Mass Transfer in the Absorption of Nitrogen Oxides in Alkaline Solutions

The absorption of mixtures of nitrogen oxides into aqueous solutions of NaOH in the range of partial pressures of 0.004- to 0.05-atm NO and 0.002- to 0.015-atm NO_2 was investigated. Absorption experiments were conducted in a gas-liquid contactor that permitted independent variation of the gas and liquid mass transfer coefficients. The results were analyzed in terms of a model which accounted for diffusion, reaction, and formation of higher oxides and oxyacids in the gas and in the liquid phases. Absorption of both HNO_2 and N_2O_3, formed in the bulk gas and within the gas diffusion film, were found to be significant. Using a rate coefficient of 8.8×10^{-3} mol/s · cm^3 · atm^3 for the formation of HNO_2 in the gas phase (England and Corcoran, 1975), a value of the absorption factor, $H\sqrt{Dk}$, for N_2O_3 of 2.5×10^{-3} mol/s cm^2 atm was determined at 25°C. This value was found to decrease with temperature and was 1.2×10^{-3} at 40°C. The use of concentrated base as an absorbent solution prevented the formation of nitric acid mist, a problem encountered in many previous studies of NO_x absorption.

Bernard L. Newman and
Giorgio Carta
Department of Chemical Engineering
University of Virginia
Charlottesville, VA 22901

Introduction

The absorption of mixtures of nitric oxide and nitrogen dioxide into aqueous alkaline media is important in many industrial processes, both in the area of pollutant emission control and in the production of inorganic nitrogen chemicals.

Absorption into solutions or slurries is conducted in the production of sodium and calcium nitrite, which are sold as specialty chemicals, and ammonium nitrite, an intermediate in the production of caprolactam. Mixtures with lower NO_x concentrations, produced as off-gases from nitric acid production or usage, are scrubbed using alkaline solutions. In addition, gas mixtures containing NO and NO_2 are contacted with alkaline compounds in the process of flue gas desulfurization, in either wet scrubbers or spray dryers. Recent developments have focused on combining scrubbing with a variety of gas-solid catalytic processes, where SO_2 and NO are oxidized to SO_3 and NO_2, compounds which are much easier to remove by alkaline scrubbing.

While the absorption of nitrogen dioxide has been studied for many years, the absorption of NO/NO_2 mixtures has been the subject of far fewer studies. Joshi et al. (1985) have recently reviewed the literature on nitrogen oxide absorption.

Nitrogen oxide chemistry

The absorption of nitrogen oxides involves a number of chemical reactions, both in the gas and liquid phases. The gas-phase reactions occurring in the process are

$$2NO + O_2 \rightarrow 2NO_2 \tag{1}$$

$$2NO_2 \rightleftharpoons N_2O_4 \tag{2}$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \tag{3}$$

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \tag{4}$$

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \tag{5}$$

Reactions 2 and 3 are very rapid and can be considered to be in equilibrium for typical absorption processes. Reaction 1 proceeds at a rate which is proportional to the square of the NO concentration and which decreases as temperature is increased. Some estimates are available for the rate of reaction 5 (England and Corcoran, 1975) and the equilibrium constant can be calculated. When the NO partial pressure is comparable to or greater than that of NO_2, the equilibrium concentration of nitric acid is very small for typical process conditions.

Correspondence concerning this paper should be addressed to G. Carta.

Reaction 4, that leads to the formation of nitrous acid, has been the subject of numerous kinetic studies, because of its importance in both chemical processing and the chemistry of the atmosphere. Table 1 summarizes the results of a number of these studies, which have yielded widely varying results. Some investigators have found a fourth-order mechanism, i.e., second order in the water partial pressure and first order in the partial pressures of NO and NO_2. The second-order dependence on water was attributed to catalysis by water adsorbed on the glass surfaces of their reactors. More recent studies have used reactors with a very large volume to surface ratio and very low NO_x partial pressures in an attempt to eliminate the occurrence of heterogeneous phenomena.

Schwartz and White (1983) have reviewed the equilibrium constants of the above reactions.

In the liquid phase, the following reactions may be considered:

$$N_2O_3 + H_2O \rightleftharpoons 2HNO_2 \qquad (6)$$

$$N_2O_4 + H_2O \rightleftharpoons HNO_3 + HNO_2 \qquad (7)$$

$$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2 \qquad (8)$$

In basic media, the neutralization of the acids is also important:

$$HNO_2 + OH^- \rightarrow H_2O + NO_2^- \qquad (9)$$

$$HNO_3 + OH^- \rightarrow H_2O + NO_3^- \qquad (10)$$

Except for the two oxyacids, HNO_2 and HNO_3, the gas-phase species have low solubilities in aqueous solutions, and the kinetics of reactions 6 through 8 must be obtained from absorption rate studies. Reactions 9 and 10 can be assumed to be instantaneous proton transfer reactions. Reaction 8 has been investigated by Lee and Schwartz (1981) who found that this reaction is important at low NO_2 partial pressures. Schwartz and White (1981) and Joshi et al. (1985) have reviewed the available information on the physical solubility of the various species in water.

Figure 1 (Carta, 1984) summarizes the mechanism of absorption of NO_x in alkaline solutions. NO is oxidized to NO_2 which is dimerized to form N_2O_4. The latter species is absorbed and leads to the formation of equimolar amounts of NO_2^- and NO_3^-. NO and NO_2 react to form N_2O_3 which is absorbed forming NO_2^-. In presence of water vapor, NO and NO_2 also react to form HNO_2 which is quickly absorbed forming again NO_2^-. Reaction 8 is neglected in this model as this reaction is significant only at very low partial pressures (Joshi et al., 1985). The occurrence of this network of reactions results in an interesting optimization problem in the production of nitrites. Tetravalent nitrogen (NO_2 and N_2O_4) must in fact accompany divalent nitrogen (NO) to permit the formation of N_2O_3 and HNO_2 which are absorbed readily to form nitrites. However, because of the occurrence of reaction 7 (and 8 at very low partial pressures), the presence of tetravalent nitrogen decreases the yield in nitrites as a result of absorption of N_2O_4. An appropriate choice of process conditions is thus needed to minimize the loss of fixed nitrogen in nitrates, while at the same time maintaining a sufficiently high rate of absorption.

Table 1. Rate Constants for Homogeneous Gas-Phase HNO_2 Formation, 25°C

Authors	Third-Order $mol/cm^3 \cdot atm^3 \cdot s$	Fourth-Order $mol/cm^3 \cdot atm^4 \cdot s$
Wayne and Yost (1951)		1.54
Leighton (1961)	3	
Graham and Taylor (1972)	8.18×10^{-4}	6.76×10^{-2}
England and Corcoran (1975)	8.83×10^{-3}	
Chan et al. (1976)	1.49×10^{-3}	
Kaiser and Wu (1977)	1.09×10^{-5}	
Sakamaki et al. (1983)	2.05×10^{-4}	
Pitts et al. (1984)	1.49×10^{-3}	

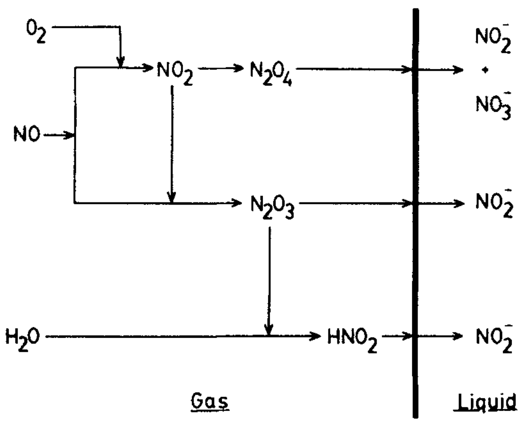

Figure 1. Diffusion/reaction network for absorption of nitrogen oxides in alkaline solutions.

