ADVANCED FUEL RECYCLE PROGRAM

A LITERATURE REVIEW OF NITROGEN OXIDE ABSORPTION
INTO WATER AND DILUTE NITRIC ACID

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ABSTRACT

The removal of gaseous nitrogen oxides from off-gas streams is important when reprocessing spent nuclear fuels. The absorption of nitrogen oxides has been the subject of several laboratory and engineering-scale experiments and the theory of nitrogen oxide absorption seems to be well established. However, previous engineering-scale experimental work is not directly applicable to proposed nitrogen oxide removal processes. A literature survey has been conducted to determine the "state of the art" in nitrogen oxide absorption. The purpose of this report is to give the results of that survey and make some general observations on nitrogen oxide absorption.

1. INTRODUCTION

The removal of nitrogen oxides from off-gas streams is important when reprocessing spent nuclear fuels, since many of the off-gas streams in a reprocessing facility will contain nitrogen oxides in sufficient concentration to interfere with further gas cleanup operations or to exceed discharge limits. Absorption of gaseous NO_2^* (the sum of the NO_2 concentration and the product of two times its equilibrium polymer concentration, N_2O_4) into water and dilute nitric acid and the gas phase oxidation reaction of NO provide the basis for one method of nitrogen oxide removal. The purposes of this report are (1) to identify the rate-limiting mechanisms associated with nonequilibrium absorption of NO_x (the sum of $NO_2^* + NO$) compounds into water or dilute nitric acid and (2) to point out the absence in the open literature of information necessary to complete the design of nitrogen oxide absorption equipment.

2. LITERATURE REVIEW

The nitrogen oxides of importance are NO_2, N_2O_4, NO, and N_2O_3. The essential chemical reactions are usually written as follows:

$$2NO_2(g) \rightleftarrows N_2O_4(g) \, , \tag{1}$$

$$N_2O_4(g) + H_2O(\ell) \rightarrow HNO_3(\ell) + HNO_2(\ell) , \qquad (2)$$

$$3HNO_2(\ell) \rightleftarrows HNO_3(\ell) + 2NO(g) + H_2O(\ell) , \qquad (3)$$

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) , \qquad (4)$$

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g) , \qquad (5)$$

$$N_2O_3(g) + H_2O(g) \rightleftarrows 2HNO_2(g) , \qquad (6a)$$

or

$$N_2O_3(g) + H_2O(\ell) \rightleftarrows 2HNO_2(\ell) . \qquad (6b)$$
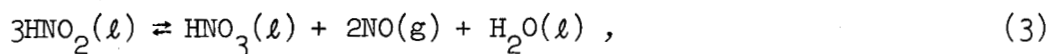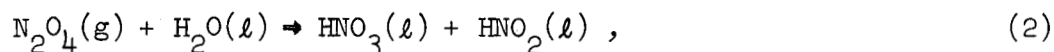
Reactions (2) and (3) are sometimes combined as

$$(3/2)N_2O_4(g) + H_2O(\ell) \rightarrow 2HNO_3(\ell) + NO(g) . \qquad (7)$$
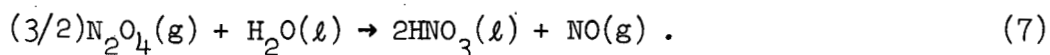
Reactions (1) through (4) adequately describe the absorption process if the gaseous NO concentration is low or the gaseous NO_2^* concentration is moderately high. If either of these conditions is not satisfied, reactions (1) through (6) may be required to describe the absorption process. The heats of reaction associated with the above reactions make the absorption a highly exothermic process.

2.1 The NO_2 - N_2O_4 Equilibrium

Bodenstein[1] studied reaction (1) at temperatures from 282 to 404 K. Data are expressed in the following equation for the log of the pressure equilibrium constant:

$$\text{Log } K_{p,1} = -\frac{2692}{T} + 1.75 \text{ Log } T + 0.00483T - 7.144 \times 10^{-6}T^2 + 3.062 , \qquad (8)$$

where

$$K_{p,1} = \frac{P_{NO_2}^2}{P_{N_2O_4}} \text{ atm .} \qquad (9)$$

Verhoek and Daniels[2] also conducted an investigation of reaction (1) but varied the temperatures from 298 to 318 K. The following equation expresses their data for the log of the pressure equilibrium constant:

$$\text{Log } K_{p,1} = 9.8698 - \frac{3198}{T} \cdot \tag{10}$$

Hoftyzer and Kwanten[3] give the following correlation for $K_{p,1}$ without temperature restrictions and based on the work of Verhoek and Daniels[2] and the JANAF Thermochemical Tables:[4]

$$K_{p,1} = 1.46 \times 10^9 \exp(6866.0/T). \tag{11}$$

2.2 The Absorption of NO_2^* into Water and Dilute Nitric Acid Accompanied by Reaction with H_2O

The hydrolysis of N_2O_4 is essentially irreversible if the absorbing fluid is water or dilute nitric acid. The equilibrium hydrolysis of N_2O_4 is not considered in this report although the subject is well covered in the literature.[5,6]

Chambers and Sherwood[7] studied the absorption of NO_2^* from nitrogen into nitric acid solutions at 298 K using both a wetted-wall column and a batch system. Acid strengths were varied up to 18.5 $\underline{M}$, and the NO_2^* partial pressure was approximately 0.05 to 0.06 atm. Assuming that reaction (3) is rapid and that the hydrolysis of N_2O_4 is accurately represented by reaction (7), they concluded that gas-phase resistance is the controlling mechanism since the rate of absorption is proportional to the approximate 0.8 power of the gas velocity. A gas-phase hydrolysis reaction of NO_2^* was assumed; analysis was accomplished by a chemical analysis of gas samples.

The effects of system temperature, NO_2^* concentration, and acid molarity on the absorption rate of NO_2^* from $NO_2^*-N_2$ gas mixtures into nitric acid was investigated by Denbigh and Prince[8] using a wetted-wall column. Temperatures of 298 and 313 K were used; NO_2^* partial pressure ranged from 0 to 0.27 atm, and acid molarity varied from 1.7 $\underline{M}$ to 13.0 $\underline{M}$. They assumed that reaction (7) describes the reaction of N_2O_4 and water. For acid strengths up to 5.7 $\underline{M}$, the absorption rate of NO_2^* is accurately represented by the

following equation in accordance with the theory representing the process of absorption combined with chemical reaction:[9]

$$R_{NO_2^*} = 2\left[\frac{\sqrt{D_{N_2O_4,H_2O}\,k_2}}{He_{N_2O_4}}\right]P_{N_2O_4} \qquad (12)$$

The experimental values for this equation are given in Table 1. They concluded that chemical reaction (7) is the rate-controlling step. Analysis was conducted on the gas phase using a calibrated photocell.

