaction to form a considerable amount of nitric acid in the presence of water vapor because the nitric acid formed in the reaction would condense out of the gas continuously. According to McHaney, the vapor-phase reaction proceeds rapidly, the half time for equilibrium being approximately 30 seconds.

The following is a brief summary of the evidence in support of the occurrence of the gas-phase reaction.

1. A mist is formed when gaseous N_2O_4 and NO_2 are brought into contact with water vapor.

2. In the commercial production of nitric acid, about 40 percent of the total nitric-acid production is formed in cooler condensers where vapors containing H_2O , NO_2 , N_2O_4 , NO , N_2 , and O_2 are cooled. The acid formed has a strength of about 40 weight percent nitric acid. It seems unlikely that all of this absorption and reaction could occur in the liquid phase formed by the condensation of pure water.

3. Experimental results obtained with a wetted-wall column indicate that the rate of N_2O_4 and NO_2 absorption into aqueous $CaCl_2$ is less than that into pure water with all other conditions held constant². If the reaction were primarily in the gas phase, this effect would be expected because of the lower vapor pressure of water. However, if the reaction were primarily in the liquid phase, the only possible explanation for reduction in the absorption rate would be a decrease in the reactivity of the water caused by the presence of $CaCl_2$.

4. When N_2O_4 and NO_2 react with aqueous $NaOH$, some NO is found in the gas phase³. If the reaction were in the liquid phase, no NO would be formed since the nitrogen oxides would react with $NaOH$ to form $NaNO_3$ and $NaNO_2$.

2. Liquid-Phase Reaction.-- There is little evidence to indicate that the liquid-phase reaction between water and NO_2 or N_2O_4 is important under ordinary conditions. Caudle and Denbigh², from experiments with a wetted-wall column, reported that neither increasing the gas-space volume nor increasing the bulk liquid volume had any effect on the rate of removal of nitrogen oxides by liquid water. The rate of removal was proportional to the interfacial area between the gas and the liquid. Therefore, the controlling resistance must lie in the gas film or in the liquid film.

In direct contradiction to the data of Chambers and Sherwood, Caudle and Denbigh reported that no NO was found in the gas phase when NO_2 and N_2O_4 reacted with aqueous solutions of NaOH . Even if Caudle and Denbigh were correct, this would not be conclusive evidence in favor of a liquid-phase reaction since the nitrogen oxides could react with water vapor in the gas phase to form HNO_3 and HNO_2 followed by immediate absorption and reaction of the HNO_2 in the liquid.

According to the results of this work, liquid water or dilute nitric acid which has been in contact with gaseous NO_2 or N_2O_4 has an appreciable oxygen demand due to the presence of dissolved NO or HNO_2 . Since the solubility of NO is not sufficiently great to account for all the oxygen demand, it must be concluded that some HNO_2 is present in the liquid phase. However, in the bubble-cap plate unit where the liquid was highly agitated, the actual amount of HNO_2 present was found to be small relative to the total amount of HNO_3 even in dilute solutions.

The evidence in support of the gas-phase reaction and in support of the liquid-phase reaction indicates that the major reaction occurs in the gas film. Gaseous NO_2 and N_2O_4 react with water vapor to form HNO_3

and HNO_2 . Most of the HNO_3 diffuses into the liquid phase while some H_2O and HNO_3 condense in the form of a mist containing small droplets of dilute nitric acid. Part of the HNO_2 decomposes in the vapor space giving NO , NO_2 , and H_2O while the rest diffuses into the liquid where the same decomposition products are obtained.

The preceding analysis of the process mechanism is consistent with the observed data. However, it should not be concluded that the liquid-phase reaction is nonexistent. Part of the HNO_2 decomposition reaction occurs in the liquid phase and undoubtedly a portion of the NO_2 and N_2O_4 diffuses into the liquid phase before reacting with water. Under ordinary conditions, the major reaction occurs in the gas film, but it may be possible to make the liquid-film or liquid-phase reaction become important by promoting the HNO_2 decomposition in this phase or by increasing the rate of oxygen absorption into the liquid.

B. Diffusion as the Controlling Mechanism

The rate of the over-all process by which nitrogen oxides are removed from gaseous mixtures by chemical reaction with water could be controlled by (a) diffusional resistances, (b) the speed of the chemical reactions, or (c) a combination of diffusional resistance and chemical reaction rate. The following diffusional resistances could be of importance in the process assuming both liquid and gas phase reactions can occur:

(a) Diffusion of NO_2 and N_2O_4 through the gas film or the liquid film.

(b) Diffusion of H_2O through the gas film or the liquid film.

(c) Diffusion of NO through the gas film or the liquid film.

(d) Diffusion of HNO_3 through the gas film or the liquid film.

(e) Diffusion of HNO_2 through the gas film or the liquid film.

(f) Diffusion of O_2 through the gas film or the liquid film.

Chambers and Sherwood³ assumed the controlling mechanism to be the physical diffusion of NO_2 and N_2O_4 through the gas film. Under these conditions, the following expression for the absorption rate, expressed as gram moles of equivalent combined nitrogen [i.e., moles of $\text{NO}_2 + 2$ (moles of N_2O_4)] per second per square centimeter of gas-liquid interfacial area, may be derived:

$$N_{\text{eNO}_2} = \frac{2D_{\text{N}_2\text{O}_4}}{x_f} \Delta C_{\text{N}_2\text{O}_4} + \frac{D_{\text{NO}_2}}{x_f} \Delta C_{\text{NO}_2} \quad (1)$$

where,

N_{eNO_2} = rate of nitrogen oxides absorption based on equivalent NO_2 removal [eNO₂ = moles of $\text{NO}_2 + 2$ (moles of N_2O_4)] , gram moles/(sec.)(sq.cm.).

$D_{\text{N}_2\text{O}_4}$ = gaseous diffusivity of N_2O_4 , sq. cm./sec.

D_{NO_2} = gaseous diffusivity of NO_2 , sq. cm./sec.

x_f = effective film thickness, cm.

$\Delta C_{\text{N}_2\text{O}_4}$ = difference in N_2O_4 concentration between main body of gas and gas-liquid interface, gram moles/cc.

ΔC_{NO_2} = difference in NO_2 concentration between main body of gas and gas-liquid interface, gram moles/cc.

Instantaneous attainment of equilibrium between NO_2 and N_2O_4 is assumed in the derivation of Equation 1. The result is the same as for the diffusion of NO_2 and N_2O_4 under conditions in which the two gases have no effect on each other.

Equation 1 cannot apply unless the chemical reactions are irreversible. Since the chemical reactions between nitrogen oxides and water are reversible under certain conditions (such as high NO concentration

or high nitric acid concentration), the general validity of Equation 1 is doubtful.

According to the experimental results of this work and the results of Caudle and Denbigh², the rate of nitrogen oxides removal (N_{eNO_2}) is directly proportional to the concentration of N_2O_4 in gases containing more than about 2 volume percent equivalent NO_2 . The ratio $D_{NO_2}/D_{N_2O_4}$ is 1.43³ and the NO_2 concentration in all the experimental runs was larger than the N_2O_4 concentration. Therefore, since NO_2 and N_2O_4 may be assumed to be always in equilibrium, ΔC_{NO_2} was larger than $\Delta C_{N_2O_4}$. Under these conditions, Equation 1 is not supported by the experimental results since Equation 1 shows that the absorption rate should be determined to a large extent by the NO_2 concentration, and it must be concluded that the diffusion of NO_2 and N_2O_4 through the gas film is not the controlling mechanism.

Using a method similar to that of Hatta⁵, differential equations based on combined diffusional resistance and chemical reaction rate as the controlling mechanism have been derived. These equations either could not be integrated or did not agree with the experimental data. A similar approach based on the two-film theory was attempted by Caudle and Denbigh using methods such as those described by Van Krevelen and Hoftijzer¹³. They were unsuccessful in developing any applicable relationships including diffusion as a controlling factor.

C. Chemical Reaction Rates as the Controlling Factor in the Over-all Mechanism

The reactions involved in the removal of nitrogen oxides from gases by reaction with water are reversible and proceed at a finite rate. Therefore, it is possible that the over-all process is controlled by the rate of the chemical reactions. On this basis, an analysis of the process has been

developed by the application of chemical kinetics, and the results agree closely with the experimental data.

Denbigh and Prince⁴ and Caudle and Denbigh² have obtained data on the rate of nitrogen dioxide removal by reaction with water. They interpreted their results on the basis of chemical kinetics based on the chemical reaction rate as the controlling factor. Their experimental results indicated that the absorption rate was proportional to the N_2O_4 concentration in the gas, and they assumed the reaction between N_2O_4 and H_2O was controlling. They also presented semi-empirical equations which took the reversibility of the reactions into account.

A complete analysis of the chemical reaction kinetics has been made in this work taking into consideration the reversible reactions involving N_2O_4 and NO_2 . The results show good agreement with experimental data. The derivation of the kinetic relationships is presented in the following section while the comparison with experimental data is presented in the section of this report dealing with experimental results.

1. Chemical Kinetics of the Nitrogen Oxides Reactions.-

Equilibrium between NO_2 and N_2O_4 is attained very rapidly and, in the following derivation, these two materials are assumed to be continuously in equilibrium. Under this condition, the important chemical reactions involved in the removal of NO_2 and N_2O_4 from gaseous mixtures by reaction with water can be written as follows:

By summation of Reactions (a) and (d),

By summation of Reactions (b) and (e),

where,

k_1 = reaction rate constant based on N_2O_4

k_2 = reaction rate constant based on HNO_2

k_3 = reaction rate constant based on NO_2

k_4 = reaction rate constant based on HNO_2

k_5 = reaction rate constant based on HNO_2

k_6 = reaction rate constant based on N_2O_4

k_7 = reaction rate constant based on HNO_2

k_8 = reaction rate constant based on NO_2

Reactions (a), (b), and (f) occur simultaneously while Reactions (d) and (e) are consecutive to Reactions (a) and (b). Reaction (a) is a bimolecular reaction and, therefore, should proceed at a faster rate than Reaction (b) which is trimolecular. However, Reaction (b) cannot be neglected because it may become important when the concentration of NO_2 is large relative to the N_2O_4 concentration. At low total concentration of equivalent NO_2 ($C_{\text{eNO}_2} = C_{\text{NO}_2} + 2C_{\text{N}_2\text{O}_4}$), only a small fraction of the total oxides is in the form of N_2O_4 . For example, at 25°C and a total pressure of one atmosphere, a gaseous mixture containing 0.1 mole percent eNO_2 has 1.3 percent of the equivalent oxides in the form of N_2O_4 ; but 43 percent of the equivalent oxides is in the form of N_2O_4 in a gaseous mixture containing 10 mole percent eNO_2 at the same temperature and total

pressure. (See Figure 6). Therefore, as the total concentration of gaseous nitrogen oxides decreases, the efficiency of the removal process should decrease because the slow Reaction (b) tends to become controlling. This has been observed experimentally in the present work. Consequently, an analysis of the overall process must include a consideration of the effects caused by Reaction (b).