Absorption of nitrogen oxides in aqueous solutions

The absorption of NO_2 in water has been studied extensively. All studies indicate that at partial pressures of NO_2 greater than about 0.002 atm the absorption of tetravalent nitrogen in water occurs via N_2O_4 following a fast, pseudofirst-order reaction mechanism. The rate of absorption is thus proportional to the square of the NO_2 partial pressure. The absorption parameter $H\sqrt{Dk}$ for N_2O_4 was found to be in the range $4.7 - 11 \times 10^{-5}$ $mol/s \cdot cm^2 \cdot atm$. Several reviews on this subject are available (Sherwood et al., 1975; Schwartz and White, 1983; Joshi et al., 1985).

There also have been a number of studies on the absorption of NO_2 into alkaline solutions (Chambers and Sherwood, 1937; Gray and Joffe, 1955; Kameoka and Pigford, 1977; Takeuchi and Yamanaka, 1978; Sada et al., 1979; Komiyama and Inoue, 1980; Weisweiler and Deiss, 1981; Aoki et al., 1982). These studies indicate little or no effect of added base on the absorption rate. This indicates that hydrolysis of N_2O_4 is the rate controlling step.

Contrary to the wealth of information on the absorption of N_2O_4, the published information on absorption of N_2O_3 is very limited. Corriveau (1971) and Hofmeister and Kolhaas (1965) found that the rate of absorption of divalent nitrogen into water is proportional to the partial pressure of N_2O_3 and assumed that the absorption process occurs with a fast pseudofirst-order reaction of N_2O_3 with water. The values of the absorption factor, $H\sqrt{Dk}$, for N_2O_3 determined by these authors were 1.59×10^{-4} and 5×10^{-4} $mol/s \cdot cm^2 \cdot atm$, respectively. Komiyama and

Inoue (1980) have investigated the absorption of NO/NO_2 mixtures diluted with nitrogen into 0.01 M NaOH and have found an approximate ¾ power dependence of the rate of absorption of divalent nitrogen on the product of the partial pressures of NO and NO_2. Aoki et al. (1982) have investigated the absorption of mixtures of NO (0.00066 to 0.012 atm) and NO_2 (5×10^{-6} to 0.002 atm) into NaOH and buffer solutions. They found that the rate of absorption of divalent nitrogen is proportional to the partial pressure of NO_2 at a given partial pressure of NO. Like previous studies, this result was attributed to absorption of N_2O_3 occurring in the fast pseudofirst-order reaction regime, but the absorption rate was two orders of magnitude greater than that predicted by the results of Corriveau (1971). In the theory proposed by the authors, the presence of the hydroxyl ions eliminated undissociated nitrous acid, which retarded the hydrolysis of N_2O_3 in Corriveau's experiments.

Carta (1984) has developed a theoretical model for absorption of NO and NO_2 into alkaline solutions. In this work it was theorized that, with a sufficiently fast rate of formation of HNO_2, the gas phase limited mass transfer of HNO_2 could be enhanced by formation of HNO_2 in the gas film. If one uses the kinetic data of England and Corcoran (1975) and the data of Corriveau (1971) for the absorption of N_2O_3 in water, enhancement can be shown to occur at high partial pressures of NO_x with the gas-side coefficients typically found in gas absorption towers.

The present study investigates experimentally the absorption of NO/NO_2 mixtures in alkaline solutions. The effects of simultaneous mass transfer and chemical reaction occurring both in the gas and in the liquid phases are investigated. Bulk condensation of nitric acid in the gas phase is eliminated in this work by using a sufficiently concentrated alkaline solution as the absorbent. A diffusion/reaction model based on the film theory is developed and numerical results are compared with experimental data obtained in a laboratory contactor. The absorption factors for absorption of N_2O_4 and N_2O_3 in the fast pseudofirst-order reaction regime are determined, using literature values for the rate constant for the formation of HNO_2 in the gas phase. Analysis of the experimental results in terms of the model shows that absorption of HNO_2 formed in the bulk gas becomes significant at low NO_2 partial pressures when NO is in excess. The presence of gas-phase mass transfer resistance reduces the partial pressure of NO_2 (and N_2O_4) at the gas-liquid interface thereby depressing considerably the formation of nitrates.

Transport Equations

When concentrated bases are used, HNO_2 is completely ionized in the liquid and does not influence transport of the other diffusing species in the liquid film. In this case, the absorption of N_2O_3 and N_2O_4 in the liquid can be assumed to follow a fast, pseudo-first order mechanism. Thus, the fluxes of N_2O_3 and N_2O_4 may be written as

$$\phi_{N_2O_3} = (H\sqrt{Dk})_{N_2O_3} P^i_{N_2O_3} \tag{11}$$

$$\phi_{N_2O_4} = (H\sqrt{Dk})_{N_2O_4} P^i_{N_2O_4} \tag{12}$$

where $P^i_{N_2O_3}$ and $P^i_{N_2O_4}$ are the partial pressures of N_2O_3 and N_2O_4 at the gas-liquid interface.

The fluxes in the gas film must be matched to those in the liquid and the bulk gas to determine the interfacial partial pressure of the diffusing species. Neglecting the presence of nitric acid in the gas phase and assuming that diffusion occurs through a stagnant gas layer of thickness δ adjacent to the gas-liquid interface, the transport equations for the gas film take the form

$$\frac{D_i}{RT}\frac{d^2P_i}{dx^2} + \sum_{n=2}^{4} (\nu_{i,+n} r_{+n} + \nu_{i,-n} r_{-n}) = 0, \quad i = 1, 6 \tag{13}$$

where the r_{+n}'s are the rates of the forward gas phase reactions 2, 3, and 4, the r_{-n}'s are the rates of the reverse of these reactions, and the $\nu_{i,n}$ the stoichiometric coefficients of species i in reaction n. The six species, i, for which these equations are written are NO, NO_2, N_2O_4, N_2O_3, HNO_2, and H_2O. By assuming that chemical equilibrium exists in the gas film for the formation of N_2O_3 and N_2O_4 according to reactions 2 and 3, two equations can be eliminated by substitution of the equilibrium conditions and addition and subtraction of equations. Four boundary conditions must be specified at each boundary of the film. Six of these are straightforward. If δ is the film thickness ($\delta = D/k^0_gRT$), and if $x = 0$ at the gas-liquid interface, then at $x = \delta$ four of the partial pressures (we used NO, NO_2, H_2O and HNO_2) are equal to the corresponding partial pressures in the bulk gas. At the gas-liquid interface ($x = 0$) the partial pressures of water and HNO_2 are those corresponding to physical equilibrium with the liquid. For a strong base absorbent, the HNO_2 back pressure is zero. The partial pressure of water is approximately equal to the saturated vapor pressure of the aqueous solution.

The two remaining boundary conditions are found by equating fluxes on the gas side of the interface to those in the liquid. For divalent nitrogen ($NO^* = NO + N_2O_3$) the boundary condition is

$$(H\sqrt{Dk})_{N_2O_3} P^i_{N_2O_3} = \frac{D_{N_2O_3}}{RT}\left(\frac{dP_{N_2O_3}}{dx}\right)_{x=0} + \frac{D_{NO}}{RT}\left(\frac{dP_{NO}}{dx}\right)_{x=0} \tag{14}$$

For tetravalent nitrogen ($NO_2^* = NO_2 + 2N_2O_4$) the boundary condition is:

$$\begin{aligned}(H\sqrt{Dk})_{N_2O_3} P^i_{N_2O_3} + 2(H\sqrt{Dk})_{N_2O_4} P^i_{N_2O_4} &= \frac{D_{N_2O_3}}{RT}\left(\frac{dP_{N_2O_3}}{dx}\right)_{x=0} + \frac{2D_{N_2O_4}}{RT}\left(\frac{dP_{N_2O_4}}{dx}\right)_{x=0} \\ &\quad + \frac{D_{NO_2}}{RT}\left(\frac{dP_{NO_2}}{dx}\right)_{x=0}\end{aligned} \tag{15}$$

As for the equations, the number of species in the boundary conditions may be reduced to four by substitution of the two equilibrium conditions for N_2O_3 and N_2O_4.