A wetted-wall column was also used by Caudle and Denbigh[10] to experimentally measure the rate of NO_2^* absorption from N_2 into water and dilute nitric acid. The variables examined were gas composition, temperature, and gas and liquid flow rates. The hydrolysis of N_2O_4 is said to occur essentially as reaction (7). No effect of liquid flow rate was observed over a range of $Re(\ell)$ from 140 to 600; no effect of gas flow rate was found over a range of $Re(g)$ from 3500 to 12,000 except for the local eddying and mixing effects in the liquid phase that seemed to be functions of the gas flow rate. The absorption rate of NO_2^* can be calculated as a linear function of the partial pressure of N_2O_4 and can be expressed by equation (12). The values of $\sqrt{D_{N_2O_4,H_2O}\,k_2}/He_{N_2O_4}$ are given in Table 1.

These investigators suggested that the hydrolysis of N_2O_4 occurs at the gas-liquid interface because (1) the absorption rate is proportional to the interfacial area and not to the volume of bulk phases; and (2) when N_2O_4 is absorbed in the column, NO is liberated primarily in the column itself with a small amount evolving from the liquor after leaving the column. The absorption rate was determined by photometric gas analysis.

Wendel and Pigford[11] studied the absorption of NO_2^* into water using a wetted-wall column and N_2 as the diluent gas. The NO_2^* partial pressure was varied up to 0.20 atm. The range of gas rates covered $Re(g)$ from 170 to 350; water rates were varied to allow contact time between gas and liquid from 0.03 to 0.3 sec; and experiments were conducted at 298 and 313 K. No effects of gas or liquid flow rates or of contact time between

Table 1. Experimental information for the absorption of N_2O_4 into water

	Temperature (K)						References
	293	298	303	308	313	318	
$\dfrac{\sqrt{D_{N_2O_4,H_2O}\, k_2}}{He_{N_2O_4}}$ $\left(\dfrac{kg \cdot mole}{atm\ m^2 sec}\right)$		$.09 \times 10^{-2}$			1.2×10^{-2}		Denbigh and Prince[a]
		1.1×10^{-3}				2.5×10^{-3}	Caudle and Denbigh[b]
		0.58×10^{-3}			0.54×10^{-3}		Wendel and Pigford[c]
		1.1×10^{-3}		1.0×10^{-3}			Dekker, Snoeck, and Kramers[d]
	$.77 \times 10^{-3}$		$.89 \times 10^{-3}$				Kramers, Blind, and Snoeck[e]
		$.903 \times 10^{-3}$					Hoftyzer and Kwanten[f]
k_2 (sec^{-1})		290.0			1340.0		Wendel and Pigford[c]
	250.0		330.0				Kramers, Blind, and Snoeck[e]
$He_{N_2O_4}$ $\left(\dfrac{atm\ m^3}{kg \cdot mole}\right)$		1.04			2.86		Wendel and Pigford[c]
	0.72		0.81				Kramers, Blind, and Snoeck[e]
$D_{N_2O_4,H_2O}$ $\left(\dfrac{m^2}{sec}\right)$	1.23×10^{-9}		1.59×10^{-9}				Kramers, Blind, and Snoeck[e]

[a] J. Chem. Soc. 53: 790-801 (1947).

[b] Trans. Faraday Soc. 49: 39-52 (1953).

[c] Am. Inst. Chem. Eng. J. 4: 249-256 (1958).

[d] Chem. Eng. Sci. 11: 61-71 (1959).

[e] Chem. Eng. Sci. 14: 115-123 (1961).

[f] Process for Air Pollution Control, 2nd Ed., 164-187 (1972).

the two reaction rates were observed. The indicated rate-controlling step was the hydrolysis of N_2O_4, expressed by reaction (7). The absorption rate data were correlated using equation (12). Experimental values are given in Table 1.

The results were interpreted using the penetration theory and assuming that reaction (7) occurs in the liquid film. From the experimental data, a pseudo first-order rate constant for reaction (7) and a Henry's law constant for N_2O_4 in water were calculated and are presented in Table 1.

Peters and Holman[12] used both nitrogen and air as the diluent gas in their wetted-wall column experiments on the absorption of NO_2^* into water and NaOH solutions, with no significant differences in results. The NO_2^* partial pressure was maintained at 0.048 atm; all runs were made at atmospheric pressure and at temperatures ranging from 301 to 329 K. Reaction (7) was assumed to apply for the reaction of N_2O_4 and water. Removal efficiency decreased significantly with increased temperature for runs using water or NaOH solutions. The following equation describes the reaction of NO_2^* and NaOH:

$$2NaOH + N_2O_4 \rightarrow NaNO_2 + NaNO_3 + H_2O . \tag{13}$$
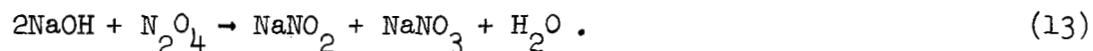
Both the gas and liquid phases were analyzed and inlet and outlet NO_2^* and HNO_3 or NaOH concentrations were determined chemically.

The presence of NO in the off-gas when an NaOH solution is the absorbent liquid may indicate a gas-phase reaction for the hydrolysis of NO_2^*. However, no proportionality of NO_2^* removal to the water vapor fugacity was found in runs in which the feed-gas stream contained water vapor. The nonproportionality of the NO_2^* removal rate to water vapor fugacity was interpreted as indicating the presence of a liquid-phase reaction; both liquid- and gas-phase reactions may contribute to NO_2^* absorption.

Carberry,[13] in a literature review in 1959, concluded that when N_2O_4 is dissolved in solvents of high dielectric strength, ionization occurs according to the reaction

$$N_2O_4(\ell) \rightarrow NO^+(\ell) + NO_3^-(\ell) , \tag{14}$$

and N_2O_4 exists in these solutions in the ionized form. In light of this conclusion, the reaction of dissolved N_2O_4 and water may be written as

$$N_2O_4(\ell) + H_2O(\ell) \rightarrow NO^+(\ell) + OH^-(\ell) + H^+(\ell) + NO_3^-(\ell) \tag{15}$$

or

$$N_2O_4(\ell) + H_2O(\ell) \rightarrow HNO_2(\ell) + H^+(\ell) + NO_3^-(\ell) . \tag{16}$$
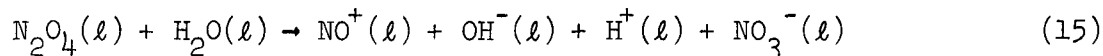
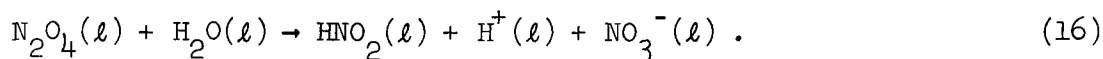The ionization of N_2O_4 not only supports the kinetic and chemical equilibrium data but also provides potent support to the argument that a purely gas-phase reaction between N_2O_4 and water vapor is an unlikely occurrence.

