Mass Transfer in Nitric Acid Absorption

The mechanism and rate limitations in aqueous nitrogen oxides absorption are reviewed and data available on chemical kinetics for performance predictions are discussed. Application of a rate relationship to characterize interphase mass transfer for the primary reactant N_2O_4 is shown, with mass transfer coefficients derived from plant-scale data. Correlations for these coefficients as functions of acid strength and temperature for both bubble cap and sieve plate designs are presented.

D. N. Miller
Engineering Department
E. I. du Pont de Nemours & Co.
Wilmington, DE 19898

Introduction

The aqueous absorption of nitrogen oxides to produce nitric acid is an operation common throughout the chemical industry. It is an essential step for nitric acid manufacture in ammonia oxidation plants and is used in many other processes where offgas abatement and nitric acid recovery are required. The chemistry, although extremely complex, has been treated extensively in the literature. Gas-liquid mass transfer of the primary reactants, however, is less well understood. In particular, data for prediction of plant-scale performance has been lacking.

In the past, it has been customary to cover the mass transfer effect in performance predictions by use of a plate efficiency. The plate efficiency has been defined as the percentage to which actual absorption of nitrogen oxides approaches equilibrium absorption. Use of a rate relationship is an approach that can provide greater accuracy both for design and as a guide in operations.

This study was undertaken to show the application of a rate expression for mass transfer of the primary reactant, N_2O_4. Rate constants for mass transfer have been extracted from plant data for bubble cap and sieve type plates. Correlations for these data as functions of acid strength and temperature have been developed for use in performance calculations.

Mechanism

The aqueous absorption of nitrogen oxides to produce nitric acid is known to be highly complex, involving reactions in both gas and liquid phases and mass transfer interchange between phases of several species (Chilton, 1968; Sherwood et al., 1975). The primary route involves N_2O_4 as the liquid phase reactant. Its formation in the gas phase, mass transfer and reaction in the liquid occur in the following sequence:

$$1.\ 2NO_{(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{2(g)}$$
$$2.\ 2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$
$$3.\ N_2O_{4(g)} \rightleftharpoons N_2O_{4(l)}$$
$$4.\ N_2O_{4(l)} + H_2O_{(l)} \rightleftharpoons HNO_{3(l)} + HNO_{2(l)}$$
$$5.\ 3HNO_{2(l)} \rightleftharpoons HNO_{3(l)} + H_2O_{(l)} + 2NO_{(g)}$$

A second route involves the liquid phase reactant N_2O_3:

$$6.\ NO_{(g)} + NO_{2(g)} \rightleftharpoons N_2O_{3(g)}$$
$$7.\ N_2O_{3(g)} \rightleftharpoons N_2O_{3(l)}$$
$$8.\ N_2O_{3(l)} + H_2O_{(l)} \rightleftharpoons 2HNO_{2(l)}$$

with subsequent decomposition of HNO_2 via reaction 5 or, possibly, with liquid phase oxidation of HNO_2:

$$9.\ 2HNO_{2(l)} + O_{2(l)} \rightleftharpoons 2HNO_{3(l)}$$

The component NO_2 can also be absorbed and react directly in the liquid phase:

$$10.\ NO_{2(g)} \rightleftharpoons NO_{2(l)}$$
$$11.\ 2NO_{2(l)} + H_2O_{(l)} \rightleftharpoons HNO_{3(l)} + HNO_{2(l)}$$

and can produce nitric acid in the gas phase:

$$12.\ 3NO_{2(g)} + H_2O_{(g)} \rightleftharpoons 2HNO_{3(g)} + NO_{(g)}$$
$$13.\ HNO_{3(g)} \rightleftharpoons HNO_{3(l)}$$

The NO_2 routes—steps 10 and 11 and steps 12 and 13—are slow relative to those involving the reactants N_2O_4 and N_2O_3, and can usually be neglected in evaluating nitric acid absorption performance.

Chemical Kinetics

The kinetics and equilibrium for the step 1 NO oxidation have been studied by Bodenstein (1918, 1922). The rate expression follows:

$$R(1) = k1\left(p_{NO}^2 p_{O_2} - \frac{p_{NO_2}}{K1}\right), \text{kPa/s} \tag{1}$$

where

$$k1 = \exp(1{,}468/T - 10.9043), \text{kPa}^{-2} \cdot \text{s}^{-1}$$

$$K1 = \exp(-8.002 + 1.75 \ln T - 0.000217T - 2{,}496/T), \text{kPa}^{-2}$$

$p_{NO}, p_{NO_2}, p_{O_2}$ = partial pressure, kPa

T = temperature, K

In the temperature regions normally involved in aqueous absorption, the reverse reaction term can be neglected.