The partial pressures of HNO_2 and H_2O in the bulk gas are determined from overall material balances. If the absorption process occurs in a CSTR with a gas volume V and the gas molar flow rate is F, the following equations may be written

$$\begin{aligned}&2k_3VP_{NO}P_{NO_2}P_{H_2O} - 2k_{-3}VP^2_{HNO_2} \\ &\quad + \frac{F}{P}(P^o_{HNO_2} - P_{HNO_2}) = A\frac{D_{HNO_2}}{RT}\left(\frac{dP_{HNO_2}}{dx}\right)_{x=\delta}\end{aligned} \tag{16}$$

$$-k_3 V P_{NO} P_{NO_2} P_{H_2O} + k_{-3} V P_{HNO_2}^2 + \frac{F}{P}(P_{H_2O}^o - P_{H_2O}) = A \frac{D_{H_2O}}{RT}\left(\frac{dP_{H_2O}}{dx}\right)_{x=\delta} \quad (17)$$

In these equations, A is the gas-liquid interfacial area in the contactor.

The solution of the diffusion equations was obtained by orthogonal collocation using shifted Chebyshev polynomials of the first kind. The bulk gas material balances, Eqs. 16 and 17, were solved simultaneously to the film equations to determine the bulk concentration of nitrous acid and water vapor. Details of the solution algorithm are given in Newman (1988).

For use in cases where formation of HNO_2 in the gas film has minor importance, a simplified mass transfer model was also developed. In this model the diffusion coefficients of NO, NO_2, N_2O_3 and N_2O_4 are assumed to be equal, and equal to the diffusion coefficient of NO_2 since this species limits the rate of absorption when NO is in excess. Under these assumptions, the film theory diffusion equations can be integrated twice, yielding

$$\phi_{NO^\bullet} = \frac{D}{\delta RT}(P_{NO^\bullet}^b - P_{NO^\bullet}^i) \quad (18)$$

$$\phi_{NO_2^\bullet} = \frac{D}{\delta RT}(P_{NO_2^\bullet}^b - P_{NO_2^\bullet}^i) \quad (19)$$

where

$$\phi_{NO^\bullet} = \phi_{NO} + \phi_{N_2O_3} \quad (20)$$

is the flux of divalent nitrogen and

$$\phi_{NO_2^\bullet} = \phi_{NO_2} + \phi_{N_2O_3} + 2\phi_{N_2O_4} \quad (21)$$

is the flux of tetravalent nitrogen (both excluding HNO_2), and $\delta = D_{H_2O}/k_g^0 RT$. The flux of HNO_2 formed in the bulk gas is given by

$$\phi_{HNO_2} = \frac{D}{\delta RT} P_{HNO_2}^b \quad (22)$$

The fluxes in the gas must be equal to the corresponding fluxes in the liquid, according to Eqs. 14 and 15. These equations can be combined with Eqs. 16 and 17 and with the equilibrium conditions for the formation of N_2O_3 and N_2O_4 to determine the partial pressures at the gas-liquid interface.

Experimental

Absorption apparatus

Absorption experiments were conducted in a stirred gas-liquid contactor of the type developed by Levenspiel and Godfrey (1974). A cross section of the reactor is shown in Figure 2. The contactor was constructed of 10.2-cm-ID Plexiglas tubing, 10.2 cm long in the liquid section, and 5.1 cm long in the gas section. Perforated Plexiglas plates of various thickness with 0.635-cm holes, were inserted between the center flanges of the reactor. Twenty or 36 evenly spaced holes were used. The gas-liquid interface in the reactor was maintained flush with the bottom surface of the plate. Four baffles, located 90 degrees apart, were attached to the bottom and sides of the liquid section. The gas compartment of the reactor was stirred by a turbine agitator with four flat blades, 8.9 cm in diameter. The liquid was stirred by a 5.1-cm diameter propeller agitator.

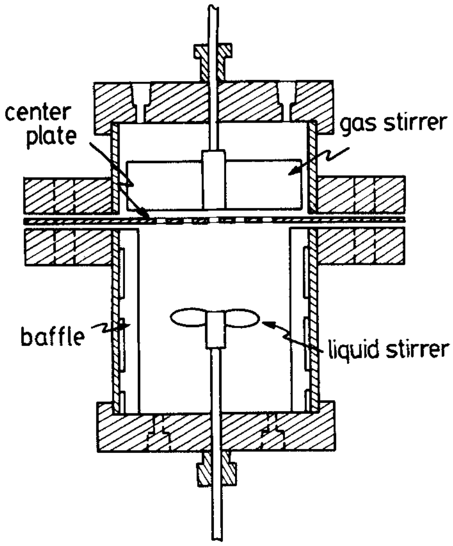

Figure 2. Cross section of experimental gas-liquid contactor.

A complete diagram of the apparatus is shown in Figure 3. The reactor was mounted inside a water bath with temperature control of ±0.5°C. The gas side of the reactor was operated with continuous flow; the liquid side was operated in the CSTR or batch mode. In experiments on the absorption of nitrogen oxides into alkaline solutions the batch-mode was most practical, since accumulation of nitrite and/or nitrate in the liquid does not affect mass transfer and control of the liquid level in the reactor is easier. For batch experiments, the absorbent solution was pumped into the reactor and the liquid level was adjusted using a syringe checking by visual observation of the holes and with an inclined sight glass tube, mounted externally to the contactor. Liquid samples were taken using a syringe at the end of a batch run. For continuous operation, a constant-head tank was used to provide a steady liquid flow. In this case the liquid level in the contactor was precisely controlled by passing the effluent flow through a leveling tank adjustable with a micrometer screw.

Nitrogen, nitric oxide, and nitrogen dioxide were obtained from cylinders and metered through rotameters. The nitrogen dioxide was vaporized by placing the cylinder in a water bath maintained at 35°C and passing the gas through a section of tubing located in the bath. The rotameter for NO_2 was also maintained at 35°C by a water jacket, in order to keep the degree of dimerization of NO_2 constant.