Dekker, Snoeck, and Kramers[14] investigated NO_2^* absorption in a wetted-wall column for contact times of 0.2 to 0.4 sec, inlet NO_2^* partial pressures of 0.03 to 0.15 atm, and operating temperatures of 298 to 308 K. The absorption rate data were correlated with an equation similar to equation (12); contact time had little effect on absorption rate. The experimental results, given in Table 1, are fairly consistent with the following model:

1. In the gas phase, NO_2 and N_2O_4 are in continuous equilibrium with each other,

2. At the gas-liquid interface, only N_2O_4 is dissolved in water, and

3. The diffusion of N_2O_4 into water is accompanied by a rapid pseudo first-order chemical reaction between N_2O_4 and water.

Absorption of NO_2^* was measured by photometric analysis of the gas phase and titration of the liquid acid phase for both HNO_3 and HNO_2.

Koval and Peters[15] examined the absorption of NO_2^* from feed-gas mixtures of NO_2^*-NO-N_2 into water at 304 K in a long wetted-wall column at atmospheric pressure. The NO_2^* partial pressure was varied up to 0.04 atm. On chemical analysis of gas and liquid phases, they noted that the presence of NO had marked effect on the HNO_3-HNO_2 split, greatly increasing the production of HNO_2 at the expense of HNO_3 production. The chemical stoichiometry is described by the following equation:

$$(2+\beta/4)N_2O_4(g) + (2+\beta/2)H_2O(\ell) \rightarrow 2HNO_3(\ell)$$

$$+ 2(1+\beta/2)HNO_2(\ell) - (\beta/2)NO(g) , \tag{17}$$
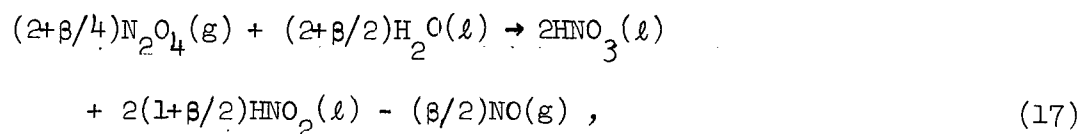
where β refers to the molar excess of HNO_2 over HNO_3. The following rate equation takes into account a varied amount of HNO_2 and best describes the experimental data:

$$R_{NO_2}^* = k(P_{N_2O_4})_i + k'(P_{NO})_i(P_{NO_2})_i - k''c_{HNO_2}^2 \tag{18}$$

Rate equation (18) allows for a significant and varied amount of HNO_2, whereas rate equation (12) does not.

Moll[16] investigated the rate of hydrolysis of N_2O_4 over a temperature range of 300 to 318 K. He injected liquid N_2O_4 directly into a flowing water stream and measured the resulting temperature rise downstream of the injection point. From these temperature profiles he determines k_2. His correlation of k_2 with the temperature from 300 to 318 K is

$$\text{Log } k_2 = 7.12 - 1375/T . \tag{19}$$

His work is the first direct evidence that the hydrolysis of N_2O_4 occurs as equation (12), a first-order reaction.

Hoftyzer and Kwanten[3] investigated the absorption of N_2O_4 by laminar jets. The variables studied were: the partial pressure of NO_2^*, 0.05 to 1.70 atm; temperature, 276 to 348 K; and acid molarity. Data were correlated using equation (12). The experimentally determined $\sqrt{D_{N_2O_4,H_2O}k_2}$ / $He_{N_2O_4}$ is given in Table 1 for 298 K, and the following correlation represents their data for temperatures form 276 to 348 K:

$$\text{Log}\left[0.98 \frac{\sqrt{D_{N_2O_4,H_2O}k_2}}{He_{N_2O_4}}\right] = -53.0 - 760/T . \tag{20}$$

They found that the value of $\sqrt{D_{N_2O_4,H_2O}k_2}/He_{N_2O_4}$ decreased with increasing acid molarity. This decrease was attributed to the increase in He with increasing ionic strength. They stated that the values of He could be corrected by using the factor $\exp(-0.075\ I)$, where I is the ionic strength defined by

$$I = 1/2 \sum_{i=1}^{n} (z_i^2 c_i) \tag{21}$$

Detournay and Jadot[17] proved the existence of a homogeneous gas-phase reaction between N_2O_4 and water vapor with a second-order reaction rate constant of 0.13 kg·mole m^{-3} sec^{-1} at 333 K. When this rate constant is compared with the rate constant for the liquid-phase hydrolysis of N_2O_4 estimated from the work of Wendel and Pigford[11] of 96.0 kg·mole m^{-3} sec^{-1}, the contribution of a gas-phase reaction of N_2O_4 and water vapor to NO$_x$ removal appears negligible.

Peters, Ross, and Klein[18] studied NO$_2^*$ absorption in a single-plate 0.19-m ID bubble-cap column equipped with seven bubble caps. The experiment was conducted at acid concentrations of 0 and 2.6 M and NO$_2^*$ partial pressures up to 0.10 atm. Runs were made at liquid flow rates of 5.0 x 10^{-6} and 10.0 x 10^{-6} m^3/sec and gas velocities of 0.36 and 0.72 m/sec in the slots. All runs were conducted at atmospheric pressure and at temperatures from 292 to 297 K. No significant difference in the results was noted from the use of nitrogen or air as the diluent gas. They assumed that reaction (7) applied for the hydrolysis of N_2O_4 and that a model developed from chemical reaction rates was adequate. The rate of removal of NO$_2^*$ was proportional to the concentration of N_2O_4 in the gas phase. Plate efficiencies are presented in Fig. 1. The fraction of entering oxides converted to nitric acid decreased as contact time between gas and liquid decreased. Liquid flow rate and the acid molarity of scrubbing liquid had no effect on plate efficiency. However, increasing the humidity in the feed gas did increase plate efficiency. They concluded that the absorption reactions occur at the gas-liquid interface.