The reaction between NO and O₂ to yield NO₂ and N₂O₄ proceeds at a relatively slow rate. This reaction has not been considered here because the analysis deals only with the nitrogen oxides removal which can be accomplished by a one-stage contact with water. The NO oxidation does not proceed at a sufficient rate to cause an appreciable change in the NO₂ concentration while in contact with the liquid. This conclusion has been verified experimentally in the bubble-cap column by substituting nitrogen for air in the entering gases.

In the following derivation, C represents the concentration in gram moles per cubic centimeter and the subscript on the C represents the particular material to which the concentration refers. The symbol t represents time in seconds.

According to Reaction (a),

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_a = k_1 (C_{N_2O_4})(C_{H_2O}) - k_2 (C_{HNO_2})(C_{HNO_3}) \quad (2)$$

According to Reaction (d),

$$\left(\frac{dC_{N_2O_4}}{dt}\right)_d = \frac{k_5}{4} (C_{HNO_2})^2 = k_6 (C_{NO})(C_{N_2O_4})^{1/2} (C_{H_2O}) \quad (3)$$

Therefore, the total change in N₂O₄ concentration caused by Reaction (a) followed by Reaction (d) is,

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_{a+d} = k_1 (C_{N_2O_4})(C_{H_2O}) - k_2 (C_{HNO_2})(C_{HNO_3}) + k_6 (C_{NO})(C_{N_2O_4})^{\frac{1}{2}}(C_{H_2O}) - \frac{k_5}{4} (C_{HNO_2})^2 \quad (4)$$

In a continuous process involving consecutive reactions, a so-called "stationary state" may be reached in which the concentrations of the intermediate reacting materials are essentially constant. Unless Reaction (d) [or (e)] is extremely slow, a stationary state will be obtained very quickly in this process and the HNO_2 concentration will change very slowly. Under these conditions, Reaction (g) applies and one mole of NO is formed [by Reaction (d)] for every $3/2$ moles of N_2O_4 which disappear [net N_2O_4 loss by Reactions (a) and (d)]. Therefore, according to Reaction (g),

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_{a+d} = \frac{3}{2} \left(\frac{dC_{NO}}{dt}\right)_d \quad (5)$$

According to Reaction (d),

$$\left(\frac{dC_{NO}}{dt}\right)_d = \frac{k_5}{2} (C_{HNO_2})^2 - 2k_6 (C_{NO})(C_{N_2O_4})^{\frac{1}{2}}(C_{H_2O}) \quad (6)$$

Combining Equations 5 and 6,

$$k_6 (C_{NO})(C_{N_2O_4})^{\frac{1}{2}}(C_{H_2O}) - \frac{k_5}{4} (C_{HNO_2})^2 = \frac{1}{3} \left(\frac{dC_{N_2O_4}}{dt}\right)_{a+d} \quad (7)$$

Combining Equations 4 and 7,

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_{a+d} = \frac{3}{4} k_1 (C_{N_2O_4})(C_{H_2O}) - \frac{3}{4} k_2 (C_{HNO_2})(C_{HNO_3}) \quad (8)$$

Since NO_2 and N_2O_4 are continuously in equilibrium, a change in N_2O_4 concentration is caused by Reaction (f). The rate of this concentration change may be represented by $\left(\frac{dC_{\text{N}_2\text{O}_4}}{dt}\right)_f$.

The net rate of change in N_2O_4 concentration caused by Reactions (a), (d), and (f) is,

$$-\left(\frac{dC_{\text{N}_2\text{O}_4}}{dt}\right)_{\text{net}} = -\left(\frac{dC_{\text{N}_2\text{O}_4}}{dt}\right)_{a+d+f} = \frac{3}{4} k_1 (C_{\text{N}_2\text{O}_4})(C_{\text{H}_2\text{O}}) - \frac{3}{4} k_2 (C_{\text{HNO}_2})(C_{\text{HNO}_3}) - \left(\frac{dC_{\text{N}_2\text{O}_4}}{dt}\right)_f \quad (9)$$

By applying the same reasoning as was used for developing Equation 9, it is possible to obtain a similar equation representing the net rate of disappearance of NO_2 . The method is as follows:

According to Reaction (b),

$$-\left(\frac{dC_{\text{NO}_2}}{dt}\right)_b = k_3 (C_{\text{NO}_2})^2 (C_{\text{H}_2\text{O}}) - 2 k_4 (C_{\text{HNO}_2})(C_{\text{HNO}_3}) \quad (10)$$

According to Reaction (e),

$$\left(\frac{dC_{\text{NO}_2}}{dt}\right)_e = \frac{1}{2} k_7 (C_{\text{HNO}_2})^2 - k_8 (C_{\text{NO}})(C_{\text{NO}_2})(C_{\text{H}_2\text{O}}) \quad (11)$$

Therefore, the total rate of change in NO_2 concentration caused by Reaction (b) followed by Reaction (e) is,

$$-\left(\frac{dC_{NO_2}}{dt}\right)_{b+e} = k_3 (C_{NO_2})^2 (C_{H_2O}) - 2 k_4 (C_{HNO_2})(C_{HNO_3}) + k_8 (C_{NO})(C_{NO_2})(C_{H_2O}) - \frac{1}{2} k_7 (C_{HNO_2})^2 \quad (12)$$

According to Reaction (h),

$$-\left(\frac{dC_{NO_2}}{dt}\right)_{b+e} = 3 \left(\frac{dC_{NO}}{dt}\right)_e \quad (13)$$

According to Reaction (e),

$$\left(\frac{dC_{NO}}{dt}\right)_e = \frac{1}{2} k_7 (C_{HNO_2})^2 - k_8 (C_{NO})(C_{NO_2})(C_{H_2O}) \quad (14)$$

Combining Equations 12, 13, and 14,

$$-\left(\frac{dC_{NO_2}}{dt}\right)_{b+e} = \frac{3}{4} k_3 (C_{NO_2})^2 (C_{H_2O}) - \frac{3}{2} k_4 (C_{HNO_2})(C_{HNO_3}) \quad (15)$$

The rate of change in NO_2 concentration due to Reaction (f) is $\left(\frac{dC_{NO_2}}{dt}\right)_f$.

The net rate of change in NO_2 concentration caused by Reactions (b), (e), and (f) is,

$$-\left(\frac{dC_{NO_2}}{dt}\right)_{net} = -\left(\frac{dC_{NO_2}}{dt}\right)_{b+e+f} = \frac{3}{4} k_3 (C_{NO_2})^2 (C_{H_2O}) - \frac{3}{2} k_4 (C_{HNO_2})(C_{HNO_3}) - \left(\frac{dC_{NO_2}}{dt}\right)_f \quad (16)$$

The rate of change in N_2O_4 concentration caused by Reaction (f) must be one-half of the rate of change in NO_2 concentration due to this reaction, or,

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_f = \frac{1}{2} \left(\frac{dC_{NO_2}}{dt}\right)_f \quad (17)$$

Equations 9, 16, and 17 may be combined to give,

$$\begin{aligned} -\left(\frac{dC_{N_2O_4}}{dt}\right)_{net} - \frac{1}{2} \left(\frac{dC_{NO_2}}{dt}\right)_{net} &= \frac{3}{4} k_1 (C_{N_2O_4})(C_{H_2O}) - \frac{3}{4} k_2 (C_{HNO_2})(C_{HNO_3}) \\ &+ \frac{3}{8} k_3 (C_{NO_2})^2 (C_{H_2O}) - \frac{3}{4} k_4 (C_{HNO_2})(C_{HNO_3}) \end{aligned} \quad (18)$$

or

$$\begin{aligned} -\frac{4}{3} \left(\frac{dC_{N_2O_4}}{dt}\right)_{net} - \frac{2}{3} \left(\frac{dC_{NO_2}}{dt}\right)_{net} &= k_1 (C_{N_2O_4})(C_{H_2O}) + \frac{k_3}{2} (C_{NO_2})^2 (C_{H_2O}) \\ &- (k_2 + k_4)(C_{HNO_2})(C_{HNO_3}) \end{aligned} \quad (19)$$

Since Reaction (f) is at continuous equilibrium,

$$K_c = \text{equilibrium constant} = \frac{C_{N_2O_4}}{(C_{NO_2})^2} \quad (20)$$

and

$$dC_{NO_2} = \frac{dC_{N_2O_4}}{2 \sqrt{K_c C_{N_2O_4}}} \quad (21)$$

Combination of Equations 19, 20, and 21 gives,

$$\begin{aligned} -\frac{4}{3} \left(\frac{dC_{N_2O_4}}{dt}\right)_{net} - \frac{1}{3 \sqrt{K_c C_{N_2O_4}}} \left(\frac{dC_{N_2O_4}}{dt}\right)_{net} &= (k_1 + \frac{k_3}{2K_c})(C_{N_2O_4})(C_{H_2O}) \\ &- (k_2 + k_4)(C_{HNO_2})(C_{HNO_3}) \end{aligned} \quad (22)$$

Only three assumptions have been made in the derivation of Equation 22. They are (1) NO_2 and N_2O_4 are in continuous equilibrium, (2) the reactions as indicated represent the important chemical process, and (3) a stationary state is rapidly obtained. All of these assumptions appear to be justified on the basis of results obtained in this work and by other investigators.