The gas effluent from the reactor was analyzed continuosly by a flow-through gas analyzer (BINOS UV-VIS, Leybold-Heraeus GMBH, Hanau), which used UV spectrophotometry to measure the NO_2 concentration, and non-dispersive IR to measure the NO concentration. The absorption flow cuvettes of the analyzer were thermostatted at 60°C to eliminate condensation and to insure reproducibility. The apparatus has two measurement ranges of 0–1% and 0–3% with an accuracy of ±2% of the full scale reading. The concentration of nitrite in solution was determined spectrophotometrically. Nitrate was analyzed by

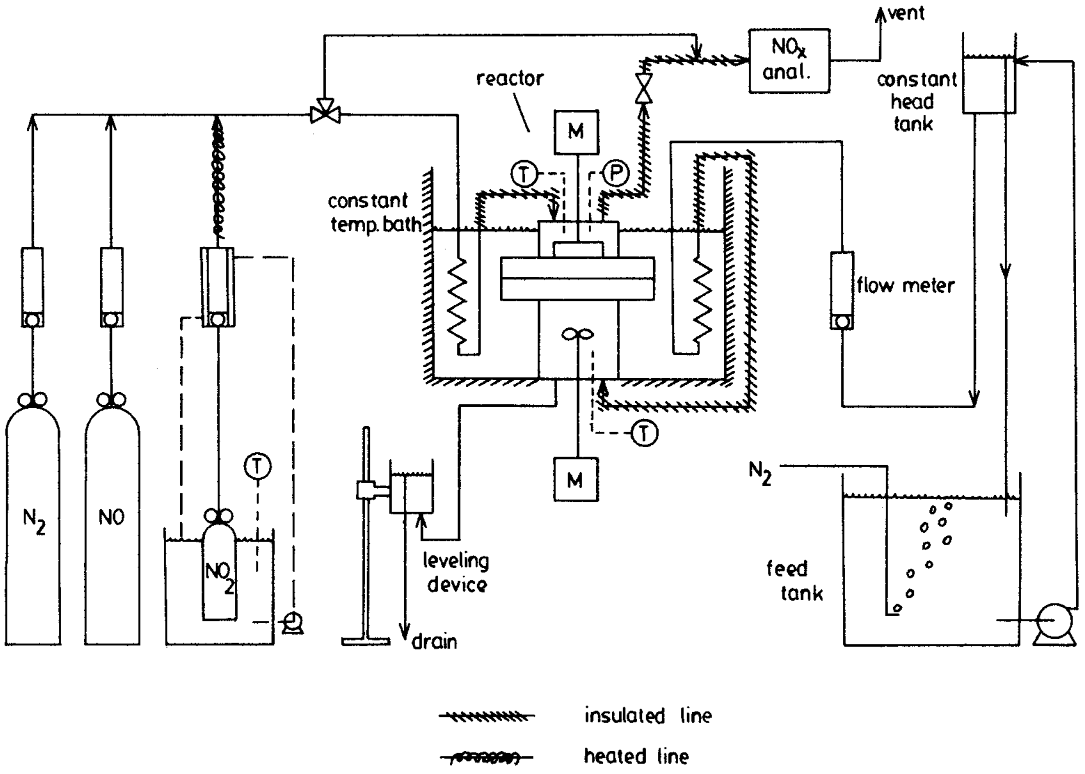

Figure 3. Experimental apparatus.

the 2,6 xylenol colorimetric technique of Hartley and Asai (1963).

Determination of mass transfer coefficients

Liquid side and gas side mass transfer coefficients were determined as functions of stirring speed, for water or dilute aqueous absorbents at 25°C and 1 atm total pressure. The liquid-side mass transfer coefficient, k_l^0, was determined by measuring the uptake of pure CO_2 into water, using a continuous water flow to minimize CO_2 accumulation in the liquid. The uptake was measured volumetrically with a soap film meter. k_l^0 was found to vary linearly with agitation rate between 1.5 and 3.5×10^{-3} cm/s in the range 200–600 rpm. These values of k_l^0 are sufficiently large to insure that hydrolysis of N_2O_3 and N_2O_4 will occur in the fast-reaction regime. The gas-side mass transfer coefficient, k_g^0, was determined by measuring the rates of evaporation of water into nitrogen and the rates of absorption of ammonia into 1 kmol/m^3 aqueous solutions of H_2SO_4. A liquid stirrer speed of 400 rpm was used for these experiments. The results are shown in Figure 4. The mass transfer coefficient appears to be again a linear function of the stirring speed, except at very low agitation rates, when the mass transfer process becomes entirely controlled by diffusion through a truly stagnant gas film. In this case the gas-side mass transfer coefficient is independent of the stirrer speed and is approximately equal to the diffusion coefficient divided by the plate thickness.

Results and Discussion

Aqueous solutions of sodium hydroxide, 24% by weight, were used as the absorbent to carry out experiments on the absorption of nitrogen oxides. At this concentration of sodium hydroxide there is no liquid-side resistance to HNO_2 absorption, and HNO_2 formed from N_2O_3 and N_2O_4 hydrolysis is instantly neutralized. Furthermore, at this concentration of sodium hydroxide, the vapor pressure of water is sufficiently low that condensation of nitric acid is prevented, even at partial pressures of NO_2 of 0.01–0.015 atm (Newman, 1988). Calculations based on equilibrium reveal that nitric acid condensation may have occurred in many published studies. In fact, in the presence of

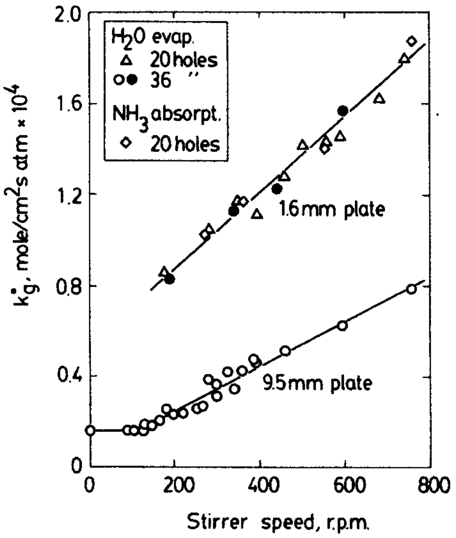

Figure 4. Gas-side mass transfer coefficient as a function of stirrer speed.

Data were determined by evaporation of water in nitrogen and absorption of ammonia into 1 kmol/m^3 sulfuric acid, 25°C, 1 atm.

pure liquid water, condensation of HNO_3 is thermodynamically possible at any NO_2 concentration level.

Absorption of NO_2

Absorption of NO_2 was studied experimentally over a range of partial pressures of 0.0045 to 0.012 atm, at constant k_g^0. The 9.5-mm-thick plate was used in these experiments to provide sufficient gas-side resistance to minimize the absorption of nitric acid formed in the bulk gas. The gas stirrer and liquid stirrer speeds were 155 and 400 rpm respectively. The flux is plotted against the interfacial partial pressure of N_2O_4 in Figure 5. The flux of tetravalent nitrogen was obtained from overall material balances and the interfacial partial pressure of N_2O_4 was calculated solving the diffusion equation for the gas film. The ratio of nitrite and nitrate concentrations in the liquid was found to be very close to unity in these experiments. A least-squares fit of the data resulted in a value of the absorption factor, $H\sqrt{Dk}$, of 3.3×10^{-5} mol/s · cm² · atm. This value is somewhat smaller than that obtained by other authors for absorption into water. Chambers and Sherwood (1937), on the other hand, found that the absorption rate decreased with NaOH concentration, and found values of $H\sqrt{Dk}$ between 2.3 and 6.0×10^{-5} for 23.6% NaOH. It is likely that two competing effects are present. As the sodium hydroxide concentration is increased there is a slight increase of the rate constant for the hydrolyic reaction of N_2O_4 (Eq. 7). However, at the same time, the solubility and diffusivity are decreased. At high concentrations of NaOH the latter effect appears to be dominant as the absorption factor, $H\sqrt{Dk}$, decreases.

Absorption of mixtures of NO *and* NO_2

Absorption rates were determined for different values of the gas-side mass transfer coefficient, k_g^0, and NO partial pressure, using a constant value of 0.01 ± 0.001 atm for the partial pressure of NO_2. The flux of nitrite produced minus that of nitrate produced is plotted in Figure 6 as a function of the gas side mass transfer coefficient, k_g^0, for different partial pressures of NO at 25°C. The liquid stirrer speed was 400 rpm in these experiments. The results for absorption of NO/NO_2 mixtures are reported here in terms of the difference between the nitrite and nitrate production rates, rather than simply the nitrite production. Since nitrite and nitrate are produced in equimolar amounts by N_2O_4 absorption, subtraction of the nitrate flux reduces the remainder by the nitrite flux produced by N_2O_4 absorption, if absorption of HNO_3 is neglected. The remaining flux, therefore, represents nitrite produced by N_2O_3 and HNO_2 absorption.