Peters[19] compared the absorption of NO$_2^*$ from air into water and dilute nitric acid (<2.6 M) in the following devices: a single-plate bubble-cap column previously described;[18] a 0.025-m ID column, packed with 1/4-in. glass raschig rings to a height of 1.17 m; a 0.14-m ID single-plate fritted bubbler column consisting of 12 medium-frit glass rods sealed into the plate; a 0.025-m ID spray tower 1.32 m in height and equipped with a single spray nozzle; and a 0.025-m ID bed of silica gel packed to a height of 0.3 m. The partial pressure of NO$_2^*$ was varied from 0.002 to 0.02 atm, but the total pressure was maintained at 1.0 atm. The temperature was maintained at 298 K.
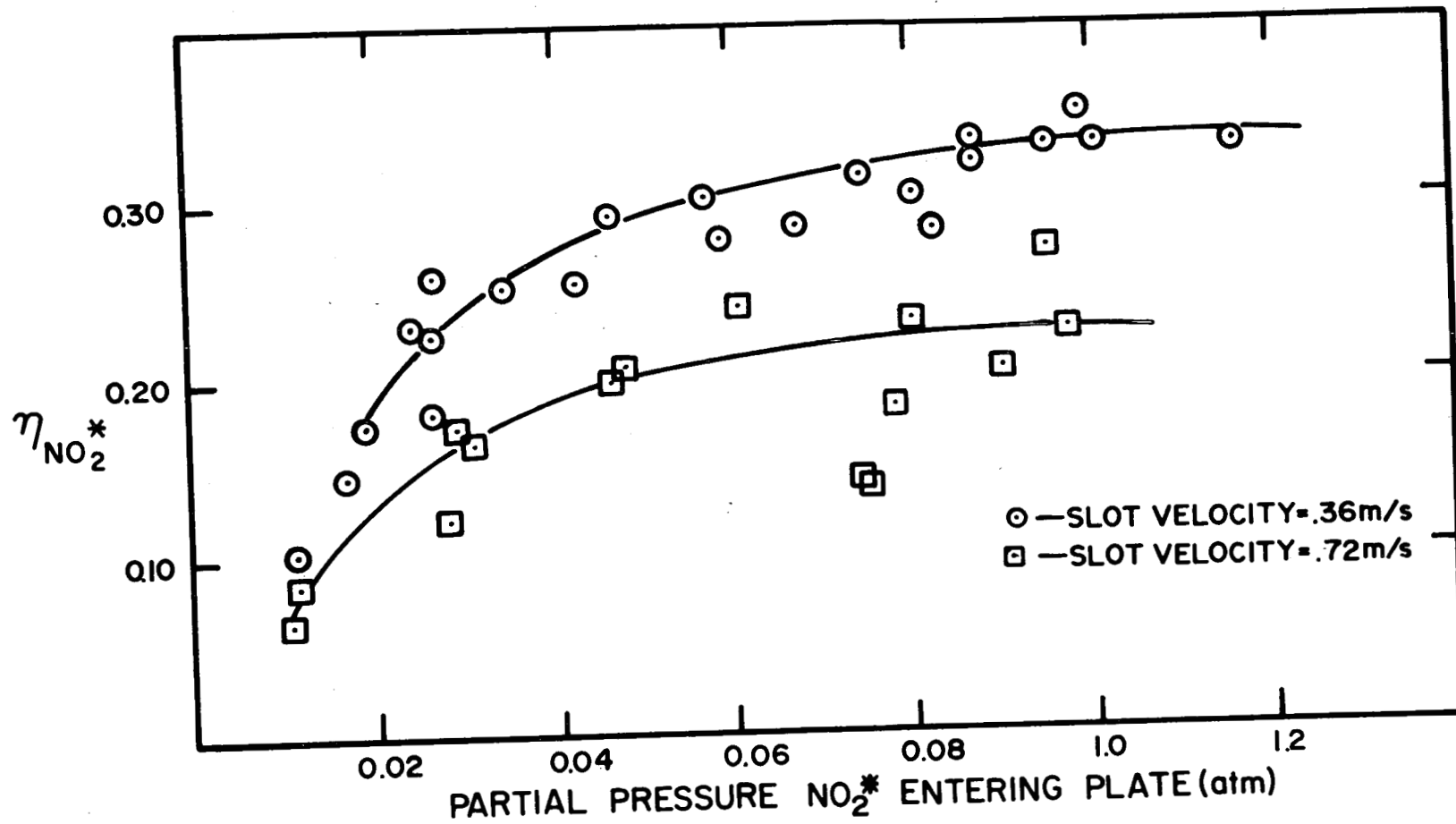
Fig. 1. Bubble-cap plate NO_2^* removal efficiencies versus NO_2^* concentration obtained by Peters, Ross, and Klein.

A. I. Ch. E. J. 1:105-11 (1955).

Efficiencies of the packed beds were reported as per 0.3 m of packing. Operating parameters were chosen to permit a fair comparison of the removal efficiencies of various types of contactors. The removal efficiency was independent of the liquid rate in the bubble-cap and fritted bubbler columns if the concentration of the liquid did not increase above 2.8 $\underline{M}$ nitric acid. The spray column was operated at a liquid rate that would yield a finely-divided mist, and the packed column was operated at approximately 90% of flooding.

The experimental results are presented in Fig. 2. The performance of the bubble-cap column improved with increasing NO_2^* concentration, and its removal efficiency is significantly surpassed only by that of the fritted bubbler column. The removal efficiency of the fritted bubbler column was higher than that of other devices except at concentrations of NO_2^* less than 0.004 atm. However, the pressure drop through the plate was about 30 times higher than that of the bubble-cap plate. Removal efficiencies with the packed column were lower than those found with the bubble-cap column or fritted bubbler column. The decrease in efficiency with reduction in NO_2^* concentration is fairly gradual, and at NO_2^* partial pressures of less than 0.002 atm, its performance is comparable to other types of equipment. The results obtained with the spray column indicate poor removal efficiencies at NO_2^* concentrations less than 0.001 atm, but at higher concentrations the spray-column efficiencies are comparable to other types of equipment. The silica gel absorber gives the best removal efficiency of the units tested at concentrations of less than 0.004 atm.

A stirred-tank reactor was used by Peters and Koval[20] to study the absorption of NO_2^* from NO_2^*-air mixtures into water. The partial pressure of NO_2^* varied from 0.4 to 4.4 atm; both the gas and liquid phases were analyzed to determine NO_2^* absorption. Removal efficiency improved with increased NO_2^* concentration and/or increased agitation. The agitator was designed to break up large gas bubbles into smaller bubbles. The data were correlated with the following rate equation:

