Controlling Mechanism in the Aqueous Absorption of Nitrogen Oxides

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The reactions involved in the removal of nitrogen oxides from gases by reaction with water are reversible and proceed at a finite rate. It is possible therefore that the over-all process is controlled by the rate of the chemical reactions. On this basis an analysis of the process has been developed by the application of chemical kinetics, with consideration of reactions involving both nitrogen dioxide and dinitrogen tetroxide. The resulting differential equation has been simplified and integrated to give a final equation which can be tested experimentally.

Theoretical methods are presented for predicting the extent of absorption of nitrogen oxides at various gas rates and concentrations and are compared with the experimental results.

The paper presents some new concepts of the factors which control the rate of absorption of nitrogen dioxide and dinitrogen tetroxide in water. An understanding of the controlling factors in the process should indicate methods for improving the design of absorption towers in nitric acid plants and aid in the design of scrubbers for removing nitrogen oxides from waste gases.

The removal of nitrogen oxides from gaseous mixtures is important in the production of nitric acid and in the cleaning of certain stack gases. The removal may be accomplished by the reaction of nitrogen dioxide (NO_2) or dinitrogen tetroxide (N_2O_4) with water to give nitric acid and nitric oxide (NO). Although the chemical reactions of the various nitrogen oxides with themselves, with oxygen, and with water have been investigated extensively during the past 40 years, very little work has been done on the actual mechanisms involved in the removal of nitrogen oxides from gaseous mixtures.

Most industrial units for the production of nitric acid use bubble-cap-plate towers or packed towers for contact between water and the gases containing nitrogen oxides, but these towers are very inefficient when the concentration of nitrogen oxides in the gases is low. Development of improved methods for recovering the oxides requires an understanding of the controlling mechanisms in the oxide-recovery process.

The nitrogen oxides of importance in processes involving reactions with aqueous solutions are NO_2, N_2O_4, and NO. Small amounts of N_2O_3 and N_2O_5 are also present in the gases, but according to Verhoek and Daniels(*9*) and Smith and Daniels(*7*) these compounds rapidly come to equilibrium with NO and NO_2 and represent only a small fraction of the total oxides at room temperatures or above.

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

$$2\,NO_2 \text{ (or } N_2O_4\text{)} + H_2O \rightarrow HNO_3 + HNO_2 \qquad (A)$$

$$2\,HNO_2 \rightarrow H_2O + NO + NO_2 \text{ (or } 1/2\,N_2O_4\text{)} \qquad (B)$$

$$2\,NO + O_2 \rightarrow 2\,NO_2 \text{ (or } N_2O_4\text{)} \qquad (C)$$

$$2\,NO_2 = N_2O_4 \qquad (D)$$

Reaction (D) reaches equilibrium very rapidly(*8*), and the equilibrium constant for this reaction is known as a function of temperature between 0° and 90°C.(*6, 9, 10*). The oxidation of NO proceeds relatively slowly although the reaction goes essentially to completion. Reaction-rate constants for the oxidation reaction have been determined by Bodenstein(*1*).

The decomposition of nitrous acid in the liquid phase does not occur rapidly unless the liquid is well agitated. Under ordinary conditions, however, this reaction is not the controlling factor in determining the rate of oxides removal, for analyses of the liquid product obtained in this work indicated only small amounts of nitrous acid relative to the amount of nitric acid.

GAS- AND LIQUID-PHASE REACTION

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

The liquid-phase reaction undoubtedly occurs to some extent. However, the results of the present work and those of Chambers and Sherwood(*3*) definitely indicate that a gas-phase reaction does occur. Perhaps the strongest support of the gas-phase reaction lies in the observable formation of a mist when gases containing NO_2 and N_2O_4 are brought into contact with a gas containing appreciable amounts of water vapor. The mist formation has been observed repeatedly in this work and was reported by Chambers and Sherwood.

In carefully controlled experimental tests carried out in conjunction with the present investigation, gaseous N_2O_4 and NO_2 were admitted to a bulb containing nitrogen and water vapor. No droplets of liquid were present in the bulb in any form before the admittance of the nitrogen oxides. As soon as

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

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

Caudle and Denbigh (*2*) in experiments with a wetted-wall column found that neither increasing the gas-space volume nor increasing the bulk liquid volume had any effect on the rate of removal of nitrogen oxides by liquid water. The rate of removal was proportional to the interfacial area between the gas and the liquid. The controlling resistance, therefore, must lie in the gas film or in the liquid film.

Under these conditions the following over-all mechanism can be postulated for the absorption process. Some of the gaseous NO_2 and N_2O_4 reacts with H_2O vapor in the gas film to form HNO_3 and HNO_2. Most of the HNO_3 diffuses into the liquid phase, and some H_2O and HNO_3 condense in the form of a mist containing small droplets of dilute nitric acid. Part of the HNO_2 decomposes in the vapor space to give NO, NO_2, and H_2O and the rest diffuses into the liquid, where the same decomposition products are obtained. Some of the NO_2 and N_2O_4 diffuses into the liquid phase before reacting with water.