The step 2 gas phase dimerization of NO_2 equilibrates rapidly. The equilibrium for this effect has also been reported by Bodenstein (1922).

$$K2 = \frac{p_{N_2O_4}}{p_{NO_2}^2}, \text{kPa}^{-1} \tag{2}$$

where

$$K2 = \exp(6{,}893/T - 25.865), \text{kPa}^{-1}$$

$P_{N_2O_4}$ = partial pressure, kPa

The liquid phase reaction steps 4 and 5 are often treated in the combined form

$$4,5.\ 3/2\, N_2O_{4(l)} + H_2O_{(l)} \rightleftharpoons 2HNO_{3(l)} + NO_{(g)}$$

Several authors have reported equilibria for this combined reaction effect (Burdick and Freed, 1921; Chambers and Sherwood, 1937; Denbigh and Prince, 1947; Epshstein, 1939).

$$K4,5 = \frac{p_{NO}}{p_{NO_2}^3} \cdot \frac{a_{HNO_3}^2}{a_{H_2O}}, \text{kmol/m}^3 \cdot \text{kPa}^2 \tag{3}$$

where

a_{HNO_3}, a_{H_2O} = activities, kmol/m^3

The gas phase NO_2 partial pressure is used as a measure of liquid phase N_2O_4 concentration. Further, it is customary to report the equilibrium ratio $K4, 5a = p_{NO}/p_{NO_2}^3$ as a function of nitric acid concentration and temperature.

Carberry (1959) has shown that, within experimental error, these data can be combined with the step 2 equilibrium to eliminate the temperature dependency:

$$K0 = \frac{K4,5a}{K2^{3/2}} = \frac{p_{NO}}{p_{N_2O_4}^{1.5}}, \text{kPa}^{-1/2} \tag{4}$$

where

$$K0 = \exp(23.39 - 134.98\, W_{HNO_3} + 434.69\, W_{HNO_3}^2 - 789.84\, W_{HNO_3}^3 + 675.65\, W_{HNO_3}^4 - 221.89\, W_{HNO_3}^5), \text{kPa}^{-1/2}$$

W_{HNO_3} = weight fraction

The step 6 gas phase equilibrium for N_2O_3 formation is reported by Hisatsune (1961):

$$K6 = \frac{p_{N_2O_3}}{p_{NO}p_{NO_2}}, \text{kPa}^{-1} \tag{5}$$

where

$$K6 = \exp(4{,}869/T - 21.61), \text{kPa}^{-1}$$

The step 8 liquid phase equilibrium can be derived from the work of Theobald (1968) as a function of nitric acid strength and temperature,

$$K8 = \frac{W_{HNO_2}^2}{p_{NO}\, p_{NO_2}\, K6}, \text{kPa}^{-1} \tag{6}$$

where

$$K8 = \exp(8{,}378/T - 4.68\, W_{HNO_3} - 38.81)/K6, \text{kP}_a^{-1}$$

W_{HNO_2} = weight fraction

Kinetic data on the possible liquid phase oxidation of HNO_2 are unavailable.

Mass Transfer

The step 1 gas phase oxidation of NO has been identified as a major rate limitation in the overall absorption mechanism (Chilton, 1968; Sherwood et al., 1975). The other chemical steps in the primary N_2O_4 route occur rapidly and can be assumed to be at equilibrium. Mass transfer of N_2O_4—step 3 in the absorption sequence—imposes a further rate limitation, however.

In the past, it has been customary to use a plate efficiency E to characterize this mass transfer effect. E has been defined as the percentage approach of actual to equilibrium absorption of NO_2 equivalent, where

$$NO_{2_{equiv}} = NO_2 + 2N_2O_4 + N_2O_3 \tag{7}$$

Andrew and Hanson (1961) report the calculation of plate efficiency based on a synthesis of small-scale data. They include the possible contributions of direct NO_2 absorption, gas phase NO_2 reaction, and formation of nitric acid mist. They conclude that direct NO_2 absorption has a contribution to plate efficiency at very low NO_x concentrations. Their data are limited to very dilute acid strengths, however, and are not quantitatively useful in evaluating overall nitric acid absorption performance.

A relationship for mass transfer of N_2O_4 can be derived based on either film or penetration theory. The step 4, 5 hydration of N_2O_4 occurs in large excess H_2O and can be considered pseudo-first-order-dependent on N_2O_4 concentration. An analytical solution based on film theory (Lewis and Whitman, 1924) was originally developed by Hatta (1928) for first-order irreversible reaction. Danckwerts (1970) reports the same for the surface renewal approaches, both the original Higbie (1935) penetration theory and the modification allowing for a distribution of contacting times (Danckwerts, 1951). Extensions to first-order reversible reaction are also reported for the case where diffusivities of reactant and product are equal (Danckwerts and Kennedy, 1954).

All these analytical solutions reduce to the following rate form for N_2O_4 absorption, where N_2O_4 reaction is fast and complete in the liquid film at the phase interface,

$$R(3) = H_{N_2O_4}\sqrt{k4,5D_{N_2O_4}}\,A\left[p_{N_2O_4} - \left(\frac{p_{NO}}{K0}\right)^{2/3}\right], \text{kmol/s} \quad (8)$$

where

$H_{N_2O_4}$ = Henry's law coefficient, kmol/m^3 · kPa

$k4, 5$ = pseudofirst-order rate constant, s^{-1}

$D_{N_2O_4}$ = effective diffusivity, m^2/s

A = interfacial area, m^2

The following rate form for N_2O_3 absorption can also be written:

$$R(7) = H_{N_2O_3}\sqrt{k8,5D_{N_2O_3}}\,A\left(p_{N_2O_3} - \frac{W^2_{HNO_2}}{K8}\right), \text{kmol/s} \quad (9)$$