$$R_{NO_2^*} = k_2 C_{N_2O_4,i} + \left[\frac{k_{5,F} k_{6b,F} C_{H_2O,i}^2}{k_{5,B} + k_{6b,F} C_{H_2O,i}^2} \right] \left(C_{NO,i} C_{NO_2,i} \right) . \qquad (22)$$
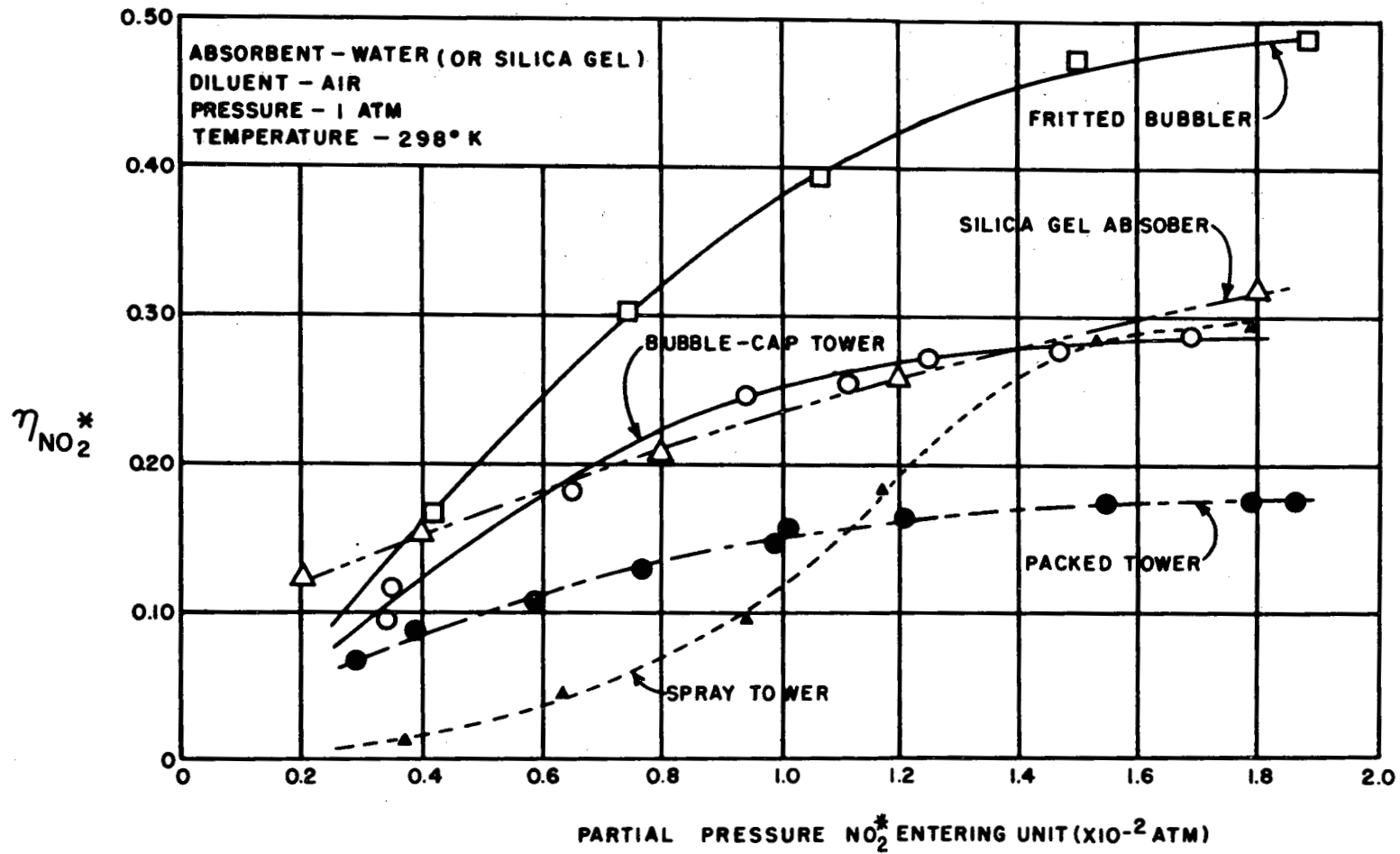
Fig. 2. Efficiency of NO_2^* removal from dilue gas with different types of equipment obtained by Peters.

Univ. of Ill. Eng. Exp. Rep. No. 14, USAEC-COO-1015, (1955).

Equation (22), in contrast to equation (12), adds a term to take care of N_2O_3 reactions.

This experiment differs from the bubble cap, sieve plate, or wetted-wall column work in that the stirred tank provides for greater gas-liquid contact time and contact area. Under these conditions the reaction of N_2O_3 with water can not be ignored.

Andrews and Hanson[21] studied the absorption of NO_2^{**} from air-NO_2^{**} and air-NO_2^{**}-NO gaseous mixtures into dilute nitric acid using a recirculating acid stream and a small single sieve-tray column at 298 K. The gas mixture NO_2^{**} is defined as the sum of concentrations NO_2^{*} plus N_2O_3 plus $(1/2)HNO_2$. The partial pressure of NO_2^{**} was varied up to 0.10 atm. For NO_2^{**} concentrations greater than 0.01 atm, the predominant absorption mechanism is the solution of N_2O_4 into the liquid followed by its rapid hydrolysis to HNO_3 and HNO_2. These investigators developed the following model for plate efficiency that correlates well with their experimental data:

$$\ln \ (1-\eta_{NO_2^{**}}) = \frac{-k^* \ a}{G} (P_{NO_2^{**},i})$$
(23)

where k^* is a combination of equilibrium, kinetic, and transfer constants. The data are presented in Fig. 3. Plate efficiencies increased slightly for NO_2^{**} absorption when NO was present in partial pressures of 0.05 atm and higher and when the NO_2^{**} partial pressure in the gas phase was less than 3 to 4 atm.

The absorption of NO_2^{*} from an inert carrier gas into water at 293 and 303 K was studied by Kramers, Blind, and Snoeck[22] using a laminar water jet. The absorption rate was determined by chemical analysis of the liquid phase for HNO_2 and HNO_3. The absorption rate data were correlated with equation (12); experimental results are given in Table 1.