2. Simplification and Integration of Rate Equations.— If the net chemical Reactions (g) and (h) are essentially irreversible, the last term

in Equation 22 may be neglected. If the irreversible reaction occurs in the gas film, the concentration of HNO_3 is very small since it diffuses rapidly into the liquid phase. Under any conditions, if the reactions are irreversible, the concentration of HNO_2 is very small.

The concentration of H_2O may be assumed as constant at any given temperature. If the reaction occurs in the gas film, the H_2O concentration is directly proportional to the H_2O vapor pressure and, if the reaction occurs in the liquid film, the H_2O concentration (or activity) is essentially constant unless there is a very large change in the acid concentration.

With these two simplifications, Equation 22 can be written as follows:

$$-\left(\frac{dC_{\text{N}_2\text{O}_4}}{dt}\right)_{\text{net}} = \frac{1}{4 \sqrt{K_c} C_{\text{N}_2\text{O}_4}} \left(\frac{dC_{\text{N}_2\text{O}_4}}{dt}\right)_{\text{net}} = A (C_{\text{N}_2\text{O}_4}) \quad (23)$$

where $A = \frac{3}{4} (k_1 + \frac{k_3}{2K_c}) (C_{\text{H}_2\text{O}})$.

For gas concentrations less than about 10 percent eNO_2 , the volumetric flow rate remains essentially constant, and, under this condition, Equation 23 may be integrated directly. The equation may be rearranged and integrated between the limits of zero time (corresponding to an original N_2O_4 concentration of $C_{\text{O}_\text{N}_2\text{O}_4}$) and the time (t) any portion of the gas is in contact with the liquid (corresponding to a final N_2O_4 concentration of $C_{\text{f}_\text{N}_2\text{O}_4}$).

$$-\int_{C_{\text{O}_\text{N}_2\text{O}_4}}^{C_{\text{f}_\text{N}_2\text{O}_4}} \frac{dC_{\text{N}_2\text{O}_4}}{C_{\text{N}_2\text{O}_4}} = \frac{1}{4 \sqrt{K_c}} \int_{C_{\text{O}_\text{N}_2\text{O}_4}}^{C_{\text{f}_\text{N}_2\text{O}_4}} \frac{dC_{\text{N}_2\text{O}_4}}{(C_{\text{N}_2\text{O}_4})^2} = A \int_0^t dt \quad (24)$$

Integration and substitution of the limits gives,

$$\ln \frac{C_{\text{O}_\text{N}_2\text{O}_4}}{C_{\text{f}_\text{N}_2\text{O}_4}} + \frac{1}{2 \sqrt{K_c}} \left[\frac{1}{(C_{\text{f}_\text{N}_2\text{O}_4})^2} - \frac{1}{(C_{\text{O}_\text{N}_2\text{O}_4})^2} \right] = A t \quad (25)$$

Equation 25 may be rearranged to give the following equation:

$$\frac{1}{(C_{fN_2O_4})^{\frac{1}{2}}} = \frac{1}{(C_{oN_2O_4})^{\frac{1}{2}}} - 2\sqrt{K_c} \ln \frac{C_{oN_2O_4}}{C_{fN_2O_4}} + B t \quad (26)$$

where $B = 2 A \sqrt{K_c}$. Therefore, if the reactions occur irreversibly and all concentration values are determined at approximately the same temperature and a constant value of t , a plot of $\frac{1}{(C_{fN_2O_4})^{\frac{1}{2}}}$ versus $\left[\frac{1}{(C_{oN_2O_4})^{\frac{1}{2}}} - 2\sqrt{K_c} \ln \frac{C_{oN_2O_4}}{C_{fN_2O_4}} \right]$ should be a straight line with a slope equal to 1.0.

The intercept at $\left[\frac{1}{(C_{oN_2O_4})^{\frac{1}{2}}} - 2\sqrt{K_c} \ln \frac{C_{oN_2O_4}}{C_{fN_2O_4}} \right]$ equal to zero should

be $B t$.

Experimental conditions in which the reactions occur essentially irreversibly may be obtained by contacting gases containing only NO_2 and N_2O_4 (plus air or nitrogen as a diluent) with dilute nitric acid or with pure water. Experimental data for various N_2O_4 concentrations have been obtained under these conditions maintaining constant gas rates (i.e., constant t) and constant temperature (i.e., constant values of A , B , and K_c). These data are plotted in a form equivalent to $\frac{1}{(C_{fN_2O_4})^{\frac{1}{2}}}$

versus $\left[\frac{1}{(C_{oN_2O_4})^{\frac{1}{2}}} - 2\sqrt{K_c} \ln \frac{C_{oN_2O_4}}{C_{fN_2O_4}} \right]$ in Figure 9, and it can be

seen that a straight line is obtained in agreement with Equation 26.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. Bubble-Cap Plate Column

1. Equipment.— Experimental data were collected using a bubble-cap plate column containing one plate with auxiliary equipment as shown in Figure 1. The bubble-cap plate was made of Lucite and was equipped with seven Lucite bubble caps and seven polystyrene gas risers. 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 slot area was 2.46 square inches. This gave a gas velocity through the slots in feet per second approximately equal to the gas rate in cubic feet per minute. The total depth of liquid on the plate was one inch and the tops of the slots were 1/2 inch below the liquid surface.

The inside diameter of the glass column was 7 1/2 inches. There was a distance of 12 inches between the bubble-cap plate and the top and bottom plates. These plates were made of stainless steel.

The Lucite parts of the equipment became cloudy with use, and experiments showed that Lucite softens considerably in nitric acid of moderate concentration. The polystyrene parts of the equipment showed good resistance toward nitric acid.

Water or aqueous nitric acid was fed to the plate from a constant-head tank, through Tygon tubing. The product liquid was delivered from the down-comer to a 20-liter bottle. Small liquid samples were taken through a glass side tube fitted with a stopcock. The liquid flow rate was determined by a rotameter and checked by volume measurements. The rotameter was calibrated against a standard rotameter.

The gaseous nitrogen oxides were diluted with nitrogen or air. The gas stream was admitted to the lower section of the column through Tygon tubing and exhausted from the upper section of the column to a hood. Sampling ports were placed in the inlet and outlet lines.

The gas flow rates were measured by glass venturi meters which were calibrated with air against standard rotameters and corrected for the difference in gas densities. From a knowledge of the equilibrium conditions between NO_2 and N_2O_4 at different temperatures, the density of the entering gas mixture, and hence the flow rate, could be determined. The venturi readings were checked by analysis of the gases.

Air was obtained from the lines in the laboratory, and nitrogen was delivered from a standard cylinder. The NO_2 (with N_2O_4) was obtained by steam-heating a cylinder containing liquid NO_2 and N_2O_4 . Flow rates were regulated by reducing valves and needle valves, those for NO_2 and the liquid being made of stainless steel. The gases were mixed in a glass mixed bulb placed in the line about a foot ahead of the entering-gas sampling point.

Pressures at the top and bottom of the column were measured by open-tube manometers containing α -bromonaphthalene, while the NO_2 -cylinder pressure was measured by a mercury manometer. The indicating fluid in the venturi manometers was also α -bromonaphthalene which is not strongly reactive with NO_2 . Temperatures at the following points were measured by means of copper-constantan thermocouples: (1) Liquid on bubble-cap plate, (2) Entering liquid, (3) Exit liquid, (4) Entering gas, (5) Exit gas.

The bubble-cap plate was equipped with a stainless-steel cooling coil, but no cooling water was needed because the liquid temperature rise

was seldom more than 1°C . Fittings were included to permit drainage of the liquid on the plate and of any condensate which collected in the lower section of the column, the entering gas line, and the exit gas line. Liquid samples were collected in small flasks or large bottles, and gas samples were taken in evacuated Gaillard bulbs fitted with three-way stopcocks.

2. Procedure.- Runs were made at liquid flow rates of 300 and 600 cc./min., gas slot velocities of 0.84, 1.18, 1.65, and 2.35 ft./sec., entering liquid compositions of 0, 15, and 30 weight percent HNO_3 and gas compositions of 1 to 12 volume percent equivalent NO_2 (equivalent $\text{NO}_2 = e\text{NO}_2 = \text{NO}_2 + 2\text{N}_2\text{O}_4$). Several runs included the addition of low-pressure steam to the lower section of the column. Otherwise, all runs were at atmospheric pressure and temperature.

Nitrogen was used as the diluent for the nitrogen oxides during the first seven runs. These runs were checked using air at the same flow conditions, and no significant difference in results was found. Consequently, air was used for the remainder of the runs. If more than one bubble-cap plate had been used or if NO had been admitted to the column with the NO_2 , there would have been a significant difference in the individual results because the air would have supplied oxygen for the oxidation of NO to NO_2 .

At the start of a run, the liquid and air flow rates were set and blank samples of each were taken. Then the NO_2 was admitted at the desired flow rate and the equipment was run until steady-state conditions were attained. The liquid flow from the column was then diverted to the collecting bottle, and liquid was collected for 10 to 20 minutes during which time the flow rates were carefully held constant. The pressures and temperatures were read, and entering and exit gas samples were taken near the beginning and near the end of the timing period. The liquid rate was determined by

measuring the amount of liquid delivered during the time of the run. The liquid sample was analysed for HNO_3 by titrating a known volume (10 or 25 cc.) with standard NaOH solution.

The gas samples were taken in evacuated bulbs to which about 5 cc. of 30 percent hydrogen peroxide had been added. The amount of sample was found by weighing, and the amount of oxides present was determined by titrating the nitric acid formed by the reactions,

Since the entering gases contained only NO_2 (including N_2O_4) and air or nitrogen, the percent $\text{NO}_2 + 2\text{N}_2\text{O}_4$ could be determined. In order to analyse the exit gases for NO and NO_2 , another sample had to be taken or the amount of H_2O_2 reacting had to be determined. However, a knowledge of the total nitrogen or air content of the exit gases was sufficient to enable calculation of the absorption efficiency.