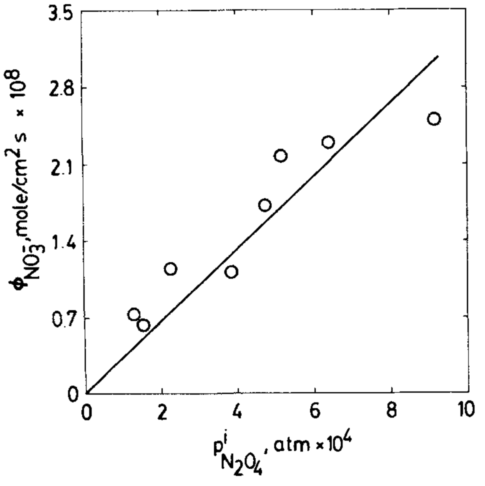

Figure 5. Nitrate flux as a function of interfacial partial pressure of N_2O_4, 25°C, 1 atm.

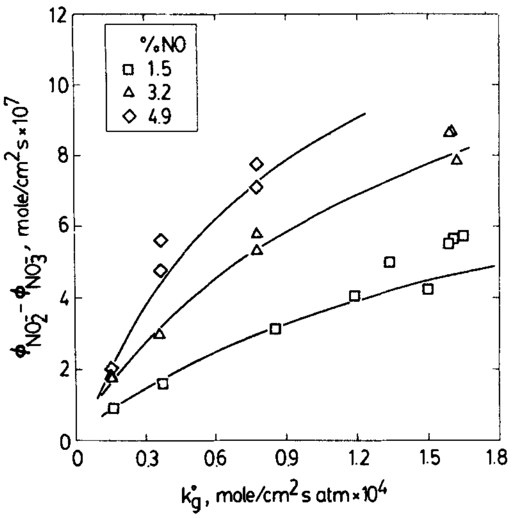

Figure 6. Nitrite flux minus nitrate flux as a function of the gas side mass transfer coefficient.

1% NO_2, 25°C, 1 atm. Lines are calculated according to par. set 1.

Calculations based on the film-theory diffusion equations, Eqs. 11–17, were compared with the experimental results. The model equations contain several reaction equilibrium constants, diffusivities, reaction rate constants, and the absorption factors for absorption of N_2O_3 and N_2O_4. The equilibrium constants used for the gas-phase reactions were those given by Carta (1984). The gas-phase diffusivities of the various species were either literature values or they were determined using available estimation methods, as indicated in Table 2. The absorption factor for absorption of N_2O_4 was obtained from our results for absorption of NO_2. The remaining two parameters are the rate coefficient for HNO_2 formation, k_3; and the group $H\sqrt{Dk}$ for absorption of N_2O_3, assuming a fast, pseudofirst-order reaction. Since there is considerable disagreement among the literature values of these parameters, they were fitted to the experimental

Table 2. Model Parameters at 25°C, 1 atm

Parameter Set	k_3 mol/cm³ · atm³ · s	$(H\sqrt{Dk})_{N_2O_3}$ mol/cm² · atm · s
1	8.83×10^{-3}*	2.50×10^{-3}
2	2.05×10^{-4}**	3.50×10^{-3}
3	0.90	1.59×10^{-4}***

$(H\sqrt{Dk})_{N_2O_4} = 3.30 \times 10^{-5}$ mol/cm² · s · atm
$D_{NO} = 0.23$†; $D_{NO_2} = 0.14$‡; $D_{N_2O_3} = 0.11$†; $D_{N_2O_4} = 0.098$‡; $D_{HNO_2} = 0.14$‡; $D_{H_2O} = 0.26$† cm²/s; $V = 411$ cm³; $A = 11.4$ cm²; $F = 2.7 \times 10^{-4} - 4.2 \times 10^{-4}$ mol/s

*England and Corcoran (1975).
**Sakamaki et al. (1983).
***Corriveau (1971).
†Fuller equation, Sherwood et al. (1975).
‡Chambers and Sherwood (1937).

results. One parameter was fitted at a time while the other parameter was selected from literature values before the fitting was performed. Each parameter was fitted from selected data which were most significant for that parameter. To determine k_3 given a literature value of $H\sqrt{Dk}$ for N_2O_3, the data used were those at low k_g^0, where the formation of HNO_2 in the gas film would have the greatest significance. To determine $H\sqrt{Dk}$ for N_2O_3 given a literature value of k_3, the data used corresponded to high values of k_g^0, where the gas-side resistance is at a minimum.

The parameters obtained using this procedure are listed in Table 2. Parameter set 1 corresponds to a situation where the bulk gas is approximately in equilibrium, but formation of HNO_2 in the gas film is significant only at very low values of the gas-side mass transfer coefficient; parameter set 2 represents a case where the flux of HNO_2 is limited by its rate of formation in the bulk gas for high values of k_g^0; parameter set 3 finally corresponds to a case where formation of HNO_2 within the gas film is important at all values of k_g^0 and significant enhancement of gas phase transport occurs. In the latter case the bulk gas is of course at equilibrium.

The experimental absorption rate data for 3.2 mol % NO are shown in Figure 7 in comparison with model predictions based on the three parameter sets listed in Table 2. Calculated fluxes based on parameter sets 1 and 2 appear to fit the data rather well at both high and low k_g^0 values. The data at high k_g^0, however, are inconsistent with calculations based on parameter set 3, for which k_3 was fitted using data at low k_g^0. Of course, a fit that on average would be better than the one shown could be obtained by using a sufficiently high value of k_3; however, this approach would result in a lack of fit at low k_g^0, and the resulting value of k_3 would be inconsistent with any previous results obtained from studies where the gas phase formation of HNO_2 was directly investigated. The calculated fluxes converge at low values of k_g^0 for all parameter sets. The reason for this behavior is that at low values of k_g^0, the formation of either HNO_2 or N_2O_3 near the gas-liquid interface becomes limited by the availability of NO_2, the limiting reactant when NO is in excess. The availability of NO_2 is limited in this case by mass transfer and diffusion of this species tends to control the overall absorption process. Since the model appears to be somewhat insensitive to the value of k_3 a best fit determination of this parameter was not attempted. Analogous results were obtained from similar calculations for data at 1.5 and 4.9% NO.

At low values of the partial pressure of NO_2 and at a low gas-side mass transfer resistance, fluxes obtained from calculations using parameter sets 1 and 2 are significantly different. Figure 8 shows calculated fluxes for these conditions in comparison with experimental results. The data appear to conform more closely to calculations based on parameter set 1.

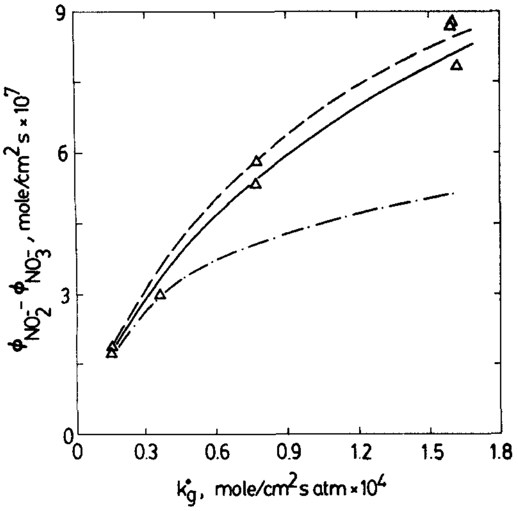

Figure 7. Nitrite flux minus nitrate flux as a function of the gas side mass transfer coefficient. Comparison of model and experimental results.