2.3 Reactions Involving Aqueous HNO_2

Abel and others[23] performed several experiments involving the kinetics of aqueous nitrous acid formation and decomposition. During the early stages of nitrous acid formation, the rate of reaction was found to be
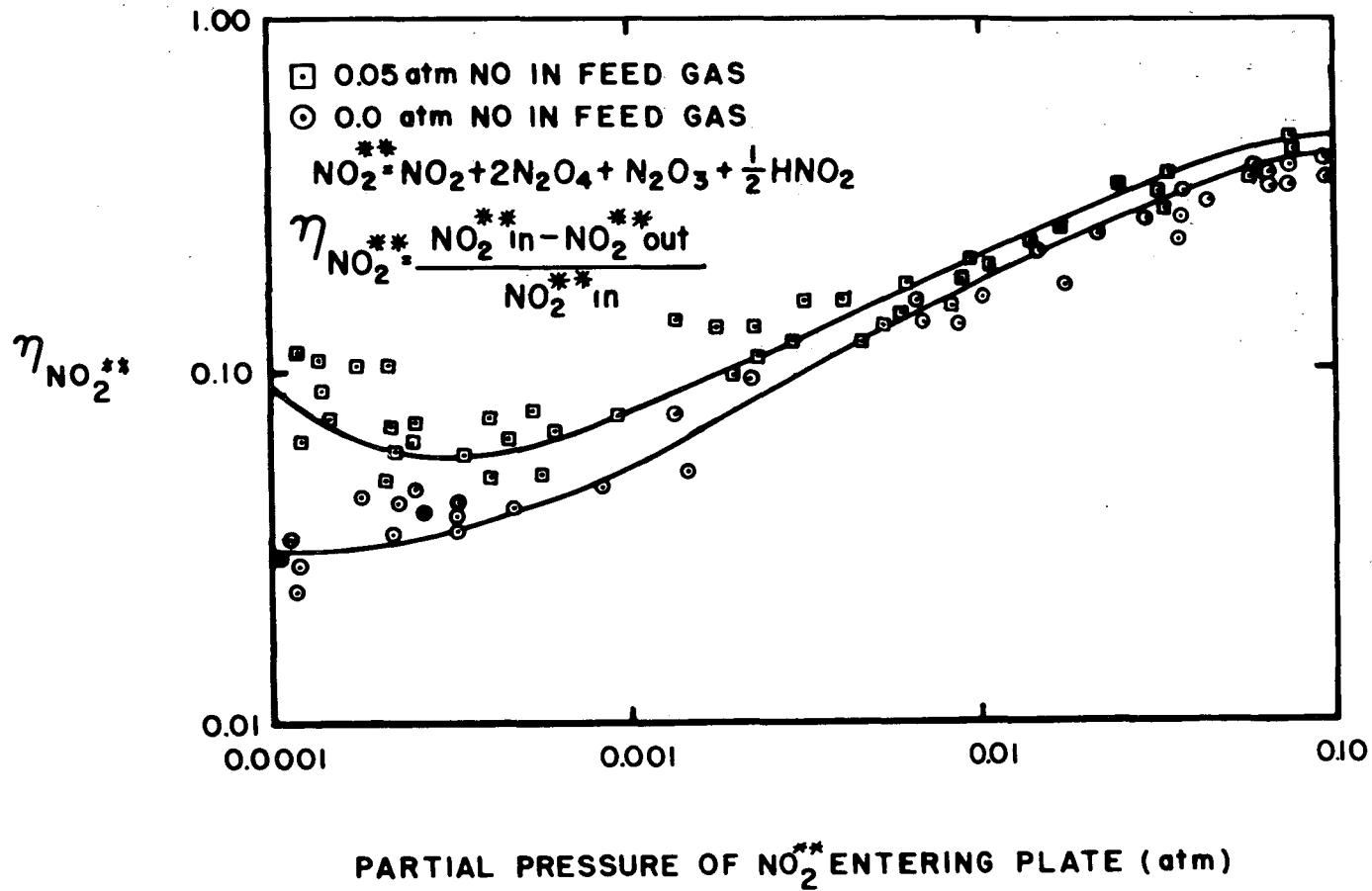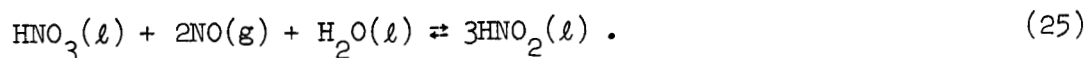
Fig. 3. Sieve-plate NO_2^{**} removal efficiencies versus NO_2^{**} concentration obtained by Andrews and Hanson.

Chem. Engr. Sci. 14:105-13 (1961).

$$\frac{dC_{HNO_2}}{dt} = k_{3,B}(C_{HNO_2})(C_{H^+})(C_{NO_3^-}) \ , \tag{24}$$

where the reaction was assumed to be

$$HNO_3(\ell) + 2NO(g) + H_2O(\ell) \rightleftarrows 3HNO_2(\ell) \ . \tag{25}$$

During the early stages of the decomposition, the following expression describes the disappearance of nitrous acid

$$-\frac{dC_{HNO_2}}{dt} = \frac{k_{3,F}(C_{HNO_2})^4}{P_{NO}^2} \ . \tag{26}$$

Abel suggests that the decomposition occurs as

$$4HNO_2(\ell) \rightleftarrows N_2O_4(\ell) + 2NO(g) + 2H_2O(\ell) \ . \tag{27}$$
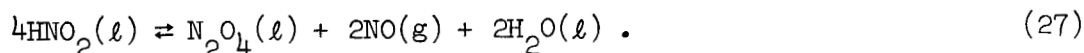
At equilibrium

$$K_3 = \frac{k_{3,F}}{k_{3,B}} = \frac{(C_{H^+})(C_{NO_3^-})(P_{NO})^2}{C_{HNO_2}^3} \ . \tag{28}$$

The experimental values of $k_{3,F}$, $k_{3,B}$, and K_3 are given in Table 2.

The stoichiometry of Abel's chemical reaction equations seems to indicate a liquid-phase equilibrium of N_2O_4. However, using Carberry's[14] conclusions concerning the ionic nature of dissolved N_2O_4, Abel's equation representing the decomposition of HNO_2 in the liquid phase may be written as

$$4HNO_2(\ell) \rightleftarrows HNO_2(\ell) + H^+(\ell) + NO_3^-(\ell) + 2NO(g) + H_2O(\ell) \ . \tag{29}$$
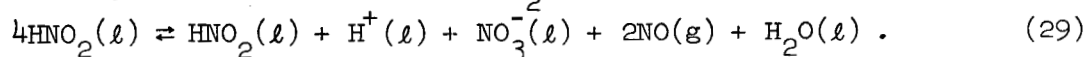
By subtracting a molecule of HNO_2 from both sides of the preceding equation, the stoichiometry becomes the same as Abel's chemical equation for the formation of HNO_2 in the liquid phase. Thus, the apparent discrepancy in Abel's use of two sets of stoichiometry for the formation and decomposition of HNO_2 in the liquid phase seems to be resolved.

Andrews and Hanson[21] calculated and verified the following equilibrium constant at 298 K:

$$\frac{(P_{NO_2})(P_{NO})}{C_{HNO_2}^2(\ell)} = 1.6 \times 10^{-2} \ \frac{atm^2 \ m^6}{kg \cdot mole^2} \ . \tag{30}$$

Table 2. Experimental results concerning aqueous HNO_2

	Temperature (K)						
	273	285	285.5	288	298	313	333
$k_{3,F}\left(\dfrac{m^9\ atm^2}{kg \cdot mole^3\ sec}\right)$	0.010	0.061			0.767	8.75	
$k_{3,B}\left(\dfrac{m^6}{kg \cdot mole^2\ sec}\right)$					0.027		
$K_{P,3}\left(\dfrac{m^3}{kg \cdot mole\ atm^2}\right)$			13.3	14.1	28.7	39.6	85.5

Z. Physik. Chem. 132: 56-77 (1928); 134: 279-300 (1928); 136: 135-45, 419-36 (1928).

2.4 The Oxidation of NO

Bodenstein[24] studied the gas-phase oxidation of gaseous NO at 273, 303, 333, and 363 K; the partial pressure of NO varied from 0.08 to 0.14 atm in excess O_2. Bodenstein confirmed the third-order kinetics consistent with the following rate equation:

$$r_4 = k_4 P_{NO}^2 P_{O_2} \ .$$

$$(31)$$

Rate constants are given in Table 3.