The analysis for both NO and NO_2 was carried out by using an additional sampling bulb containing a known amount of potassium permanganate in sulfuric acid. Under these conditions, the oxides react as follows:

The excess permanganate can be back-titrated with ferrous sulfate as shown below.

The permanganate titration gives the ratio of NO_2 to NO , and this combined with the results from the peroxide bulb gives the total amount of each oxide present in the sample. Good accuracy could not be obtained with this method, principally because a precipitate of MnO_2 formed in the sampling

bulbs and was difficult to remove quantitatively.

The observed exit gas analyses differed considerably from the calculated values based on the liquid analyses. By collecting samples of liquid product under H_2O_2 , it was determined that a slight discrepancy was caused by NO being given up by the liquid. However, a large error in the exit-gas analyses was due to the admittance of a significant amount of mist to the sampling bulbs. It was not possible to determine the amount of mist to make the necessary corrections. The mist also obviated the possibility of analysing the exit gases by photometric methods because the mist would critically interfere with the cell readings. Consequently, all results were reported on the basis of the liquid flow rate, the entering and exit liquid analyses, the air flow rate, and the entering gas analysis.

3. Method of Reporting Absorption Efficiencies.- Absorption efficiencies were reported as Murphree efficiencies based on the total oxide content of the entering and exit gases as shown by the following equation:

$$E = \frac{y_1 - y_2}{y_1 - y_2^*} \quad (100) \quad (27)$$

where,

y_1 = mole fraction ($NO_2 + 2N_2O_4 + NO$) in gases entering plate.

y_2 = mole fraction ($NO_2 + 2N_2O_4 + NO$) in gases leaving plate (calculated from liquid analysis).

y_2^* = mole fraction ($NO_2 + 2N_2O_4 + NO$) in gases leaving plate if theoretical conversion were obtained.

The theoretical conversion of the overall reaction,

was calculated by the method of Sherwood and Pigford¹⁰ using extrapolated

values of the equilibrium constant from Chambers and Sherwood¹⁰. When water (0 percent HNO₃) was used as the absorbent and the entering gases contained only NO₂ (with N₂O₄) and nitrogen or air, the calculated theoretical conversion was practically 66 2/3 percent based on the total gaseous oxides. This indicates the reaction is essentially irreversible under these conditions because one mole of NO theoretically can be liberated for every 3 moles of eNO₂ entering the system.

The relative amounts of NO₂ and N₂O₄ in the entering and exit gases were determined from the equilibrium constants for the reaction,^{10,15}

B. Venturi Atomizer

The venturi atomizer used in these studies was built by M. C. Tassler¹² for work on CO₂ desorption. Figure 2 shows the major parts of the equipment. It was constructed of molded Lucite sheeting. The diameter of the duct was 3 1/4 inches while the diameter of the venturi injection throat was 1.11 inches. Five adjustable injection points were located at the upstream end of the injection throat. Only the center injection point was used for most of the runs. Inlets for injecting NO₂, NO, and steam into the air stream were included in the equipment.

A stainless-steel collection tube, as shown in Figure 3, was used for obtaining liquid samples. The concentric outer tube supplied nitrogen as a shield to prevent entrance of the main gas stream into the collection tube. Runs to determine the effect of nitrogen flow rate on the concentration of the collected liquid indicated that a very low nitrogen flow rate was desirable and that the liquid should be collected slowly to minimize the inclusion of gas.

040 032

Liquid samples were obtained by inserting the collection tube into the duct and lining up the tube with the injection point. The liquid sample was collected under nitrogen in a 50-milliliter Erlenmeyer flask. The liquid spray was sampled at points 0.41 inches, 1.12 inches, and 2.85 inches from the liquid injection point. The cyclone effluent was also sampled and analysed.

In the experimental tests on oxygen absorption, the Winkler⁸ method was used to determine the amount of dissolved oxygen. In the NO₂ absorption runs, the liquid sample was analysed for total acid content and for oxygen deficiency. The oxygen deficiency was determined by the addition of an excess of potassium permanganate to the acidified sample. The solution was allowed to stand for 15 minutes. Potassium iodide was then added, and the solution was back-titrated with standard sodium thiosulfate.

IV. DISCUSSION OF RESULTS

A. Bubble-Cap Plate Column

1. Efficiency.- At a given set of flow conditions, the efficiency of absorption was found to increase as the percentage of eNO_2 (i.e., $NO_2 + 2N_2O_4$) in the entering gases increased. Plots of efficiency versus entering gas composition for various gas flow rates indicate that the plate efficiency starts at zero, climbs rapidly at low concentrations of eNO_2 , and tends to level off above 4 to 6 percent eNO_2 . These curves are shown in Figures 4 and 5.

At low eNO_2 concentrations only a small fraction of the total oxides is in the form of N_2O_4 , as is shown in Figure 6. Therefore, if the chemical reactions of NO_2 and N_2O_4 with water are controlling, the efficiency of absorption would be expected to be lower at low eNO_2 concentrations because the bimolecular reaction between N_2O_4 and H_2O proceeds at a faster rate than the reaction between NO_2 and H_2O . The experimental data corroborate Caudle and Denbigh's² conclusion that the reaction between N_2O_4 and H_2O controls the rate of nitrogen oxides removal from gaseous mixtures.

Plots of plate efficiency versus the concentration fractions $\frac{2N_2O_4}{eNO_2}$ and $\frac{NO_2}{eNO_2}$ are shown in Figure 7. These plots show that the absorption efficiency increases as the fraction of N_2O_4 in the gases increases. The efficiency in Figure 7 appears to approach zero before the percentage of N_2O_4 becomes zero. This would be possible because, in the low eNO_2 range, the NO_2 absorption becomes important, this oxide being by far the more abundant at low concentrations. The curve then should follow the dotted line as shown.

For any given gas composition, the plate efficiency was found to increase with decreasing gas flow rate. This relationship is reasonable since lower flow rates allow more time of contact between gas and liquid. At the lowest gas flow rate (0.84 ft./sec. slot velocity), the efficiency was much lower than would be expected. This may have been due to the formation of large bubbles which reduced the gas-liquid interfacial area. Figure 4 shows that at 10 volume percent eNO_2 in the entering gases, the efficiencies at gas slot velocities of 1.18, 1.65, and 2.35 ft./sec. were 50, 46, and 38 percent, respectively. At a concentration of 2 percent eNO_2 in the entering gases, the efficiencies at these slot velocities were 26, 24, and 18 percent, respectively.

The liquid rate had no pronounced effect on the plate efficiency as shown by comparing the runs at liquid rates of 300 and 600 cc./min. The use of 15 and 30 percent nitric acid as the absorbing media also had no appreciable effect on the efficiency. This result is to be expected since the theoretical conversion of NO_2 to HNO_3 over 30 percent acid differs from that over water by less than 5 percent under the conditions of these experiments. The theoretical conversion over water was $66 \frac{2}{3}$ percent while that over 30 percent nitric acid was 62 percent. Results for these runs are plotted in Figure 5.

The curves of efficiency versus the fractions of N_2O_4 and NO_2 show how the absorption efficiency varies for a given slot velocity. When the gases contain small amounts of nitrogen oxides, as at the upper plates of a bubble-cap absorption tower, the absorption efficiency is poor. The curve of efficiency versus entering gas composition can be used to estimate the performance of atmospheric pressure columns containing more than one plate if similar flow conditions are used. It is believed that commercial

42 035

towers which employ the same type of gas-liquid contact will also show approximately the same magnitude of absorption efficiencies if suitable allowances are made for higher pressure operation.

2. Rate of Removal of Oxides from Gases.- Figure 8 shows that the rate of removal of nitrogen oxides from gases is directly proportional to the concentration of N_2O_4 in the gases when the reactions occur irreversibly. However, it is difficult to determine the exact shape of the curve at low N_2O_4 concentrations and the direct proportionality relationship may not apply at low N_2O_4 concentrations.

3. General Observations.- A mist was observed in the upper section of the equipment and in the exit gas line during all the runs. The mist appeared to be heaviest at high gas concentrations of eNO_2 . Samples of the mist deposited in the exit line were found to contain HNO_3 , but the original concentration could not be determined because all such samples were in contact with the exit gas stream for several minutes before being withdrawn.

A small amount of brown gas (NO_2) appeared over the liquid product during all of the runs except those with the most dilute gas. When a sample of the liquid was taken in an evacuated bulb, the gas above the liquid did not turn brown until air was admitted, showing that NO was being given off and then oxidized to NO_2 . Collection of the liquid under hydrogen peroxide showed this NO to constitute about 12 percent of the total NO given off at high gas concentrations and a small fraction at lower concentrations. This NO is evidently from the decomposition of HNO_2 in the liquid phase.

The temperature of the liquid remained nearly constant during the

passage across the plate, but the gas temperature rose 10 to 15°C while passing through the column. Some of the temperature rise may have been caused by condensation of H₂O in the mist, but an exothermic reaction also undoubtedly occurred to some extent in the gas phase.

4. Chemical Reaction Rate as the Controlling Mechanism.-

Equations expressing the rate of removal of nitrogen oxides from gases based on chemical reaction rates as the controlling factor in the over-all mechanism have been derived in this work. When the reactions occur irreversibly, the differential rate equations may be simplified and integrated to give a final form which can be checked by experimental data. Considering both the reaction between H₂O and N₂O₄ and the reaction between H₂O and NO₂, the following simplified equation was derived:

$$\frac{1}{(C_{fN_2O_4})^{\frac{1}{2}}} = \frac{1}{(C_{oN_2O_4})^{\frac{1}{2}}} - 2\sqrt{K_c} \ln \frac{C_{oN_2O_4}}{C_{fN_2O_4}} + B t \quad (26)$$

where

$C_{fN_2O_4}$ = concentration of N₂O₄ in gases leaving the liquid-contact region.

$C_{oN_2O_4}$ = concentration of N₂O₄ in gases entering the liquid-contact region.

K_c = equilibrium constant for $2 NO_2 = N_2O_4$.

B = a constant at any temperature. A function of the reaction rate constants, the water concentration, and the equilibrium constant for NO₂ and N₂O₄.

t = time any portion of the gas is in contact with the liquid.