3.2% NO, 1% NO_2, 25°C, 1 atm. ——: par. set 1; ----: par. set 2; -·-·-: par. set 3.

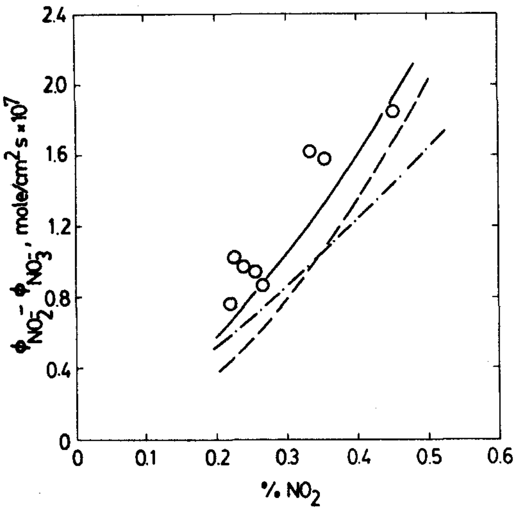

Figure 8. Nitrite flux minus nitrate flux as a function of %NO_2. Comparison of model and experimental results.

P_{NO}/P_{NO_2} = 2.4, k_g^0 = 1.6 × 10^{-4} mol/s · cm² · atm, 25°C, 1 atm. ——: par. set 1; ----: par. set 2; -·-·-: par. set 3.

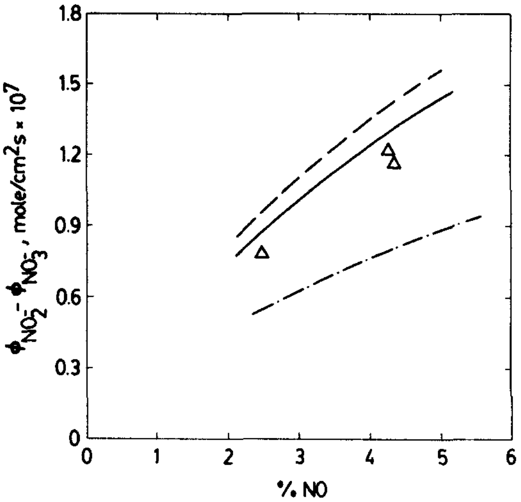

Figure 9. Nitrite flux minus nitrite flux as a function of %NO. Comparison of model and experimental results.

1.5% NO_2, k_g^0 = 1.6 × 10^{-4} mol/s · cm² · atm, 25°C, 1 atm. ——: par. set 1; ----: par. set 2; -·-·-: par. set 3.

The maximum value of the partial pressure of NO_2 was limited in the experiments by the need to avoid condensation in the reactor. A maximum of 0.015 atm for P_{NO_2} was estimated based on nitric acid/water vapor-liquid equilibrium data and the vapor pressure of the 24% sodium hydroxide solution. Figure 9 shows experimental and calculated fluxes of nitrite minus nitrate at $k_g^0 = 1.6 \times 10^{-4}$ mol/s · cm² atm and a partial pressure of NO_2 of 0.015 atm with varying partial pressures of NO. The experimental results are again in fairly good agreement with calculations based on parameter set 1.

Figure 10 shows the flux of nitrate as a function of k_g^0 at a partial pressure of NO_2 of 0.01 ± 0.001 atm, 25°C, and several levels of NO partial pressure. The experimental data are compared to calculations based on parameter set 1, although calculations for the different parameter sets gave only slightly different results. As the partial pressure of NO is increased at constant k_g^0, while the nitrite flux is increased the nitrate flux is reduced. In fact, as the NO partial pressure is increased, increasing quantities of NO_2 are required for N_2O_3 formation. The result is an increased gradient in the NO_2 partial pressure across the gas film, which results in an extremely low partial pressure of N_2O_4 at the gas-liquid interface. Calculated partial pressure profiles across the gas film are shown in Figure 11. The presence of mass transfer resistance reduces the NO_2 partial pressure at the gas-liquid interface to very low values and depresses the formation of nitrates. The concentration profile of HNO_2 is non-linear showing that some enhancement in the gas phase transport of this species occurs.

Calculations showing the effect of gas-phase mass transfer resistance on nitrite produced by absorption of N_2O_3, N_2O_4, and HNO_2 are shown in Figure 12. The calculations shown are based both on the exact film diffusion model, Eqs. 11–15, as well as on the approximate model described by Eqs. 18–22. At high values of k_g^0 the two models diverge (although not significantly) in the prediction of the flux of N_2O_3, because of differences in the diffusivities of the various species, which are not taken into account in the simplified model. For these conditions, HNO_2 formation in the film is negligible. At low values of k_g^0, when the flux of N_2O_3 is limited by the diffusion of NO_2, the two models diverge in the prediction of the flux of HNO_2 as the simplified model does not account for formation of this species within the gas film. For the conditions investigated, the nitrite flux is over twenty five times greater than the nitrite flux for high values of k_g^0 and low partial pressure of NO. The nitrite flux increases instead to over one hundred times the nitrate flux at low values of k_g^0. Finally, the effect of partial pressure of NO_2 is given in Figure 13 which shows the calculated contribution of the various species to the formation of nitrite. These calculations are based on parameter set 1. It is interesting to note that at low partial pressures of NO_2, for a constant ratio of NO/NO_2, HNO_2 becomes the primary source of nitrite.

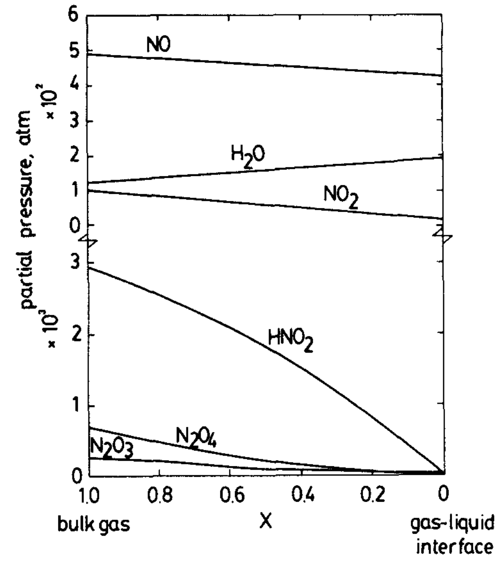

Figure 11. Calculated partial pressure profiles across the gas film based on parameter set 1.

4.9% NO, 1% NO_2, $k_g^0 = 1.5 \times 10^{-5}$ mol/cm² · atm · s, 25°C, 1 atm.

The absorption of mixtures of NO and NO_2 at 40°C and a

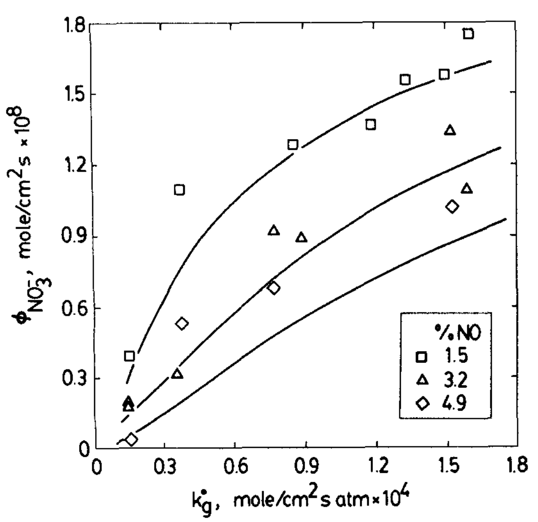

Figure 10. Nitrate flux as a function of gas side mass transfer coefficient. Comparison of model and experimental results.