Under conditions comparable to those of Bodenstein, Hasche and Patrick[25] examined the kinetics of the gas-phase reaction of NO and O_2 at 273 and 303 K and found that a third-order reaction occurs consistent with equation (31). The reaction appears to be catalyzed by the presence of glass wool. Reaction rate constants are given in Table 3.

Treacy and Daniels[26] also found a third-order reaction consistent with equation (31) in their analysis of gas-phase reaction kinetics of NO and O_2 at 273, 298, and 338 K. The NO partial pressure varied from 0.006 to 0.02 atm and the O_2 partial pressure varied from 0.026 to 0.006 atm; reaction rate constants are given in Table 3.

The reaction rate constant of Morrison, Rinker, and Corcoran[27], who investigated the gas-phase oxidation of NO at 300 K is also presented in Table 3. The NO concentration varied from 2 to 75 ppm; the oxygen concentration ranged from 0.03 to 0.25 atm. The reaction appeared to proceed as a third-order reaction consistent with equation (31).

Greig and Hall[28] used similar parameters to investigate the gas-phase oxidation of NO. Temperatures used were 293, 322, 352, and 372 K; the partial pressure of NO varied from 0.05 to 0.11 atm, and the partial pressure of O_2 ranged from 0.01 to 0.28 atm. This group also confirmed third-order kinetics consistent with equation (31). Rate constants are presented in Table 3.

2.5 Reactions Involving N_2O_3

Verhoek and Daniels[2] studied the equilibrium reaction

$$N_2O_3(g) \rightleftarrows NO_2(g) + NO(g)$$

$$(5a)$$

Table 3. Experimental values for the reaction rate constant for the oxidation of NO

	Temperature (K)											References
	273	293	298	300	303	322	333	338	352	363	372	
k_5 (atm^{-2} sec^{-1})	34.75				22.95		14.86			10.16		Bodenstein[a]
	43.24				26.19							Hasche and Patrick[b]
	25.9		13.4					9.75				Treacy and Daniels[c]
				21.47								Morrison, Rinker, and Corcoran[d]
		34.8				24.1			18.2		15.0	Greig and Hall[e]

[a] Z. Elektrochem. 24: 183-201 (1918).

[b] J. Am. Chem. Soc. 47: 1207-1214 (1925).

[c] J. Am. Chem. Soc. 77: 2033-2036 (1955).

[d] Ind. Eng. Chem. Fund. 5: 175-181 (1966).

[e] Trans. Faraday Soc. 63: 655-661 (1967).

and calculated the following equilibrium constants:

Temperature (K)	K_p (1/atm)
298	1.67
308	2.83
318	4.53

At room temperature and above the equilibrium concentration of N_2O_3 is very low.

Wayne and Yost[29], who studied reaction (6a) at 298 K, found that the forward reaction for the gas-phase hydrolysis of N_2O_3 is catalyzed by water and proceeds at third-order kinetics with a rate constant of 1.1×10^5 atm^{-2} sec^{-1}. The backward reaction is also catalyzed by water and proceeds as a third-order reaction with a rate constant of 6.6×10^{-4} atm^{-2} sec^{-1}. The dissociation rate of N_2O_3, reaction (5), proceeds with a first-order rate of 150 sec^{-1}.

2.6 Multiple Plate Absorbers

Currently, little published information exists on research involving the absorption of gaseous NO_x compounds into water or dilute nitric acid in engineering-scale absorption columns. However, information is available on engineering-scale and larger column performances involving the absorption of gaseous NO_x into nondilute nitric acid solutions. This literature usually originates in the nitric acid production industry; however, some data presented in these reports is pertinent to the design of NO_x absorption equipment in which the hydrolysis reaction is considered essentially irreversible.

Peters[19] studied NO_2^* absorption from air into water and dilute nitric acid (<2.6 M) in a three-stage bubble-cap column. A typical plate was described above. The distance between the plates was 0.3 m; the partial pressure of NO_2^* in the feed varied from 0.005 to 0.08 atm. Distilled water was fed into the top of the column at a rate of 5.0×10^{-6} m^3/sec. The gas flow rate was 5.9 m^3/sec. Other operating conditions were as described above. The efficiencies of the three plates are presented in Fig. 4. The efficiency increases as the gas moves up the tower for any given NO_2^* partial pressure in the feed.
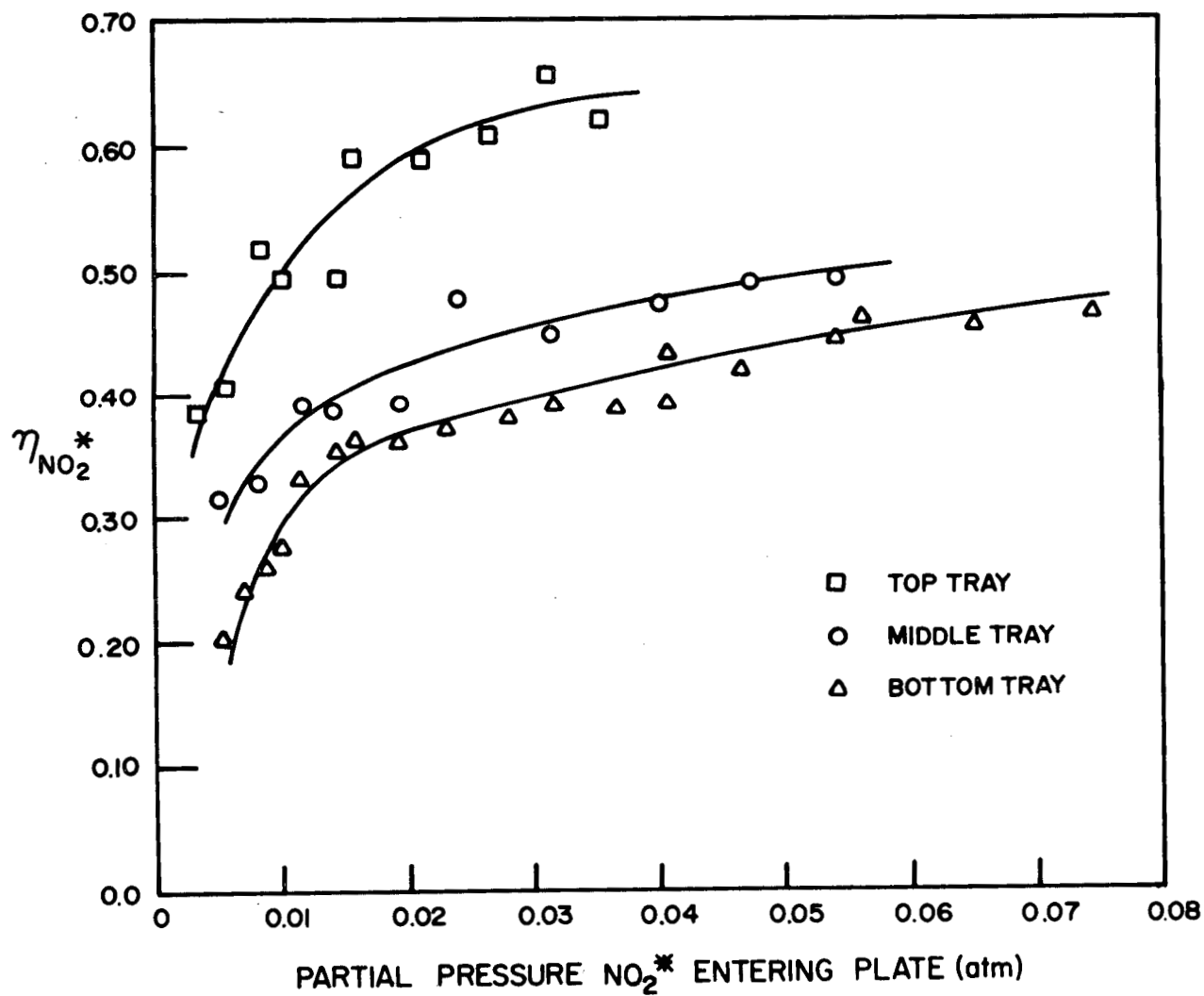
ORNL DWG 77-288 RI