The concentration terms in Equation 26 can be expressed in more convenient units of partial pressure to give the following simplified equation:

$$\frac{1}{(p_{fN_2O_4})^{\frac{1}{2}}} = \frac{1}{(p_{oN_2O_4})^{\frac{1}{2}}} - 2\sqrt{K_3} \ln \frac{p_{oN_2O_4}}{p_{fN_2O_4}} + F t \quad (28)$$

where

p = partial pressure, atm.

$$K_3 = \frac{p_{N_2O_4}}{(p_{NO_2})^2} \text{ atm.}^{-1}$$

F = a constant at any temperature.

According to Equation 28, a plot of $\frac{1}{(p_{fN_2O_4})^{\frac{1}{2}}}$ versus $\left[\frac{1}{(p_{oN_2O_4})} - 2\sqrt{K_3} \ln \frac{p_{oN_2O_4}}{p_{fN_2O_4}} \right]$ based on experimental data should be a straight line

if the data were obtained under conditions in which the reactions were essentially irreversible, the temperature was constant (i.e., constant values of F and K_3), and the gas flow rate was constant (i.e., constant value of t). Experimental data obtained under these conditions are shown in Figure 9 where K_3 is assumed as constant at 8.0 (corresponding to an average temperature of 22.8°C). The intercept of the line at

$\left[\frac{1}{(p_{oN_2O_4})^{\frac{1}{2}}} - 2\sqrt{K_3} \ln \frac{p_{oN_2O_4}}{p_{fN_2O_4}} \right]$ equal to zero is F t, and the slope

of the line is 1.0. The numerical value of the intercept can be used to predict the curve for a similar plot at the same temperature with a

different contact time assuming the gas-liquid interfacial area does not change appreciable. This was done for a different contact time at which experimental data were available. The predicted curve is shown in Figure 10, and the experimental data for the particular contact time are presented on the same plot. There is good agreement between the experimental data and the predicted curve.

Figure 11 shows the variation of $\frac{P_{O_{N_2O_4}}}{P_{f_{N_2O_4}}}$ with change in concentration of eNO_2 in the entering gases. It can be seen that the value of $\frac{P_{O_{N_2O_4}}}{P_{f_{N_2O_4}}}$ is approximately constant at eNO_2 concentrations higher than about 5 percent, but at lower concentrations its value decreases rapidly.

B. Venturi Atomizer.

1. Oxygen Absorption.- The absorption of oxygen by deaerated water in a venturi atomizer was studied at a throat gas velocity of 348 feet per second and a liquid injection rate of 95.2 cc. per minute. Data were obtained at various nitrogen flow rates surrounding the impact liquid sampling tube, and these data were extrapolated to zero nitrogen flow.

Figure 12 shows the variation in amount of absorption, expressed as the fractional approach to the equilibrium oxygen concentration, with distance from the liquid injection point. At a distance of 2.85 inches from the liquid injection point, 87.5 percent of the equilibrium concentration of oxygen had been absorbed by the liquid. This distance represents a time of 6.8×10^{-4} seconds.

Values of the mass transfer coefficient, K_{La} , were calculated

from the data of Figure 12 and are presented in Figure 13. To calculate K_{La} , it was necessary to assume an absorption volume. Tassler¹², using the same equipment, assumed this volume was equivalent to a cylinder of 0.25-inch cross-sectional diameter and of length equal to the distance from the liquid injection point. This assumption appears to be reasonable. The liquid was injected through a 1/16-inch o.d. hypodermic needle axially to the flow of gas through the throat. The liquid spray passing through the length of the throat was assumed to occupy a volume equivalent to a cylinder with a diameter of 0.25 inches. The exact method for calculating K_{La} is shown in the Appendix under sample calculations.

Experimental values of K_{La} were found to vary from 16,750 lb. moles/(hr.)(cu.ft.)(lb. moles/cu.ft.) at a distance of 1/8 inch from the injection point to 2000 at distances beyond 3 inches from the injection point. These values agree closely with those obtained by Tassler for CO_2 desorption. The values of K_{La} are very large, indicating high rates of oxygen absorption in the venturi atomizer as compared to conventional absorption methods.

Simultaneous NO_2 and O_2 Absorption.— The venturi atomizer was used to study the simultaneous absorption of NO_2 and O_2 in water. Most of the tests were carried out at a gas composition of 2.1 percent eNO_2 .

A very large interfacial area relative to the liquid volume exists between the gas and liquid phases in a venturi atomizer. Therefore, any HNO_3 and HNO_2 formed in the gas film should immediately be absorbed by the liquid. An appreciable amount of N_2O_4 and NO_2 may also be absorbed into the liquid film before reacting with water.

The liquid product should contain HNO_3 and HNO_2 along with some dissolved NO. The decomposition of HNO_2 occurs at a limited rate and the

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solubility of NO in aqueous solutions is very low. Consequently, the HNO_2 should be present in the liquid to a greater extent than NO. Some oxygen is also absorbed by the liquid and this oxygen can react with the NO available in the liquid phase. Because of the very high rate of oxygen absorption in the atomizer, it would be possible for all the NO to be oxidized to NO_2 in the liquid phase. Under these conditions, no NO would be evolved from the liquid and the overall reaction can be written as follows:

where n is the number of moles of eNO_2 reacting and x is the number of moles of oxygen which are absorbed and react in the liquid phase.

In the experimental work, the total acid content and the oxygen deficiency of the liquid samples were determined. By assuming that the oxygen demand was due primarily to HNO_2 , it was possible to determine the amount of HNO_2 and HNO_3 in the liquid sample. The number of moles of oxygen which were absorbed and reacted in the liquid phase was determined from the following equation:

$$x = \frac{\text{moles HNO}_3 - \text{moles HNO}_2}{4}$$

Figures 14a, b, and c show the variation of total acid, nitric acid, and nitrous acid concentrations with distance from the liquid injection point at different liquid injection rates. These figures also show the total amount of oxygen absorbed per liter of solution at the various distances from the injection point assuming no NO escapes from the liquid phase. In these runs, the gas rate and gas composition were held constant at 341 feet per second and approximately 2.1 percent eNO_2 , respectively. The acid concentrations in all the runs increased rapidly with distance from the injection point showing a high rate of eNO_2 removal from the gases. The HNO_2

concentration increased rapidly close to the injection point and then tended to become constant at greater distances.

In Figure 15, the amount of oxygen absorbed in pure water is compared with the amount of oxygen actually absorbed to react with NO or HNO_2 , assuming no NO escapes from the liquid phase. At distances greater than 1/2 inch from the injection point, the amount of oxygen absorbed for reaction with NO or HNO_2 was greater than that absorbed in pure water. The apparent increase in the rate of oxygen absorption in the presence of NO_2 is probably due to reaction of the oxygen during the absorption.

A mixture of NO and NO_2 with air was used in the venturi atomizer to determine the effect of NO on absorption. The gases entering the venturi throat contained 0.73 percent NO and 1.4 percent eNO_2 . As indicated in Figure 16, the absorption rates of nitrogen oxides obtained with this mixture showed no significant difference from the absorption rates obtained using air containing 2.1 percent eNO_2 with no NO.

Steam Injection.- A stainless-steel steam injection tube was installed 13.8 inches upstream from the liquid injection point. Measurements of absorption rates were made with various steam and liquid injection rates and gas velocities of 341 and 170 feet per second. The gas concentration was approximately 2.1 percent eNO_2 . In general, the results indicated that the steam caused an increase in the rate of absorption of nitrogen oxides from the gases. The results are presented in graphical form in Figure 17.

SUMMARY AND CONCLUSIONS

The factor which controls the mechanism in the removal of nitrogen oxides from gaseous mixtures is the rate of the chemical reactions involved. The major chemical reactions occur between N_2O_4 and H_2O vapor and between NO_2 and H_2O vapor in the gas film to yield HNO_3 and HNO_2 . Part of the HNO_2 decomposition takes place in the liquid phase. Equipment used for removing nitrogen oxides from gases should permit a large contact area between the gas and liquid in order to promote the gas-film reactions. Since some of the HNO_2 decomposes to give NO in the liquid phase, it should be possible to oxidize the NO while still in the liquid phase. This liquid-phase oxidation would require a very high rate of oxygen absorption such as can be obtained in a venturi atomizer.

The efficiency of removal of nitrogen oxides from gases decreases as the concentration of eNO_2 in the gases decreases. At low concentrations of eNO_2 , a large fraction of the oxides is in the form of NO_2 . The reaction between N_2O_4 and H_2O occurs at a faster rate than the reaction between NO_2 and H_2O ; therefore, the removal efficiency would be expected to decrease as the fraction of oxides in the form of NO_2 increases. Since increased pressure favors the formation of N_2O_4 from NO_2 , the removal efficiency of absorption towers operating at high pressures should be better than for towers operating at lower pressures.

For any given gas composition, the removal efficiency decreases with increasing gas rate. In the bubble-cap column used in this work, the efficiencies of recovery of nitrogen oxides from a gas containing 10 percent eNO_2 were 50, 46, and 38 percent, respectively, at gas slot velocities of 1.18, 1.65, and 2.35 ft./sec. At 2 percent eNO_2 the efficiencies were 26, 21, and 18 percent, respectively, at the three gas velocities. The

liquid rate and the concentration of nitric acid in the liquid had no significant effect on the efficiency of removal.

Experimental results obtained with a venturi atomizer showed that this device gives much higher oxygen absorption coefficients than conventional equipment because of the large liquid surface per unit volume of gas. Tests with steam injection into the entering gases indicated that the presence of steam promoted the gas-phase reaction between N_2O_4 (or NO_2) and H_2O to give increased rates of nitrogen oxides removal from the gases.

According to the results of this work, conventional bubble-cap towers are inefficient for removing nitrogen oxides from gases containing small amounts of these oxides. The removal efficiency could be increased by increasing the fraction of oxides present as N_2O_4 , by increasing the gas-liquid contact area, or by promoting the chemical reactions in the liquid phase.

Further work will be done on the kinetics of the liquid-phase reactions and means for catalyzing the overall absorption rate. The bubble-cap column operation will be studied further with respect to the use of multiple stages, and additional work will be carried out on methods for obtaining the maximum absorption efficiency in a venturi atomizer.