Parameter set 1. 1% NO_2, 25°C, 1 atm.

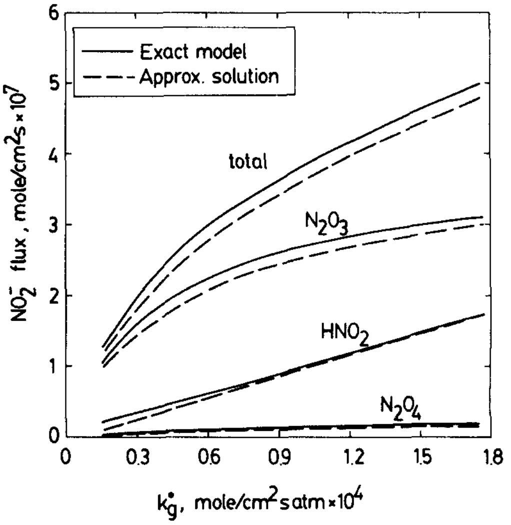

Figure 12. Calculated contribution of absorbing species to nitrite flux as a function of the gas-side mass transfer coefficient.

1.5% NO, 1% NO_2, 25°C, 1 atm.

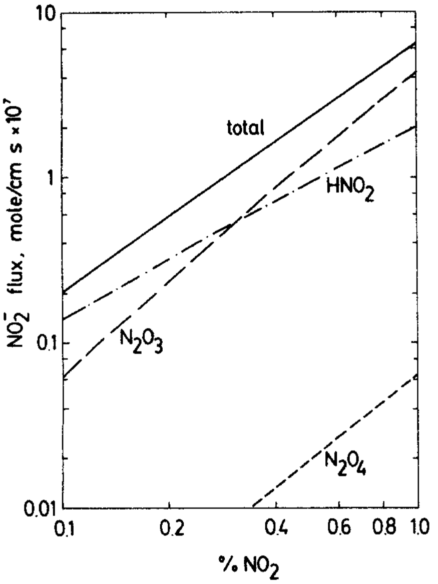

Figure 13. Calculated contribution of absorbing species to nitrite flux as a function of NO_2 concentration.

Constant value of $P_{NO}/P_{NO_2} = 2.4$, $k_g^0 = 1.6 \times 10^{-4}$ mol/cm² · atm · s, 25°C, 1 atm.

partial pressure of NO_2 of 0.01 ± 0.001 atm was also investigated as a function of the gas-side mass transfer coefficient for different values of the partial pressure of NO ranging from 0.015 to 0.049 atm. The film diffusion model was again fitted to the experimental results in a manner similar to that used for the data at 25°C. Calculations based on a value of 8.8×10^{-3} mol/cm³ · atm³ · s for the rate constant for HNO_2 formation, k_3, and a value of 1.2×10^{-3} mol/cm² · atm s for the absorption factor for N_2O_3, $H\sqrt{kD}$, were found to be in best agreement with the experimental data. A value of $H\sqrt{kD}$ for N_2O_4 equal to the value found at 25°C was found to provide a good fit of the nitrate absorption data at 40°C. For the model calculations, the gas-phase diffusivities and the mass transfer coefficient were corrected for the effect of temperature using existing correlations (Sherwood et al., 1975). This correction, however, did not exceed 8% for our experiments. The fluxes obtained at low k_g^0 values are similar in magnitude to those obtained at 25°C. However, at high k_g^0, the flux is significantly reduced by elevating the temperature. At high values of k_g^0, the flux of nitrite minus that of nitrate is approximately equal to the flux that can be calculated by assuming that the nitrous acid in equilibrium in the bulk gas diffuses alone through the gas film. These results confirm the conclusion reached for the lower temperature data that formation of nitrous acid in the gas film is only moderately important and that the absorption process is dominated by the absorption of nitrous acid formed in the bulk gas and nitrogen trioxide that diffuses in equilibrium with NO and NO_2 through the gas film.

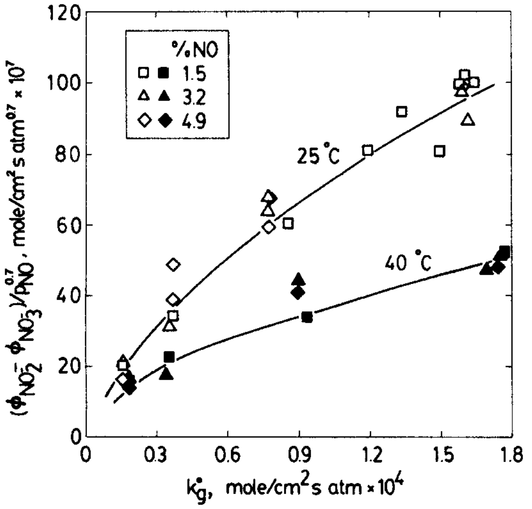

Figure 14. Nitrite flux minus nitrate flux divided by $P_{NO}^{0.7}$ as a function of the gas-side mass transfer coefficient.

1% NO_2, 1 atm.

The data obtained at a partial pressure of NO_2 of 0.01 ± 0.001 atm at 25 and 40°C can be plotted as single lines for each temperature for all values of the partial pressure of NO by dividing the flux of nitrite minus that of nitrate by the partial pressure of NO to the 0.7 power as shown in Figure 14. This is an empirical relationship, representing an averaging of effects of formation and diffusion of N_2O_3 and HNO_2 and mass transfer limitations caused by the NO_2 concentration gradient in the gas film.

Concluding Remarks

The results of this study indicate that a value of $H\sqrt{Dk}$ for N_2O_3 absorption of 2.5×10^{-3} mol/s · cm² · atm and a value of 8.8×10^{-3} mol/s · cm³ · atm³ for the rate constant for the homogeneous gas-phase formation of HNO_2 accurately describe the absorption of mixtures of nitrogen oxides in concentrated NaOH in a partial pressure range of 0.015- to 0.05-atm NO and 0.002- to 0.015-atm NO_2 at 25°C.

The value obtained for $H\sqrt{Dk}$ for N_2O_3 is about ten times larger than that obtained by Corriveau (1971). This difference may be accounted for on the grounds that the reverse of reaction 6 may have been important in Corriveau's studies, thereby reducing the observed absorption rates. The viscosity and ionic strength effects of the 24% sodium hydroxide solution used in our studies may account for the lower absorption rates that we obtained compared to those obtained by Aoki et al. (1982). The viscosity and ionic strength effects would lower both the diffusion coefficient and the solubility of N_2O_3 in the liquid. More importantly, Aoki et al. neglected the effect of HNO_2 absorption in the evaluation of their results. While the approximate first power dependence of the nitrite flux on $P_{NO} \times P_{NO_2}$ that they obtained would tend to indicate the dominance of N_2O_3 absorption, it also corresponds to the effect of the partial pressures on the forward formation rate of HNO_2. Therefore, HNO_2 absorption should be considered, especially if the gas phase is far enough from equilibrium that the reverse reaction can be neglected.

Selectivity for nitrite formation compared to nitrate formation is increased by a high ratio of the partial pressures of NO and NO_2. When the gas-phase mass transfer resistance is significant and NO is in excess over NO_2, selectivity is further enhanced as the partial pressure of NO_2 at the gas-liquid interface is greatly reduced relative to the partial pressure value in the bulk gas. In situations where the process is limited by NO_2

diffusion through the gas film, selectivity in the production of nitrites is enhanced by an increase in temperature. The nitrite flux is only affected to a small degree by temperature, since it is limited by NO_2 diffusion. However, the nitrate/nitrite ratio is reduced because of the greater temperature dependence of the equilibrium constant for formation of N_2O_4, compared with the equilibrium constant for formation of N_2O_3, combined with an increase in the rate of absorption of HNO_2.