Fig. 4. Effect of NO_2^* concentration in entering gases on plate efficiency with a three-plate bubble-cap column obtained by Peters. Univ. of Ill. Eng. Exp. Rep. No. 14, USAEC-COO-1015, (1955).

An industrial-scale bubble-cap column was used by Fauser[30] to measure the effects of temperature and pressure on NO_2^* absorption. He found that absorption rates increase with decreasing operating temperatures (288 to 259 K) and with increasing operating pressures (up to 5 atm).

Taylor, Chilton, and Handforth[31] studied the effects of temperature and pressure on NO_x absorption in a pilot-plant-scale bubble-cap column. Column efficiency increased by reducing the operating temperature or by increasing the operating pressure. The column performance was accurately predicted using Bodenstein's data for the oxidation of NO and existing equilibrium data for the NO_2-N_2O_4 equilibrium.

Atroshchenko, Konvisar, and Kordysh[32] studied the absorption of NO_x compounds in a 0.03-m ID bubble-cap column. Murphree plate efficiency generally increases with increasing NO_2^* partial pressures and with increasing interplate distance. Atroshchenko, Konvisar, and Ivakhnenko[33] later investigated the effect of plate hole size, the ratio of open area to total plate area, and the gas flow rate on gaseous NO_x absorption in a sieve-plate column. In general, they discovered that plate efficiencies increase with decreased plate open area and decreased gas flow rates.

Nitric acid production was examined by Hellmer[34] using a semi-industrial-scale sieve-plate column with cooling coils located in the bubble layer of the plates. The acid concentration was varied along with the NO_2^* concentration. According to Hellmer, it is possible to calculate the number of plates necessary for a given HNO_3 outlet acid concentration and entering NO_2^* concentration using literature rate constants for reactions (4) and (7). Murphree plate efficiencies ranged from 23 to 65% for acid concentrations varying from 0 to 15 M. At partial pressures of NO_2^* from near zero to 0.25 atm, Murphree plate efficiencies varied from 23 to 67%.

Chilton[35] gives a fairly complete review of the Dupont Pressure Process of nitric acid production.

3. SUMMARY

The predominant mechanism for nitrogen oxide absorption at NO_2^* partial pressures greater than 0.01 atm is the solution and hydrolysis of N_2O_4 to HNO_2 and HNO_3. However, if gas-liquid contact time is extended, or if high concentrations of gaseous NO are present during gas-liquid contact, the solution and hydrolysis of N_2O_3 and/or the solution of HNO_2 then appear to be competitive absorption mechanisms. The dissociation of liquid HNO_2 cannot necessarily be assumed to occur rapidly. In a recirculating system, a steady-state HNO_2 concentration in equilibrium with the gas phase has been reported. The gas-phase oxidation of NO proceeds rather slowly and requires sufficient gas space and relatively cool temperatures to proceed. The absorption reactions are very exothermic, and absorption generally decreases with increasing temperature.

Currently, a void exists in the literature in the area of applying the available kinetic data for nitrogen oxide systems to the overall design of large-scale equipment for the absorption of gaseous NO_x into water or dilute nitric acid. The following characteristics are desirable for NO_x absorption equipment: (1) discrete and optimal gas-liquid contact for N_2O_4 absorption, (2) intermittant and discrete gas spaces for NO oxidation, and (3) low operating temperatures.

Plate towers as NO_x absorption devices seem to be the choice of the nitric acid industry[3]. However, packed towers continue to be used by some European manufacturers of nitric acid[3]. Both of these applications are for high-pressure (>5.0 atm) absorption. For scrubbing gaseous NO_x compounds at essentially atmospheric pressure, the choice for absorption equipment seems to be the plate column. At sufficiently low gaseous concentrations of NO_x, the packed column seems to be a reasonable alternative.

4. NOTATION

a	Interfacial area, m^2/m^3
B	Backward reaction
C_n	Liquid phase concentration of component n, $kg \cdot moles/m^3$
d	Differential
$D_{n,j}$	Diffusivity of component n in phase j, m^2/sec
F	Forward reaction
G	Superficial gas velocity, m^3/sec
He	Henry's Law constant, $atm \ m^3/kg \cdot mole$
i	Gas-liquid interface
I	Ionic strength $kg \cdot mole/m^3$
k*	Mass transfer rate constant of NO_2^*, $m^2/(atm \ sec)$
k, k', k"	Mass transfer constants containing appropriate Henry's Law and equilibrium constants
k_n	Reaction rate constant for nth reaction
$K_{p,n}$	Pressure equilibrium constant for nth reaction
NO_2^*	$NO_2 + 2N_2O_4$
NO_2^{**}	$NO_2 + 2N_2O_4 + N_2O_3 + (1/2)HNO_2$
NO_x	$NO_2 + 2N_2O_4 + NO$
P	Pressure, atm
P_n	Partial pressure of component n, atm
r_n	Chemical reaction rate of nth reaction, atm/sec
R_n	Mass transfer rate of component n, $kg \cdot mole/(m^2 \ sec)$
Re(n)	Reynolds number for nth phase, dimensionless
t	Time, sec
T	Temperature, K

Z_n Ionic charge of species n

β Molar excess of HNO_2 over HNO_3

$\eta_{NO_2^*}$ Plate efficiency, NO_2^* absorbed/NO_2^* entering

$\eta_{NO_2^{**}}$ Plate efficiency, NO_2^{**} absorbed/NO_2^{**} entering

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