TABLE OF NOMENCLATURE

A	=	A constant at any temperature.
B	=	A constant at any temperature.
C	=	Concentration, gram moles/cc.
C _f	=	Final concentration, gram moles/cc.
C _o	=	Original concentration, gram moles/cc.
D	=	Diffusivity, sq. cm./sec.
e	=	2.7183.
eNO ₂	=	Equivalent NO ₂ = NO ₂ + 2N ₂ O ₄ .
E	=	Absorption efficiency = $\frac{y_1 - y_2}{y_1 - y_2} \times (100)$.
F	=	A constant at any temperature.
k	=	Reaction rate constant, units depend on reaction involved.
K	=	Equilibrium constant, units depend on reaction involved.
K _{La}	=	Mass transfer coefficient, lb. moles/(hr.)(cu. ft.)(lb. moles/cu. ft.).
n	=	Number of moles of eNO ₂ which react.
N _{eNO₂}	=	Rate of nitrogen oxides absorption based on equivalent NO ₂ removal, gram moles/(sec.)(sq. cm.).
N _L	=	Rate of nitric acid formation, gram moles/min.
p	=	Partial pressure, atm.
p _f	=	Final partial pressure, atm.
p _o	=	Original partial pressure, atm.
t	=	Time, seconds.
x	=	Number of moles of oxygen which are absorbed and react in the liquid phase.
x _f	=	Effective film thickness, cm.
y ₁	=	Mole fraction (NO ₂ + 2N ₂ O ₄ + NO) in gases entering plate.

TABLE OF NOMENCLATURE (CONTINUED)

y_2 = Mole fraction ($\text{NO}_2 + 2\text{N}_2\text{O}_4 + \text{NO}$) in gases leaving plate.

y_2^* = Mole fraction ($\text{NO}_2 + 2\text{N}_2\text{O}_4 + \text{NO}$) in gases leaving plate
if theoretical conversion were obtained.

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APPENDIX

SAMPLE CALCULATIONS FOR BUBBLE-CAP PLATE COLUMN

The following sample calculations for the bubble-cap plate column indicate the methods used for calculating the items listed below:

- (1) The absorption efficiency in the bubble-cap column.
- (2) The amounts of NO_2 and N_2O_4 in the gases.

These calculations are for run number 43 in which the following data were obtained:

Data for Run Number 43

Pressures: NO_2 cylinder - 2.0 cm. Hg.

Base of tower - 7.6 cm. α -bromonaphthalene.

Top of tower - 6.3 cm. α -bromonaphthalene.

Operating pressure - 1 atmosphere.

Temperature: Entering liquid - 24°C .

Exit liquid - 24°C .

Entering gas - 14°C .

Exit gas - 29°C .

Air - 25°C .

Entering liquid composition = 0 % HNO_3

Exit liquid rate = 307 cc./min.

Exit liquid composition = 0.00731 g. HNO_3 /cc. product.

Entering air rate = 1.11 ft.³/min.

Entering gas composition = $y_1 = 8.08$ mole % ($\text{NO}_2 + 2\text{N}_2\text{O}_4$)

= 8.08 % eNO_2 .

Calculation of y_2 = Mole % Oxides Leaving Plate

Basis: 1 mole in = 1 mole out.

Overall equation: $3\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{NO}$.

$$\begin{aligned} N_L &= \text{g. moles HNO}_3 \text{ produced per min.} \\ &= \frac{0.00731 \text{ g. HNO}_3}{\text{cc. product}} \times \frac{307 \text{ cc.}}{\text{min.}} \times \frac{1 \text{ mole}}{63 \text{ g.}} = 0.0356 \end{aligned}$$

G. moles air entering per min.

$$= \frac{1.11 \text{ ft.}^3}{\text{min.}} \times \frac{0.0755 \text{ lb.}}{\text{ft.}^3} \times \frac{1 \text{ lb.-mole}}{29 \text{ lbs.}} \times \frac{454 \text{ g. moles}}{1 \text{ lb.-mole}} = 1.31.$$

G. moles eNO_2 entering per min.

$$= \frac{1.31 \text{ moles air}}{\text{min.}} \times \frac{8.08 \text{ moles NO}_2}{91.9 \text{ moles air}} = 0.1153.$$

Total moles gas entering per min.

$$= 1.31 + 0.1153 = 1.425.$$

Moles NO leaving plate per min. = $1/2 N_L$

$$= 1/2 \times 0.0356 = 0.0178.$$

Moles eNO_2 leaving plate per min. = moles entering - $3/2 N_L$

$$= 0.1153 - 3/2 \times 0.0356 = 0.0619.$$

Total moles oxides leaving plate per min.

$$= 0.0178 + 0.0619 = 0.0797.$$

y_2 = mole percent oxides leaving plate = $\frac{\text{moles oxides}}{\text{total moles}} \times 100$

$$= \frac{0.0797}{1.425} = 5.60 \%$$

Calculation of y_2^* = Mole % Oxides Leaving Plate If Equilibrium Were Established

Basis: 1 mole in = 1 mole out.

Assuming that equilibrium between NO , NO_2 , N_2O_4 , and the liquid is reached on the plate, the following material balance applies:

Component

Partial Pressures (atm.)

	<u>Entering Plate</u>	<u>Leaving Plate</u>
NO	$(P_{NO})_1$	$(P_{NO})_2 = K_1 (P_{NO_2})_2^3$
NO ₂ }		$(P_{NO_2})_2$
N ₂ O ₄ }	$(P_{N_2O_4})_1$	$(P_{N_2O_4})_2 = K_3 (P_{NO_2})_2^2$

where K_1 is the partial equilibrium constant $K_1 = \frac{P_{NO}}{(P_{NO_2})^3}$ as plotted by Sherwood and Pigford¹⁰ against temperature and concentration (straight line extrapolation employed) and K_3 is the equilibrium constant for $2NO_2 = N_2O_4$ as given by Wenner^{10, 15}.

Since 3 times the moles of NO given off equals the moles of NO₂ absorbed, the following equation applies:

$$3 \left[K_1 (P_{NO_2})_2^3 - (P_{NO})_1 \right] = (P_{N_2O_4})_1 - \left[2K_3 (P_{NO_2})_2^3 + (P_{NO_2})_2 \right] \quad \text{(Equation A)}$$

Percent acid on plate (average) = 0.35 %.

Temperature = 24° C.

$K_1 = 5.63 \times 10^{-8} \text{ atm.}^{-2}$ (From Figure 18).

$K_3 = 7.0 \text{ atm.}^{-1}$ (From Figure 19).

$(P_{NO})_1 = 0 \text{ atm.}$

$(P_{N_2O_4})_1 = 0.0808 \text{ atm.}$ (partial pressure equals mole fraction at one atm.)

Substituting these values into Equation A gives an equation involving only $(P_{NO_2})_2$ as the unknown.

By trial and error $(P_{NO_2})_2 = 0.000362 \text{ atm.}$

$(P_{NO})_2 = 0.02675 \text{ atm.}$

$(P_{N_2O_4})_2 = 0$

$y_2^* =$ mole percent oxides leaving plate if equilibrium were attained = $(P_{NO_2})_2 + (P_{NO})_2 = 0.0271$.

$$\text{Theoretical absorption} = \frac{0.0808 - 0.0271}{0.0808} \times 100 = 66.5 \%$$

$$\text{Efficiency} = \frac{y_1 - y_2}{y_1 - y_2^*} = \frac{0.0808 - 0.0560}{0.0808 - 0.0271} \times 100 = 46.1 \%$$

Calculation of the Amounts of NO₂ and N₂O₄ in the Gases

Entering the Plate

$$(P_{\text{eNO}_2})_1 = 0.0808 \text{ atm.}$$

or

$$(P_{\text{NO}_2})_1 + (P_{\text{N}_2\text{O}_4})_1 = 0.0808 \text{ atm.}$$

and

$$\frac{(P_{\text{N}_2\text{O}_4})_1}{(P_{\text{NO}_2})_1^2} = K_3 = 7.0$$

$$\text{Therefore, } \frac{0.0808 - (P_{\text{NO}_2})_1}{(P_{\text{NO}_2})_1^2} = 0.0808$$

$$\text{and } (P_{\text{NO}_2})_1 = 0.0482 \text{ atm.}$$

$$(P_{\text{N}_2\text{O}_4})_1 = 0.163 \text{ atm.}$$

$$\frac{(P_{\text{NO}_2})_1}{(P_{\text{eNO}_2})_1} = \frac{0.0482}{0.0808} = 0.597$$

$$\frac{2 (P_{\text{N}_2\text{O}_4})_1}{(P_{\text{eNO}_2})_1} = \frac{2 \times 0.163}{0.0808} = 0.403$$

Similarly, values of these fractions can be calculated for the exit gas.

Note: The assumption that the mole fraction reported as (NO₂ + 2N₂O₄) is equal to the partial pressure P_{eNO_2} introduces a slight error. The sample shows there are 0.808 moles eNO₂ per 0.919 moles air. This corresponds approximately to 0.0482 atm. NO₂ and 0.0163 atm. N₂O₄ as shown in the preceding calculations. But this adds to 0.919 + 0.0482 + 0.0163 = 0.9835 atm. instead of 1.0 atm. If the calculated values are multiplied by $\frac{1}{0.9835}$ and checked, the answers obtained are

$$(P_{NO_2})_1 = 0.0490 \text{ atm.}$$

$$(P_{N_2O_4})_1 = 0.0166 \text{ atm.}$$

Since the error involved is less than 2 %, the calculations as shown above are satisfactory.