where

$H_{N_2O_3}$ = Henry's law coefficient, kmol/m^3 · kPa

$k8, 5$ = pseudofirst-order rate constant, s^{-1}

$D_{N_2O_3}$ = effective diffusivity, m^2/s

Several experimental measurements of $H_{N_2O_4}\sqrt{k4,5D_{N_2O_4}}$ in dilute acid have been reported (Wendel and Pigford, 1958; Dekker et al., 1959; Kramers et al., 1961; Gerstacker, 1961; Corriveau, 1971; Kameoka, 1973), and one for $H_{N_2O_3}\sqrt{k8,5D_{N_2O_3}}$ (Corriveau, 1971). More recent experimental measurements of $H_{N_2O_4}\sqrt{k4,5D_{N_2O_4}}$ in strong nitric acid have also been reported (Lefers and van den Berg, 1982). These measurements were made in small-scale wetted-wall or wetted-sphere contactors and liquid jets. Contact times were kept short. Reactant nitrogen oxides feeds were diluted in nitrogen with no oxygen present. Gas-liquid interfaces were well defined, with liquid film mass transfer presumed to occur by molecular diffusion.

Results

In this study, $H_{N_2O_4}\sqrt{k4,5D_{N_2O_4}}$ factors have been extracted from plant data. These data are summarized in Table 1, along with the physical characteristics of the columns from which the data were obtained. Three data sets are shown for bubble cap plate units, and three for a sieve plate design.

The column performance simulation used in these calculations proceeds stepwise, plate to plate, from the bottom up to the top of a unit. Inputs include the gas feed rate and composition, the liquid effluent acid rate and composition, and the plate temperature profile. Both the aerated liquid holdup on each tray and the gas in the spaces between trays are assumed to be completely back-mixed. Check computations show that any partial staging of either phase on individual trays does not, because of the large number of trays in a typical column, affect calculated concentration profiles significantly.

Equation 8, for $R(3)$, along with $K0$ from Eq. 4 is used to calculate N_2O_4 mass transfer for the first plate. An iterative calculation, using the Wegstein procedure (Franks, 1972), is then made with the component balances, adjusting $R(3)$ for the exit $p_{N_2O_4}$ and p_{NO} values. The test for closure is based on $NO_{2_{equiv}}$ absorbed.

If desired, the calculation for N_2O_3 absorption can be made concurrently using Eq. 9 for $R(7)$ and Eq. 6 for $K8$. The N_2O_3 absorption effect is small relative to N_2O_4, however, and can be omitted without appreciable error in most column simulations.

The gas rate and composition leaving the liquid phase on the plate and the acid rate and composition coming from the plate above are then available. The gas phase composition is next calculated using Eqs. 1 and 2, and Eq. 5 if N_2O_3 absorption is followed. This also is an iterative balance using the Wegstein procedure to establish exit p_{NO}, p_{NO_2}, $p_{N_2O_4}$, and $p_{N_2O_3}$ values, the test for closure being NO conversion.

These calculations are repeated plate by plate to establish composition profiles through a column. Where side stream feeds are introduced, the liquid phase balances are adjusted for nitric and water additions at those points. If necessary an adjustment is made to the acid effluent rate and the profiles recalculated to match pure water input to the top plate.

Trial-and-error adjustments to the N_2O_4 $H\sqrt{kD}$ coefficients in Eq. 8 have been made plate to plate for the six test cases detailed in Table 1. These adjustments were made to establish the best fits of calculated to measured plate acid strengths and exit gas NO_x concentrations.

In calculating the N_2O_4 $H\sqrt{kD}$ mass transfer coefficients, interfacial area values were obtained using the relationship reported by Andrew (1961):

$$A = 325\,u_g^{1/2}\,S^{-1/6}\,\pi\,d^2/4, \text{ m}^2 \quad (10)$$

where

u_g = superficial gas velocity, m/s

S = bubble cap slot or sieve hole submergence, m

d = column diameter, m

Discussion

The mass transfer coefficients show a strong dependence on acid strength and temperature. Best-fit relationships for the two plate types follow:

Bubble Cap Plate

$$\begin{aligned} H_{N_2O_4}\sqrt{k4,5D_{N_2O_4}} = \exp\Big(&-\frac{1{,}500}{T} - 4.3790 \\ &- 23.279W_{HNO_3} + 130.42W^2_{HNO_3} \\ &- 370.87W^3_{HNO_3} + 486.94W^4_{HNO_3} \\ &- 236.54W^5_{HNO_3}\Big), \text{ kmol/m}^2\cdot\text{kPa}\cdot\text{s} \end{aligned}$$

$$R^2_A = 0.862 \quad (11)$$

Table 1a. Nitric Acid Absorption, Bubble Cap Column, 3.20 m dia.