DIFFUSION AS THE CONTROLLING FACTOR IN THE OVER-ALL MECHANISM

The rate of the over-all process by which nitrogen oxides are removed from gaseous mixtures by chemical reaction with water could be controlled by (*a*) diffusional resistances, (*b*) the speed of the chemical reactions, or (*c*) a combination of diffusional resistance and chemical reaction rate.

Chambers and Sherwood (*3*) assumed the controlling mechanism to be the physical diffusion of NO_2 and N_2O_4 through the gas film; consequently the following expression for the absorption rate, expressed as gram moles of equivalent combined nitrogen [i.e., moles of NO_2 + 2(moles of N_2O_4)] per second per square centimeter of gas-liquid interfacial area, may be derived:

$$N_{eNO_2} = \frac{2D_{N_2O_4}}{x_f}\Delta C_{N_2O_4} + \frac{D_{NO_2}}{x_f}\Delta C_{NO_2} \qquad (1)$$

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

According to the experimental results of this work and the results of Caudle and Denbigh (*2, 4*), the rate of nitrogen oxides removal (N_{eNO_2}) at any given gas rate is directly proportional to the concentration of N_2O_4. The ratio $D_{NO_2}/D_{N_2O_4}$ is 1.43 (*3*), and the NO_2 concentration in all the experimental runs was higher than the N_2O_4 concentration; therefore, as NO_2 and N_2O_4 may be assumed to be always in equilibrium, ΔC_{NO_2} was greater than $\Delta C_{N_2O_4}$. Under these conditions Equation (1) is not supported by the experimental results, for Equation (1) shows that the absorption rate should be determined to a large extent by the NO_2 concentration; therefore, it can be concluded that the diffusion of NO_2 and N_2O_4 through the gas film is not the controlling factor in the over-all mechanism.

By the employment of a method similar to that of Hatta (*5*), differential equations based on combined diffusional resistance and chemical-reaction rate as the controlling factor in the over-all mechanism have been derived. These equations either could not be integrated or did not agree with the experimental data. A similar approach based on the two-film theory was attempted by Caudle and Denbigh using methods such as those described by Van Krevelen and Hoftijzer (*8*). They were unable to develop any applicable relationships including diffusion as a controlling factor.

CHEMICAL-REACTION RATES AS THE CONTROLLING FACTOR IN THE OVER-ALL MECHANISM

The reactions involved in the removal of nitrogen oxides from gases by reaction with water are reversible and proceed at a finite rate. It is possible, therefore, that the rate of aqueous absorption is controlled by the rate of the chemical reactions. On this basis, an analysis of the process can be developed by the application of chemical kinetics, and the results agree closely with the experimental data.

The important chemical reactions involved in the removal of NO_2 and N_2O_4 from gaseous mixtures by reaction with water can be written as follows:

$$N_2O_4 + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} HNO_2 + HNO_3 \qquad (a)$$

$$2\,NO_2 + H_2O \underset{k_4}{\overset{k_3}{\rightleftarrows}} HNO_2 + HNO_3 \qquad (b)$$

$$2\,HNO_2 \underset{k_6}{\overset{k_5}{\rightleftarrows}} NO + 1/2\,N_2O_4 + H_2O \qquad (c)$$

$$2\,HNO_2 \underset{k_8}{\overset{k_7}{\rightleftarrows}} NO + NO_2 + H_2O \qquad (d)$$

$$2\,NO_2 = N_2O_4 \quad \text{(continuous equilibrium)} \qquad (e)$$

By summation of reactions (*a*) and (*c*),

$$3/2\,N_2O_4 + H_2O \rightarrow 2\,HNO_3 + NO \qquad (f)$$

By summation of reactions (*b*) and (*d*),

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO \qquad (g)$$

The k's in the preceding equations represent the reaction-rate constants for the forward and reverse reactions.

Equilibrium between NO_2 and N_2O_4 is attained very rapidly, and in the following derivation these two materials are assumed to be continuously in equilibrium. Reactions (*a*), (*b*), and (*e*) occur simultaneously, and reactions (*c*) and (*d*) are consecutive to reactions (*a*) and (*b*). Reaction (*a*), being a bimolecular reaction, should proceed at a faster rate than reaction (*b*), which is trimolecular; however, reaction (*b*) cannot be neglected because it may become important when the concentration of NO_2 is large relative to the N_2O_4 concentration.