Notation

A = gas-liquid interfacial area, cm^2
D_j = diffusion coefficient for species j, cm^2/s
H = Henry's law constant, $mol/cm^3 \cdot atm$
$H\sqrt{Dk}$ = absorption factor for fast pseudofirst-order reaction, $mol/s \cdot cm^2 \cdot atm$
F = gas molar flow rate, mol/s
k_g^0 = gas-side mass transfer coefficient in the absence of reaction, $mol/s \cdot cm^2 \cdot atm$
k_l^0 = liquid-side mass transfer coefficient in the absence of reaction, cm/s
k_{+n} = reaction rate constant for forward reaction n
k_{-n} = reaction rate constant for reverse reaction n
P_j = partial pressure of component j, atm
P_j^b = partial pressure of component j in the bulk gas, atm
P_j^i = partial pressure for component j at the gas-liquid interface, atm
P_j^o = partial pressure for component j at reactor inlet, atm
r_{+n} = rate of forward reaction n, $mol/cm^3 \cdot s$
r_{-n} = rate of reverse reaction n, $mol/cm^3 \cdot s$
T = temperature, K
V = gas phase reaction volume, cm^3
x = distance from gas-liquid interface, cm

Greek letters

δ = diffusion film thickness, cm
$\nu_{i,+n}$ = stoichiometric coefficient for component j in forward reaction n
$\nu_{i,-n}$ = stoichiometric coefficient for component j in reverse reaction n
ϕ_j = flux of component j, $mol/cm^2 \cdot s$

Literature Cited

Aoki, M., H. Tanaka, H. Komiyama, and H. Inoue, "Simultaneous Absorption of NO and NO_2 into Alkaline Solutions," *J. Chem. Eng. Japan*, **15**, 362 (1982).

Carta, G., "Role of HNO_2 in the Absorption of Nitrogen Oxides in Alkaline Solutions," *Ind. Eng. Chem. Fund.*, **23**, 260 (1984).

Chambers, F. S., and T. K. Sherwood, "Absorption of Nitrogen Dioxide by Aqueous Solutions," *Ind. Eng. Chem.*, **29**, 1415 (1937).

Chan, W. H., R. J. Nordstrom, G. G. Calvert, and J. Shaw, "Kinetic Study of HONO Formation and Decay Reactions in Gaseous Mixtures of HONO, NO NO_2, H_2O, and N_2," *Env. Sci. Tech.*, **10**, 674 (1976).

Corriveau, C. E., "The Absorption of N_2O_3 in Water," Master's Thesis, Univ. of California, Berkeley, CA (1971).

England, C., and W. H. Corcoran, "The Rate and Mechanism of the Air Oxidation of Parts-per-Million Concentrations of Nitric Oxide in the Presence of Water Vapor," *Ind. Eng. Chem. Fund.* **14**, 55 (1975).

Graham, R. F., and B. J. Tyler, "Formation of Nitrous Acid in a Gas-phase Stirred Flow Reactor," *J. Chem. Soc., Faraday I*, **68**, 683 (1972).

Gray, P., and A. D. Joffe, "The Reactivity and Structure of Nitrogen Dioxide," *Chem. Rev.*, **55**, 1069 (1955).

Hartley, A. M., and R. I. Asai, "Spectrophotometric Determination of Nitrate with 2,6 Xylenol Reagent," *Anal. Chem.*, **35**, 1207 (1963).

Hofmeister, H. K., and R. Kohlhaas, "Die Absorption von NO-NO_2-Mischungen durch einen lamainaren Wasserstrahl," *Ber. Buns.*, **69**, 232 (1965).

Joshi, J. B., V. V. Mahajani, and V. A. Juvekar, "Absorption of NO_x Gases," *Chem. Eng. Comm.*, **33**, 1 (1985).

Kaiser, C. H., and E. W. Wu, "A Kinetic Study of the Gas Phase Formation and Decomposition Reactions of Nitrous Acid," *J. Phys. Chem.*, **81**, 1701 (1977).

Kameoka, V., and R. L. Pigford, "Absorption of Nitrogen Dioxide into Water, Sulfuric Acid, Sodium Hydroxide, and Alkaline Sodium Sulfite Aqueous Solutions," *Ind. Eng. Chem. Fund.*, **16**, 163 (1977).

Komiyama, H., and H. Inoue, "Absorption of Nitrogen Oxides into Water," *Chem. Eng. Sci.*, **35**, 154 (1980).

Leighton, P. A., *Photochemistry of Air Polution*, p. 184, Academic Press, New York (1961).

Levenspiel, O., and J. H. Godfrey, "A Gradientless Contactor for Experimental Study of Interphase Mass Transfer with/without Reaction," *Chem. Eng. Sci.*, **29**, 723 (1974).

Newman, B. L., "Absorption of Nitrogen Oxides in Alkaline Solutions," PhD Dissertation, Univ. of Virginia, Charlottesville, VA (1988).

Pitts, Jr., J. N., E. Sanhueza, R. Atkinson, W. P. L. Canter, A. M. Winer, G. W. Harris, and C. N. Plum., "An Investigation of the Dark Formation of Nitrous Acid in the Environmental Chamber," *Int. J. Chem. Kinetics*, **16**, 919 (1984).

Sada, E., H. Kumazawa, and M. A. Butt, "Single and Simultaneous Absorptions of Lean Sulfur Dioxide and Nitrogen Dioxide into Aqueous Slurries of Calcium Hydroxide or Magnesium Hydroxide Particles," *J. Chem. Eng. Japan*, **12**, 111 (1979).

Sakamaki, F., S. Hatakeyama, and H. Akimoto, "Formation of Nitrous Acid and Nitric Oxide in the Heterogenous Dark Reaction of Nitrogen Dioxide and Water Vapor in a Smog Chamber," *Int. J. Chem. Kinetics*, **15**, 1013 (1983).

Schwartz, S. E., and W. H. White, "Solubility Equilibria of the Nitrogen Oxides and Oxyacids in Dilute Aqueous Solutions," *Advances in Environmental Science and Engineering*, Vol. 4, Pfaffin, J. R. and E. N. Ziegler, Eds., Gordon-Breach Science Publisher, New York (1981).

Schwartz, S. E., and W. H. White, "Kinetics of Reactive Dissolution of Nitrogen Oxides into Aqueous Solution," *Advances in Environmental Science and Technology*, Vol. 12, J. Nriagu, Ed., Wiley, New York (1983).

Sherwood, T. K., R. L. Pigford, and C. R. Wilke, *Mass Transfer*, McGraw-Hill, New York (1975).

Takeuchi, H., and Y. Yamanaka, "Absorption of SO_2 and NO_2 in Aqueous Solutions of NaOH and Na_2SO_3," *Ind. Eng. Chem. Proc. Des. Dev.*, **17**, 389 (1978).

Wayne, L. G., and D. M. Yost, "Kinetics of the Rapid Gas Phase Reaction between NO, NO_2, and H_2O," *J. Chem. Phys.*, **19**, 41 (1951).

Weisweiler, W., and K. H. Deiss, "Measurement of Absorption Rate of Nitrogen Dioxide in Water in a Falling Film Absorber," *Ger. Chem. Eng.*, **4**, 79 (1981).

Manuscript received Dec. 12, 1987, and revision received Apr. 5, 1988.