Plate Spacing m	on Plate Nos.
0.330	1–7
0.336	8–13
0.346	14–15
0.808	16–22
0.799	23–27
0.786	28–35

Feed Gas, kmol/s		
NO	0.0000983	0.00223
NO_2	0.0316	0.0284
O_2	0.0312	0.01208
N_2	0.385	0.346
Side Stream Acid, kg/s	0.277 (60.7% acid) on Pl. 10 1.604 (42.8% acid) on Pl. 18	0.280 (58.2% acid) on Pl. 10 1.721 (38.8% acid) on Pl. 18
Pressure kPa	736	736
Nitric Acid Rate, kg/s (as 100% acid)	2.82	2.71

Plate No.	Temp. °C	Acid, %		Exp. $H\sqrt{k4, 5D}$ kmol/m^2 · kPa · s	Temp. °C	Acid, %		Exp. $H\sqrt{k4, 5D}$ kmol/m^2 · kPa · s
		Meas.	Calc.			Meas.	Calc.	
1	28	67.5	67.5	0.00000465	45	60.4	60.4	0.00000634
2	20	64.4	66.5	465	39	58.2	59.5	634
3	15	—	65.8	465	37	—	58.1	641
4	12	61.3	65.0	465	35	55.7	56.5	648
5	10	—	64.1	465	33	—	54.7	655
6	9	61.1	63.1	465	32	52.1	52.8	662
7	9	—	62.0	465	32	—	50.8	677
8	11	50.8	60.7	465	32	48.0	48.9	691
9	9	—	59.2	450	32	—	46.8	713
10	9	—	57.6	450	32	44.4	45.0	761
11	9	—	55.3	450	32	—	41.9	816
12	9	—	53.4	450	32	—	40.1	889
13	9	—	51.4	450	32	—	38.5	964
14	9	52.2	49.1	458	32	29.9	36.9	0.00001060
15	7	—	47.1	465	32	—	35.5	1204
16	5	—	45.1	487	31	—	34.3	1301
17	4	—	43.3	501	30	—	33.1	1445
18	1	—	41.5	522	31	—	32.0	1590
19	4	—	34.2	556	31	—	18.02	1806
20	3	30.5	29.5	600	31	15.27	15.23	1975
21	2	—	25.0	648	31	—	12.90	221
22	1	—	21.0	718	31	—	10.92	246
23	1	—	17.37	804	30	—	9.24	277
24	1	—	14.55	915	30	—	7.71	311
25	1	10.30	11.99	0.00001036	30	5.65	6.61	359
26	1	—	9.75	1180	30	—	5.56	409
27	4	7.60	7.82	1325	31	3.92	4.62	465
28	1	—	6.30	1518	30	—	3.82	535
29	2	—	4.87	1782	30	2.32	3.07	619
30	2	—	3.93	1975	30	—	2.54	691
31	1	2.23	3.07	226	30	1.50	2.03	768
32	1	—	2.27	253	30	—	1.55	874
33	1	0.62	1.56	282	30	0.48	1.10	988
34	1	—	0.98	325	30	—	0.70	0.0001108
35	1	—	0.46	366	30	—	0.32	1132
Off-gas NO_x, ppmv								
Meas.	990				2,000			
Calc.	986				2,045			

Table 1b. Nitric Acid Absorption, Bubble Cap Column, 3.81 m dia.

Plate Spacing m	on Plate Nos.
0.305	1–21
0.457	22–23
0.610	24–25
0.914	26–30

Feed Gas, kmol/s	
NO	0.00394
NO_2	0.0605
O_2	0.01856 (0.0276 addn on Pl. 4)
N_2	0.759 (0.1040 addn on Pl. 4)
Side Stream Acid, kg/s	4.46 (43.5% acid) on Pl. 12
Pressure kPa	936
Nitric Acid Rate, kg/s (as 100% acid)	10.05 (84% as 56.9% acid from Pl. 5 16% as 67% acid from Pl. 1)

Plate No.	Temp. °C	Acid, % Meas.	Acid, % Calc.	Exp. $H\sqrt{k4,5D}$ kmol/m² · kPa · s
1	30.3	67.0	67.0	0.00001542
2	28.6	—	66.9	1542
3	27.3	—	64.9	1542
4	26.4	—	57.3	1542
5	25.7	56.9	56.5	1542
6	35.8	—	56.0	1542
7	37.7	—	55.5	1542
8	39.2	—	54.5	1542
9	40.3	—	53.6	1542
10	40.1	—	50.6	1566
11	41.6	—	48.1	1590
12	41.9	—	45.9	1638
13	41.9	37.5	44.3	1686
14	40.9	—	40.4	1758
15	39.8	34.0	36.3	1782
16	39	—	32.4	1831
17	38.5	28.5	28.8	1879
18	38.3	—	25.6	1975
19	38.2	21.5	22.6	210
20	38	—	20.0	212
21	37.7	—	17.76	217
22	37.6	—	15.75	226
23	37.5	8.50	13.96	238
24	37.2	—	12.24	248
25	36.9	—	10.67	267
26	36.4	—	9.14	296
27	35.9	—	7.70	311
28	36.2	—	6.53	325
29	36.2	—	5.47	352
30	35.9	—	4.47	395
31	35.6	—	3.53	450
32	36.2	—	2.64	508
33	36.7	—	1.87	578
34	36.8	—	1.17	641
35	36.8	—	0.55	706