Sample Calculations for the Venturi Atomizer

Calculation of Mass Transfer Coefficient, $K_L a$, for Oxygen

Absorption

A. Slope of curve (Figure 12) at 0.125"

$$\text{Slope} = \frac{1.65 \text{ g. mole } O_2}{(\text{g. mole } O_2 \text{ eq.})(\text{inch})}$$

B. Absorption volume taken as a cylinder of length 0.125" and diameter 0.25".

Cross-sectional area of absorption volume

$$A = \frac{\pi(0.25)^2}{4} = 0.0491 \text{ in.}^2$$

C. Liquid Flow Rate:

$$L = 95.2 \text{ g./min.}$$

D. Driving Force:

$$D = 1 - (\text{Fractional absorption at } 0.125") \text{ (Figure 12)}$$

$$D = 1 - 0.3 = 0.7 \frac{\text{g. moles } O_2}{\text{g. moles } O_2 \text{ eq.}}$$

E. Mass Transfer Coefficient:

$$\begin{aligned} K_L a &= \frac{(\text{Slope}) (\text{Liquid Flow Rate})}{(\text{Cross-Sectional area}) (\text{Driving Force})} \\ &= \frac{(1.65)(95.2)}{(0.0491)(0.7)} = 4560 \frac{\text{g. moles } O_2}{(\text{min.})(\text{in.})^3 \frac{\text{g. mole } O_2}{\text{g.}}} \\ &= 4560 \times \frac{1728 \text{ in.}^3}{1 \text{ ft.}^3} \times \frac{60 \text{ min.}}{1 \text{ hr.}} \times \frac{1 \text{ ft.}^3}{28.31 \text{ liter}} \times \frac{1 \text{ liter}}{1000 \text{ g.}} \\ &= 16,750 \frac{\text{lb. moles}}{(\text{hr.})(\text{ft.})^3 (\text{lb. moles/ft.}^3)} \end{aligned}$$

Figure 1. Experimental Equipment for Bubble-Cap Plate Column.

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Figure 2. Venturi Atomizer.

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Figure 3. Sample-Collection Tube for Venturi Atomizer.

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Figure 4

Figure 5

Figures 4 and 5. Effect of eNO_2 Concentration in Entering Gases on Absorption Efficiency. (One Atmosphere Pressure and 25°C Average Temperature in Bubble-Cap Column).

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Figure 6. Effect of eNO_2 Concentration on Fraction of Total Oxides Present as N_2O_4 .

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Figure 7. Variation of Efficiency with Fraction N_2O_4 and NO_2 in the Oxides in Bubble-Cap Column.

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Figure 8. Effect of N_2O_4 Concentration on Rate of Oxides Removal in Bubble-Cap Column (One Atm. Pressure and 25°C Average Temp.).

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(p = partial pressure, atm.; $K_3 = 8$)

Figure 9. Experimental Test for Validity of Reaction Rate Equations (Bubble-Cap Column).

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$$\frac{1}{\sqrt{P_{\text{O}} \text{N}_2\text{O}_4}} = 2 \sqrt{K_3} \ln \frac{P_{\text{O}} \text{N}_2\text{O}_4}{P_{\text{F}} \text{N}_2\text{O}_4}$$

(p = partial pressure, atm.; $K_3 = 8$)

Figure 10. Predicted Curve for Relationship Between Entering and Exit N_2O_4 Concentrations (Bubble-Cap Column).

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Figure 11. Effect of Gas Concentration on Ratio of Original N_2O_4 Partial Pressure to Final N_2O_4 Partial Pressure (Bubble-Cap Column).

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Figure 12. Oxygen Absorption in Venturi Atomizer.

Figure 13. Mass Transfer Coefficients for Oxygen Absorption in Venturi Atomizer.

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Figure 14-a. Liquid rate = 60 cc./min.

Figure 14-b. Liquid rate = 99.5 cc./min.

Figures 14-a and 14-b. Absorption of NO_2 and N_2O_4 by Water in Venturi Atomizer (Gas Concentration = 2.1 Percent eNO_2 . Throat Gas Velocity = 341 ft./sec.).

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58

Figure 14-c. Liquid rate = 185 cc./min.

Figure 14-c. Absorption of NO₂ and N₂O₄ by Water in Venturi Atomizer
(Gas Concentration = 2.1 Percent eNO₂. Throat Gas
Velocity = 341 ft./sec.).

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Figure 15. Comparison Between Oxygen Absorption in Pure Water and in a Water Solution Containing HNO_3 and HNO_2 in Venturi Atomizer.

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Figure 17. Effect of Steam Injection Rate on Acid Concentration Obtained in Venturi Atomizer.

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Figure 18. Equilibrium of NO₂ and NO Over Nitric Acid (Reference 10).

$$K_1 = \frac{P_{NO}}{(P_{NO_2})^2} \text{ atm.}^{-2}$$

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Figure 19. Equilibrium Between NO_2 and N_2O_4 (References 10 and 15).

$$K_3 = \frac{p_{\text{N}_2\text{O}_4}}{(p_{\text{NO}_2})^2} \text{ atm.}^{-1}$$

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Table I
TABULATED DATA AND RESULTS FOR BUBBLE-CAP PLATE
(Part 1)

Total Pressure=1atmosphere										
Run No.	Plate Temp.	Air Temp.	Ent. Liq. Comp.	Exit Liq. Rate	HNO ₃ Pro-duced	Gas Rate	Gas Slot Vel.	Ent. Gas Comp. (mole fraction)		
	(°C)	(°C)	(% HNO ₃)	($\frac{\text{cc.}}{\text{min.}}$)	($\frac{\text{g.}}{\text{cc.}} \times 10^2$)	($\frac{\text{ft.}^3}{\text{min.}}$)	($\frac{\text{ft.}}{\text{sec.}}$)	(NO ₂ + 2N ₂ O ₄)	(NO ₂)	(N ₂ O ₄)
25	21	23	0	293	0.0362	1.16	1.13	0.0115	0.0097	0.0009
18	23	23*	0	309	0.0700	1.14	1.11	0.0170	0.0140	0.0015
19	25	23.5	0	298	0.144	1.15	1.12	0.0270	0.0210	0.0030
68	22.5*	23.5	0	301	0.258	1.19	1.16	0.0346	0.0250	0.0048
63	22.5	25	0	291	0.337	1.19	1.16	0.0431	0.0295	0.0068
71	22	31	0	302	0.390	1.22	1.19	0.0462	0.0307	0.0078
46	21.5	24.5	0	303	0.593	1.24	1.21	0.0671	0.0400	0.0136
43	24	25	0	307	0.730	1.21	1.18	0.0808	0.0482	0.0163
44	21.5	24	0	306	0.754	1.21	1.18	0.0814	0.0458	0.0178
70	23*	23*	0	304	0.841	1.20	1.17	0.0870	0.0500	0.0185
69	23*	23*	0	300	0.878	1.20	1.17	0.0873	0.0500	0.0185
56	20	25	0	299	1.050	1.23	1.20	0.102	0.0510	0.0253
45	26	25.5	0	305	1.164	1.24	1.21	0.116	0.0650	0.0257
27	20.5	23.5	0	610	0.0482	1.18	1.15	0.0187	0.0146	0.0020
28	22	25	0	608	0.252	1.23	1.20	0.0588	0.0365	0.0110
30	22.5	23.5	0	605	0.477	1.22	1.19	0.0954	0.0521	0.0217
57	18	25	0	595	0.541	1.23	1.20	0.0992	0.0475	0.0259
38	23	23.5	15	284	0.180	1.19	1.16	0.0247	0.0191	0.0028
37	23*	23*	15	290	0.188	1.19	1.16	0.0270	0.0205	0.0032
36	23.5	23.5	15	288	0.221	1.19	1.16	0.0271	0.0207	0.0032
66	23.5	23.5	15	289	0.533	1.17	1.14	0.0585	0.0376	0.0105
42	25	27	15	282	0.727	1.18	1.15	0.0741	0.0460	0.0140
41	25	25	15	292	0.962	1.22	1.19	0.0971	0.0560	0.0205
10	19.5	23*	0	308	0.089	1.58	1.54	0.0184	0.0144	0.0020
65	22.5	21.5	0	293	0.116	1.68	1.64	0.0177	0.0144	0.0017

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- 83 -

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65

Table I (Cont'd)
TABULATED DATA AND RESULTS FOR BUBBLE-CAP PLATE
(Part 1)

Total Pressure=1atmosphere

Run No.	Plate Temp.	Air Temp.	Ent. Liq. Comp.	Exit Liq. Rate	HNO ₃ Produced	Gas Rate	Gas Slot Vel.	Ent. Gas Comp. (mole fraction)		
	(°C)	(°C)	(% HNO ₃)	(cc./min.)	(g./cc.) X 10 ²	ft. ³ /min.	ft./sec.	(NO ₂ + 2N ₂ O ₄)	(NO ₂)	(N ₂ O ₄)
60	23*	23*	0	295	0.707	1.71	1.67	0.0611	0.0390	0.0110
58	19.5	26	0	294	1.18	1.68	1.64	0.0925	0.0475	0.0225
64	23*	23*	0	294	0.057	0.865	0.845	0.0188	0.0152	0.0018
62	25	28.5	0	299	0.330	0.845	0.825	0.0523	0.0358	0.0083
55	29	30	0	290	0.666	0.870	0.850	0.104	0.0635	0.0202
9	20	23*	0	318	0.038	2.26	2.20	0.0110	0.0094	0.0008
11	20	23*	0	280	0.065	2.11	2.06	0.0125	0.0104	0.00106
8	21	23*	0	315	0.185	2.26	2.20	0.0280	0.0205	0.0037
7	20	23*	0	305	0.290	2.30	2.24	0.0290	0.0205	0.0042
16	20.5	23*	0	296	0.306	2.37	2.31	0.0305	0.0217	0.0044
15	22	23*	0	290	0.570	2.45	2.39	0.0463	0.0308	0.0078
61	26.5	28.5	0	290	0.601	2.43	2.37	0.0474	0.0338	0.0068
14	22.5	23*	0	280	0.915	2.46	2.40	0.0605	0.0377	0.0114
12	22	23*	0	320	1.08	2.36	2.30	0.0780	0.0452	0.0164
59	23*	23*	0	299	1.57	2.43	2.37	0.0948	0.0530	0.0210
6	19	23*	0	290	1.23	2.44	2.38	0.0905	0.0460	0.0222
13	25	23*	0	330	1.28	2.61	2.55	0.0968	0.0560	0.0204
2	29	23*	0	290	1.60	2.60	2.54	0.0982	0.0610	0.0186
3	26	23*	0	290	1.73	2.68	2.62	0.0982	0.0580	0.0202
4	27.5	23*	0	290	1.70	2.67	2.61	0.1044	0.0620	0.0211

* Nitrogen used instead of air.