Off-gas NO_x, ppmv	
Meas.	2,300
Calc.	2,167

Sieve Plate

For $W_{HNO_3} > 0.05$

$$H_{N_2O_4}\sqrt{k4,5D_{N_2O_4}} = \exp\left(-\frac{1{,}500}{T} - 2.7648 - 39.614\,W_{HNO_3} + 181.98\,W_{HNO_3}^2 - 429.65\,W_{HNO_3}^3 + 496.99\,W_{HNO_3}^4 - 223.24\,W_{HNO_3}^5\right),\ \text{kmol/m}^2\cdot\text{kPa}\cdot\text{s}$$

$$R_A^2 = 0.958 \qquad (12)$$

For $W_{HNO_3} < 0.05$

$$H_{N_2O_4}\sqrt{k4,5D_{N_2O_4}} = \exp\left(-\frac{1{,}500}{T} + 0.2548 - 315.73\,W_{HNO_3} + 9256.2\,W_{HNO_3}^2 - 95{,}602\,W_{HNO_3}^3\right),\ \text{kmol/m}^2\cdot\text{kPa}\cdot\text{s}$$

$$R_A^2 = 0.888 \qquad (13)$$

R_A^2 represents the fractional improvement of the correlation over use of a mean value for all experimental points. A value of 1.0 represents perfect correlation; zero, no improvement over the mean.

Plots of N_2O_4 mass transfer coefficients calculated for 25°C are shown vs. acid strength in Figure 1. Below 20% acid strength, the coefficients for the two plate types diverge, becoming much higher for sieve as compared to bubble cap plate design. Characteristic liquid phase energy contents can be calculated on the plates using gas velocities and liquid density:

$$P/V = 0.00981\, u_{gs}\, \rho_l,\ kW/m^3$$

where

P/V = power input per unit volume, kW/m³
u_{gs} = gas slot velocity, m/s
ρ_l = liquid density, kg/m³

Both superficial and slot velocities in the sieve and bubble cap test cases of Table 1 are roughly comparable, and energy contents calculated using these operating parameters do not differ appreciably. There is a physical problem, however, in the placement of caps with cooling coils on bubble cap trays. Because of the physical constraints, the distribution of gas injection points is less uniform and gas-liquid contacting less effective with bubble caps than with sieves. This difference has increasing importance as nitrogen oxides concentrations diminish to very low values.

It will also be noted in Table 1 for the sieve plate test data, that roughly the upper one-third of the columns operated with less than 1% acid strengths. Corresponding calculated gas phase NO_x concentrations are lower than 1,000 ppmv. It is possible that in this region, as suggested by Andrew and Hansen (1961), the controlling mass transfer mechanism shifts to direct absorption and reaction of NO_2.

Also shown in Figure 1 is the range of published dilute acid

Table 1c. Nitric Acid Absorption, Sieve Tray Column, 3.05 m dia.

Feed Gas, kmol/s			
NO	0.000229	0.0001877	0.000226
NO_2	0.01885	0.01861	0.01780
O_2	0.01188	0.01387	0.01110
N_2	0.1947	0.218	0.200
Side Stream Acid, kg/s	0.705 (34.5% acid) on Pl. 5	0.695 (34.6% acid) on Pl. 5	0.736 (34.4% acid) on Pl. 5
Pressure kPa	681	681	756
Nitric Acid Rate, kg/s (as 100% acid)	1.437	1.414	1.384

Plate No.	Temp. °C	Acid, %		Exp. $H\sqrt{k4, 5D}$ $\text{kmol/m}^2 \cdot \text{kPa} \cdot \text{s}$	Temp. °C	Acid, %		Exp. $H\sqrt{k4, 5D}$ $\text{kmol/m}^2 \cdot \text{kPa} \cdot \text{s}$	Temp. °C	Acid, %		Exp. $H\sqrt{k4, 5D}$ $\text{kmol/m}^2 \cdot \text{kPa} \cdot \text{s}$
		Meas.	Calc.			Meas.	Calc.			Meas.	Calc.	
1	30.8	57.9	57.9	0.00000816	45.8	57.6	57.6	0.00000988	36.4	57.2	57.2	0.00000889
2	30.3	52.0	51.7	816	35.7	52.5	52.9	0.00001012	23.7	50.7	51.1	915
3	31.8	—	45.2	831	38.3	—	46.8	1084	25.0	—	43.5	0.00001012
4	33.2	39.4	39.2	860	40.9	41.0	41.1	1180	27.0	37.5	36.7	1180
5	33.8	—	34.3	915	41.8	—	36.2	1301	27.2	—	31.5	1349
6	34.5	30.0	30.6	0.00001012	42.7	33.0	32.3	1493	27.5	23.3	27.7	1469
7	33.7	—	22.5	1180	42.6	—	25.3	1758	25.0	—	16.81	205
8	32.9	18.14	18.04	1445	42.5	22.0	20.6	205	24.3	12.20	12.35	275
9	32.2	—	14.14	1831	42.3	—	16.60	253	23.0	—	9.01	381
10	30.6	11.05	11.05	238	41.8	14.20	13.34	337	21.5	6.40	6.63	535
11	29.9	—	8.60	366	41.4	—	10.63	450	20	—	4.92	718
12	29.9	6.83	6.58	535	40.7	9.26	8.44	619	17.6	3.44	3.70	0.0001060
13	29.1	—	5.04	804	40.4	—	6.68	860	17	—	2.77	1542
14	28.7	—	3.86	0.0001156	39.6	—	5.27	0.0001277	16	—	2.13	226
15	28.3	3.32	2.98	1686	38.7	5.05	4.12	1782	15.2	1.48	1.64	337
16	28.1	—	2.30	238	38.6	—	3.21	246	15.1	—	1.27	479
17	28	—	1.79	352	38.4	—	2.52	352	15	—	0.99	706
18	27.7	—	1.41	494	38	—	2.00	494	14.8	—	0.78	0.001060
19	27.4	—	1.10	706	37.7	—	1.56	706	14.5	—	0.60	1542
20	27.2	0.09	0.84	0.001060	37.3	1.49	1.19	959	14.1	0.42	0.46	219
21	27.2	—	0.62	1782	37.2	—	0.89	0.001277	14	—	0.35	311
22	27.3	—	0.45	246	37.2	—	0.65	1782	13.9	—	0.26	438
23	27.3	—	0.31	359	37.2	—	0.45	238	13.7	—	0.18	633
24	27.4	0.02	0.19	501	37.1	0.46	0.27	318	13.5	0.12	0.11	888
25	27.4	—	0.09	706	32.8	0.19	0.13	424	13.1	—	0.05	0.01204
Off-gas NO_x, ppmv												
Meas.	438				747				290			
Calc.	549				683				315			

N_2O_4 mass transfer coefficients (Wendel and Pigford, 1958; Dekker et al., 1959; Kramers et al., 1961; Gerstacker, 1961; Corriveau, 1971; Kameoka, 1973); along with two higher acid strength values (Lefers and van der Berg, 1982). The plant $H\sqrt{kD}$ data at comparable acid strengths are substantially higher than the literature values. A contributing factor to these differences was the omission in all the literature data analyses of a reverse driving force term for equilibrium liquid phase reaction. The back-reaction effect is particularly important if contact times are short and HNO_2 decomposition incomplete. The Lefers data were obtained with 25 and 40% acid strengths. In this case, inclusion of the driving force limits not only would increase the $H\sqrt{kD}$ values but also would moderate the sharp drop reported in the 25 to 40% concentration range.

Also, all the small-scale test work was done with nitrogen rather than air as the feed gas NO_x diluent. Oxygen in the plant gases may contribute to enhanced N_2O_4, N_2O_3, and NO_2 mass transfer by liquid phase HNO_2 oxidation. A few comparative runs in the laboratory equipment with air rather than nitrogen as the carrier gas are needed to provide quantitative confirmation.

In addition, there are important phase contacting differences between the laboratory and plant absorption units. The laboratory equipment was carefully chosen to present a quiescent, laminar film at the phase interface. In the plant units, gas is broken up in small bubbles and forced through the liquid. The increased liquid energy contents produced in plant contacting increase the effective diffusivities of the absorbed components, thereby further augmenting mass transfer.

Corriveau (1971) reports the value 0.1569×10^{-4} $\text{kmol/m}^2 \cdot \text{kPa} \cdot \text{s}$ for $H_{N_2O_3}\sqrt{k8, 5D_{N_2O_3}}$ obtained in his test equipment at 25°C. His comparable value for $H_{N_2O_4}\sqrt{k4, 5D_{N_2O_4}}$ is 0.562×10^{-5} $\text{kmol/m}^2 \cdot \text{kPa} \cdot \text{s}$. If it is assumed that plant-scale mass transfer coefficients follow the ratio of Corriveau's values for N_2O_3 relative to N_2O_4, then N_2O_3 absorption performance can be calculated plate to plate for a typical column. This has been done for the second set of bubble cap performance data—Table 12, and the results plotted in Figure 2.

Figure 2 illustrates acid strength profiles typical in nitric acid absorption. Whereas, moving up through the column, nitric acid concentrations decrease plate to plate, nitrous acid increases to a maximum and then decreases. Nitrous acid levels persist to a point higher in the column at lower temperature, but disappear for all practical purposes below 25–30% HNO_3 acid strength.

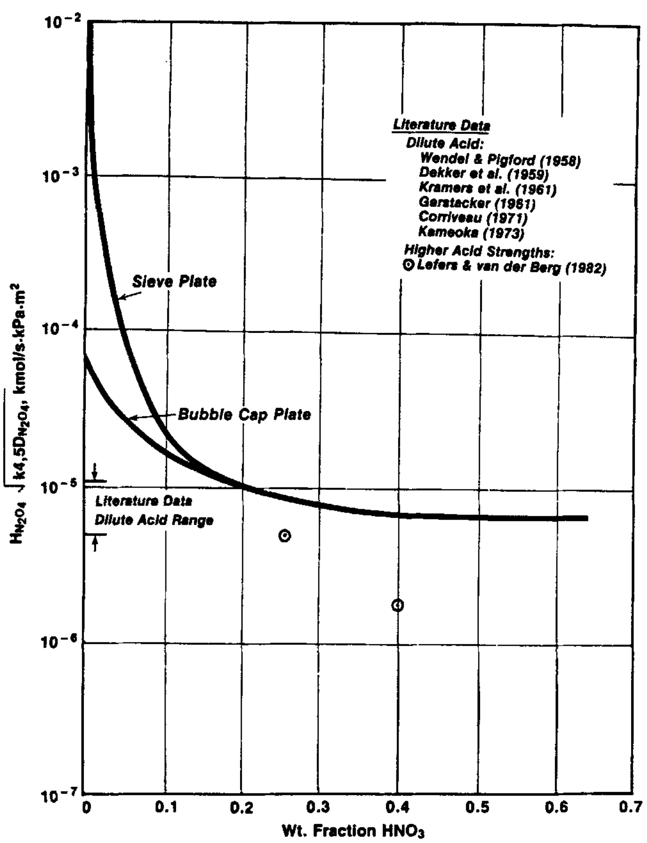

Figure 1. N_2O_4 **mass transfer coefficients vs. nitric acid strength at 25°C.**