* Estimated temperature.

Note: The results of several runs are not included in Tables I and II for the following reasons:

(a) Condensate entered the entering gas sampling bulbs in several runs, making

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66

calculations impossible.

(b) The initial 15 % nitric acid runs gave erratic results because the method of analysis was not perfected.

(c) It was very difficult to determine the amount of nitric acid produced in the 10% 30 % acid run because the solution increased only slightly in acidity. However, the exit-gas sample checked the exit-gas samples of water runs at the same flow conditions; so it was assumed that the use of 30 % acid did not change the absorption efficiency significantly.

(d) One series of three runs at 1.2 cu. ft./min. was consistent within itself but yielded efficiencies far lower than the other runs at this flow rate. An experimental error was assumed.

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Table II
TABULATED DATA AND RESULTS FOR BUBBLE-CAP PLATE
(Part 2)

Total Pressure=1 atmosphere

Run No.	Exit Gas Composition (mole fraction)				Ent. Frac- tion $\frac{N_2O_4}{2N_2O_4 + eNO_2}$	Exit Frac- tion $\frac{N_2O_4}{2N_2O_4 + eNO_2}$	Effi- ciency %	Rate of Absorption (g. mole HNO ₃ /min.)
	(NO + NO ₂ + 2N ₂ O ₄)	(NO ₂ + 2N ₂ O ₄)	(NO ₂)	(N ₂ O ₄)				
25	0.0103	0.0097	0.0084	0.00065	0.157	0.134	16	0.00168
18	0.0145	0.0132	0.0113	0.00100	0.177	0.151	22	0.00343
19	0.0221	0.0196	0.0161	0.00172	0.222	0.175	28	0.00680
68	0.0258	0.0215	0.0170	0.00225	0.278	0.209	38	0.0123
63	0.0320	0.0265	0.0202	0.0032	0.315	0.241	38.5	0.0156
71	0.0329	0.0262	0.0198	0.0032	0.337	0.244	43	0.0187
46	0.0477	0.0379	0.0262	0.0059	0.405	0.312	43.5	0.0285
43	0.0560	0.0435	0.0305	0.0065	0.433	0.299	46	0.0356
44	0.0583	0.0456	0.0302	0.0078	0.437	0.342	43	0.0366
70	0.0588	0.0447	0.0305	0.0070	0.425	0.313	49	0.0406
69	0.0580	0.0435	0.0300	0.0068	0.425	0.313	50	0.0418
56	0.0680	0.0507	0.0315	0.0096	0.500	0.379	50	0.0499
45	0.0776	0.0585	0.0395	0.0095	0.440	0.325	50	0.0564
27	0.0154	0.0137	0.0113	0.0012	0.214	0.175	26	0.00467
28	0.0422	0.0340	0.0243	0.0049	0.374	0.288	42	0.0243
30	0.0637	0.0479	0.0318	0.0080	0.455	0.334	50	0.0458
57	0.0640	0.0464	0.0282	0.0091	0.522	0.392	53	0.0511
38	0.0190	0.0161	0.0135	0.00135	0.226	0.168	35	0.00810
37	0.0209	0.0178	0.0146	0.0016	0.237	0.180	35	0.00865
36	0.0200	0.0164	0.0137	0.00135	0.237	0.165	40	0.0101
66	0.0408	0.0321	0.0238	0.00415	0.359	0.258	46	0.0244
42	0.0505	0.0390	0.0285	0.0053	0.378	0.272	48.5	0.0326
41	0.0662	0.0508	0.0350	0.0079	0.422	0.311	48.5	0.0446

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68

Table II (Cont'd)
TABULATED DATA AND RESULTS FOR BUBBLE-CAP PLATE
(Part 2)

Total Pressure = 1 atmosphere

Run No.	Exit Gas Composition (mole fraction)				Ent. Fraction $\frac{N_2O_4 + 2N_2O_4}{eNO_2}$	Exit Fraction $\frac{N_2O_4 + 2N_2O_4}{eNO_2}$	Efficiency %	Rate of Absorption (g. mole HNO_3 /min.)
	$(NO + NO_2 + 2N_2O_4)$	$(NO_2 + 2N_2O_4)$	(NO_2)	(N_2O_4)				
10	0.0162	0.0150	0.0120	0.0015	0.217	0.200	24	0.00435
65	0.0150	0.0136	0.0115	0.0010	0.192	0.147	23	0.00538
60	0.0448	0.0364	0.0261	0.0051	0.360	0.280	40	0.0331
58	0.0645	0.0507	0.0312	0.0097	0.486	0.382	45	0.0550
64	0.0161	0.0148	0.0125	0.0012	0.191	0.162	21	0.00267
62	0.0393	0.0327	0.0249	0.0040	0.318	0.244	38	0.0157
55	0.0735	0.0580	0.0410	0.0084	0.388	0.290	44	0.0307
9	0.0103	0.0099	0.0085	0.0007	0.145	0.141	9.5	0.00192
11	0.0114	0.0108	0.0092	0.0008	0.170	0.148	13	0.00289
8	0.0246	0.0228	0.0174	0.0027	0.264	0.236	18	0.00925
7	0.0240	0.0215	0.0163	0.0026	0.290	0.242	26	0.0141
16	0.0254	0.0228	0.0172	0.0028	0.288	0.246	25	0.0144
15	0.0370	0.0325	0.0235	0.0045	0.337	0.277	29	0.0262
61	0.0376	0.0327	0.0251	0.0038	0.287	0.232	31	0.0277
14	0.0460	0.0390	0.0270	0.0059	0.377	0.303	35	0.0407
12	0.0635	0.0538	0.0347	0.0096	0.420	0.357	35	0.0548
59	0.0689	0.0559	0.0363	0.0098	0.443	0.351	41	0.0745
6	0.0718	0.0620	0.0355	0.0132	0.490	0.425	31	0.0566
13	0.0746	0.0640	0.0415	0.0112	0.421	0.350	33	0.0670
2	0.0745	0.0625	0.0435	0.0095	0.380	0.304	36	0.0740
3	0.0741	0.0620	0.0415	0.0103	0.410	0.332	37	0.0800
4	0.0800	0.0677	0.0452	0.0113	0.405	0.334	35	0.0780

* Nitrogen used instead of air.

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69

Table III

DATA FOR OXYGEN ABSORPTION WITH VENTURI ATOMIZER
(at N₂ shielding rate of zero by extrapolation
from finite shielding rates)

<u>Position inches from liquid injection point</u>	<u>Fraction Absorbed Mole O₂/(Mole O₂ at equilibrium)</u>
0.445	0.591
1.103	0.768
2.84	0.876

Equilibrium concentration of O₂ in water at 70°F. and 750 mm. Hg
total pressure is 2.8×10^{-4} moles O₂/liter H₂O.

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70

Table IV

DATA FOR $\text{NC}_2 - \text{O}_2$ ABSORPTION WITH VENTURI ATOMIZER

Gas Velocity Through Throat = 341 ft./sec.

Position inches from injection point	Liquid Rate g./min.	Gas Composition % eNO_2	Total Acid Concn. moles/liter	HNO_2 Concn. m./l.	HNO_3 Concn. m./l.	O_2 Absorbed m./l.
0.41	60	2.05	0.00960	0.0026	0.0070	0.0011
1.12	60	2.05	0.0131	0.0033	0.0098	0.0016
0.41	99.5	2.06	0.00312	0.0013	0.00182	0.00012
1.12	99.5	2.06	0.00884	0.0034	0.00544	0.00051
2.85	99.5	2.06	0.0189	0.0063	0.0126	0.0016
0.41	185	2.06	0.00165	0.00057	0.00108	0.00013
1.12	185	2.06	0.00515	0.00177	0.00338	0.00040
2.85	185	2.06	0.0113	0.0038	0.0075	0.00093

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71

Table V

DATA FOR NO₂ - NO - O₂ ABSORPTION WITH VENTURI ATOMIZER

Gas Composition NO₂ = 1.4 % ; NO = 0.73 %

<u>Position inches from liquid injection point</u>	<u>Liquid Rate g./min.</u>	<u>Total Acid Concn. moles/liter</u>
0.41	60	0.0077
0.41	99.5	0.00468
1.12	99.5	0.00900
2.85	99.5	0.0171
0.41	185	0.00221
1.12	185	0.00468
2.85	185	0.0101

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Table VI

DATA FOR STEAM INJECTION WITH VENTURI ATOMIZER

Liquid Rate = 185 g./min.

Position inches from liquid injection point	Steam Rate g./min.	Gas Comp. % eNO ₂	Gas Rate ft./sec.	Total Acid Conc. moles/liter
0.41	0	1.94	170	0.001275
0.41	6.8	1.94	170	0.001765
0.41	19.4	1.94	170	0.001765
0.41	36.3	1.94	170	0.0043
1.12	0	1.94	170	0.00471
1.12	6.8	1.94	170	0.00676
1.12	19.4	1.94	170	0.00686
1.12	36.3	1.94	170	0.0223
2.85	0	1.94	170	0.00805
2.85	6.8	1.94	170	0.0149
2.85	19.4	1.94	170	0.0174
2.85	36.3	1.94	170	0.0465
0.41	0	2.06	341	0.00165
0.41	6.8	2.50	341	0.00555
0.41	19.4	2.22	341	0.00269
0.41	36.3	2.22	341	0.00236
1.12	0	2.06	341	0.00515
1.12	6.8	2.50	341	0.0113
1.12	19.4	2.22	341	0.00699
1.12	36.3	2.22	341	0.00606
2.85	0	2.06	341	0.0113
2.85	6.8	2.50	341	0.0120
2.85	19.4	2.22	341	0.0200
2.85	36.3	2.22	341	0.0252
Additional Points				
0.41	6.8	2.10	341	0.00118
1.12	6.8	2.10	341	0.00785
2.85	6.8	2.10	341	0.0169