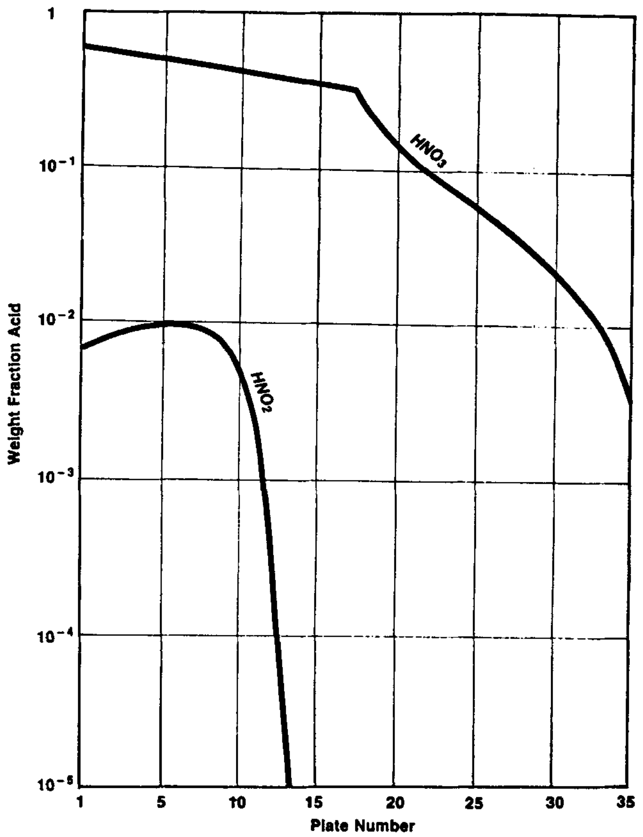

Figure 2. HNO_3 **and** HNO_2 **weight fraction vs. plate number. Bubble cap column with 30°C cooling water**

This observation is the basis for the approach of Bolme (1977) and Bolme and Horton (1979) to off-gas NO_x reduction. Off-gas NO_x levels can be further reduced by contacting with 25–30% acid recirculated from the primary absorber. The additional NO_x picked up in this stream can be removed in a steam stripping, recompressed, and fed back to the primary column.

Steps 6 through 8 in the mechanism described previously are involved in this supplemental recovery operation. It should be noted, however, that $H_{N_2O_3}\sqrt{k8,5D_{N_2O_3}}$ values higher by at least an order of magnitude than those obtained from the Corriveau (1971) ratio, are needed to explain the off-gas NO_x reductions that are claimed possible. Here again, a liquid phase oxidation effect may be operative.

Conclusions

Mass transfer of N_2O_4 is a primary rate-limiting consideration in aqueous nitric acid absorption. Plate efficiency, defined as the percentage approach of actual to equilibrium absorption, has been used in past performance evaluations. Use of a rate expression based on film or penetration theory with rapid liquid phase reaction can provide improved accuracy.

Mass transfer coefficients for N_2O_4 have been obtained from plant-scale absorption data. These values were found to be strongly dependent on temperature and acid strength, and at acid strengths under 20% HNO_3 to be dependent on plate design. Sieve trays show better mass transfer performance then bubble caps in this acid concentration range. Cooling coils are needed on most absorption trays. The better distribution of gas injection points possible with cooling coils on sieves provides the demonstrated advantage.

Plant mass transfer coefficients are higher than those reported in the small-scale laboratory tests. Omission of a reverse film reaction term in the laboratory data analyses—particularly for those tests involving higher nitric acid concentrations—contributes to the differences. The laboratory tests were run with nitrogen rather than air as a diluent feed gas. Mass transfer enhancement by liquid phase oxidation of HNO_2 for N_2O_4, N_2O_3, and at low gas phase NO_x concentrations for NO_2, may also have been a factor in the observed improvement in plant performance.

Finally, higher liquid phase energy contents resulting from gas-liquid contacting on the plant scale, produce further mass transfer advantages.

Notation

A = interfacial area, m²
a = activity, kmol/m³
D = diffusivity, m²/s
d = column diameter, m
E = plate efficiency, %
H = Henry's law coefficient, kmol/m³ · kPa
$k1$ = reaction rate constant for NO oxidation, $kPa^{-2}s^{-1}$
$k4, 5$ = reaction rate constant for N_2O_4 hydrolysis, s^{-1}
$k8, 5$ = reaction rate constant for N_2O_3 hydrolysis, s^{-1}
$K0 = (p_{NO}/p_{N_2O_4}^{1.5}) \cdot (a_{HNO_3}^2/a_{H_2O})$, $kPa^{-1/2}$
$K1 = (p_{NO_2}/p_{NO}^2\, p_{O_2})$, kPa^{-2}

$K2 = (p_{N_2O_4}/p^2_{NO_2})$, kPa^{-1}
$K4, 5 = (p_{NO}/p^3_{NO_2}) \cdot (a^2_{HNO_3}/a_{H_2O})$, $(kmol/m^3 \cdot kPa^2)$
$K4, 5a = (p_{NO}/p^3_{NO_2})$, kPa^{-2}
$K6 = (P_{N_2O_3}/p_{NO}\, p_{NO_2})$, kPa^{-1}
$K8 = (W^2_{HNO_2}/p_{NO}\, p_{NO_2})$, kPa^{-2}
P = power input, kW
p = partial pressure, kPa
R^2_A = multiple correlation coefficient
S = bubble cap slot or sieve hole submergence, m
T = temperature, K
u_g = superficial gas velocity, m/s
u_s = bubble cap slot or sieve hole velocity, m/s
V = volume, m^3
W = weight fraction
ρ_l = liquid density, kg/m^3

Literature cited

Andrew, S. P. S., "Aspects of Gas/Liquid Mass Transfer," *Alta Technologie Chemica Processi di Scambio,* Acedemia Nationale dei Lincei, Rome, 153 (1961).

Andrew, S. P. S., and D. Hanson, "The Dynamics of Nitrous Gas Absorption," *Chem. Eng. Sci.,* **14,** 105 (1961).

Bodenstein, M., "The Rate of the Reaction between Nitric Oxide and Oxygen," *Zeit. Elektrochem.,* **34,** 183 (1918).

———, "Formation and Dissociation of the Higher Nitrogen Oxide," *Zeit. Physik. Chem.,* **100,** 68 (1922).

Bolme, D. W., "Removal of Nitrogen Oxides from Industrial Gases by Use of Oxidizing Solutions in which Nitrates are the Oxidants," U. S. Patent 4,053,555 (1977).

Bolme, D. W., and A. Horton, "The Humphreys and Glasgow/Bolme Nitric Acid Process," *Chem. Eng. Prog.,* **75,** 95 (1979).

Burdick, C. L., and E. S. Freed, "The Equilibrium between Nitric Oxide, Nitrogen Peroxide, and Aqueous Solutions of Nitric Acid," *J. Am. Chem. Soc.,* **43,** 518 (1921).

Carberry, J. J., "Chemical Equilibrium and Kinetics in the Nitrogen Oxides-Water System," *Chem. Eng. Sci.,* **9,** 2 (1959).

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

Chilton, T. H., *Strong Water,* MIT, Cambridge, MA (1968).

Corriveau, C. E., "The Absorption of N_2O_3 into Water," M.S. Thesis, Univ. California, Berkeley (1968).

Danckwerts, P. V., "Significance of Liquid Film Coefficients in Gas Absorption," *Ind. Eng. Chem.* **43,** 1460 (1951).

———, *Gas-Liquid Reactions,* McGraw-Hill, New York (1970).

Danckwerts, P. V., and A. M. Kennedy, "Kinetics of Liquid Film Processes in Gas Absorption. I: Models of the Absorption Process," *Trans. Inst. Chem. Eng.* **32,** Supp. 1, S49 (1954).

Dekker, W. A., E. Snoeck, and H. Kramers, "The Rate of Absorption of NO_2 in Water," *Chem. Eng. Sci.,* **11,** 61 (1959).

Denbigh, K. G., and A. J. Prince, "Kinetics of Nitrous Gas Absorption in Aqueous Nitric Acid," *J. Chem. Soc.,* 790 (1947).

Epshstein, D. A., "Equilibrium $NO - NO_2 - HNO_3 - H_2O$ at 0°C," *J. Gen. Chem. USSR,* **9,** 792 (1939).

Gerstacker, Discussion, *Chem. Eng. Sci.,* **14,** 124 (1961).

Franks, R. G. E., *Modeling and Simulation in Chemical Engineering,* Wiley, New York (1972).

Hatta, S., "On the Absorption Rate of Gases by Liquids," *Tohoku Imperial Univ. Tech. Rept.,* **8,** (1928).

Kameoka, Y., "The Absorption of Nitrogen Oxides into Water and Aqueous Solutions," M.S. Thesis, Univ. California, Berkeley (1973).

Kramers, H., M. P. P. Blind, and E. Snoeck, "Absorption of Nitrogen Tetroxide by Water Jets," *Chem. Eng. Sci.,* **14,** 115 (1961).

Higbie, R., "The Rate of Absorption of a Pure Gas into Still Liquid," *Trans. AIChE,* **31,** 365 (1935).

Hisatsune, I. C., "Thermodynamic Properties of Some Oxides of Nitrogen," *J. Phys. Chem.,* **65,** 2249 (1961).

Lefers, J. B., and P. J. van den Berg, "Absorption of NO_2/N_2O_4 into Diluted and Concentrated Nitric Acid," *Chem. Eng. J.,* **23,** 211 (1982).

Lewis, W. K., and W. G. Whitman, "Absorption Symposium—Principles of Gas Absorption," *Ind. Eng. Chem.,* **16,** 1215 (1924).

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

Theobald, H., "Measurements Concerning the Nitric Acid/Nitrous Gas Equilibrium," *Chem. Ingr. Tech.,* **40,** 763 (1968).

Wendel, M. M., and R. L. Pigford, "Kinetics of Nitrogen Tetroxide Absorption in Water," *AIChE J.,* **4,** 3, 249 (1958).

Manuscript received Nov. 3, 1986, and revision received Jan. 27, 1987.