At low total concentrations of equivalent NO_2 ($C_{eNO_2} = C_{NO_2} + 2C_{N_2O_4}$), only a small fraction of the total oxides is in the form of N_2O_4. For example, at 25°C. and a total pressure of 1 atm., a gaseous mixture containing 0.1 mole % eNO_2 has only 1.3% of the equivalent oxides in the form of N_2O_4. At the same temperature and pressure, however, a gaseous mixture containing 10 mole % $_eNO_2$ has 43% of the equivalent oxides in the form of N_2O_4. This effect of total oxides concentration on fraction of oxides present as N_2O_4 is shown in Figure 1. As the total concentration of gaseous nitrogen oxides decreases, the efficiency of the removal process should decrease because of the reduction in the fraction of total oxides present as N_2O_4.

The reaction between NO and O_2 to yield NO_2 and N_2O_4 proceeds at a relatively slow rate. This reaction has not been considered here because the analysis deals only with the nitrogen oxides removal which can be accomplished by a one-stage contact with water. The NO oxidation does not proceed at a rate sufficient to cause an appreciable change in the NO_2 concentration while in contact with the liquid on a bubble-cap plate. This conclusion has been verified experimentally in the bubble-cap column used for this work by substituting nitrogen for air in the entering gases.

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

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

According to reaction (c),

$$\left(\frac{dC_{N_2O_4}}{dt}\right)_c = \frac{k_5}{4}\,(C_{HNO_2})^2 - k_6\,(C_{NO})\,(C_{N_2O_4})^{\frac{1}{2}}(C_{H_2O}) \qquad (3)$$

Therefore, the rate of change in N_2O_4 concentration caused by reaction (a) followed by reaction (c) is

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

In a continuous process involving consecutive reactions, a so-called "stationary state" may be reached in which the concentrations of the intermediate reacting materials are essentially constant. Unless reaction (c), or (d), is extremely slow, a stationary state will be obtained very rapidly in this process and the HNO_2 concentration will change very slowly. Under these conditions reaction (f) applies, and 1 mole of NO is formed [by reaction (c)] for every 3/2 moles of N_2O_4 which disappear [net N_2O_4 loss by reactions (a) and (c)]. Therefore according to reaction (f),

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_{a+c} = \frac{3}{2}\left(\frac{dC_{NO}}{dt}\right)_c \qquad (5)$$

According to reaction (c),

$$\left(\frac{dC_{NO}}{dt}\right)_c = \frac{k_5}{2}\,(C_{HNO_2})^2 - 2k_6\,(C_{NO})\,(C_{N_2O_4})^{\frac{1}{2}}(C_{H_2C}) \qquad (6)$$

If Equations (4), (5), and (6) are combined,

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_{a+c} = \frac{3}{4}k_1(C_{N_2O_4})\,(C_{H_2O}) - \frac{3}{4}\,k_2\,(C_{HNO_2})\,(C_{HNO_3}) \qquad (7)$$

Because NO_2 and N_2O_4 are continuously in equilibrium, a change in N_2O_4 concentration is caused by reaction (e). The rate of this concentration change may be represented by $(dC_{N_2O_4}/dt)_e$. The net rate of change in N_2O_4 concentration caused by reactions (a), (c), and (e) is

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_{net} = -\left(\frac{dC_{N_2O_4}}{dt}\right)_{a+c+e} = \frac{3}{4}k_1\,(C_{N_2O_4})\,(C_{H_2O}) - \frac{3}{4}k_2(C_{HNO_2})\,(C_{HNO_3}) - \left(\frac{dC_{N_2O_4}}{dt}\right)_e \qquad (8)$$

By applying the same reasoning as was used for developing Equation (8), one can obtain the following equation representing the net rate of change in NO_2 concentration caused by reactions (b), (d), and (e):

$$-\left(\frac{dC_{NO_2}}{dt}\right)_{net} = -\left(\frac{dC_{NO_2}}{dt}\right)_{b+d+e} = \frac{3}{4}k_3\,(C_{NO_2})^2(C_{H_2O}) - \frac{3}{2}k_4\,(C_{HNO_2})\,(C_{HNO_3}) - \left(\frac{dC_{NO_2}}{dt}\right)_e \qquad (9)$$

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

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_e = \frac{1}{2}\left(\frac{dC_{NO_2}}{dt}\right)_e \qquad (10)$$

As reaction (e) is always at equilibrium,

$$K_c = \text{equilibrium constant} = \frac{C_{N_2O_4}}{(C_{NO_2})^2} \qquad (11)$$

$$dC_{NO_2} = \frac{dC_{N_2O_4}}{2\sqrt{K_c\,C_{N_2O_4}}} \qquad (12)$$

Combination of Equations (8), (9), (10), (11), and (12) gives

$$-\frac{4}{3}\left(\frac{dC_{N_2O_4}}{dt}\right)_{net} - \frac{1}{3\sqrt{K_c\,C_{N_2O_4}}}\left(\frac{dC_{N_2O_4}}{dt}\right)_{net} = \left(k_1 + \frac{k_3}{2K_c}\right)(C_{N_2O_4})\,(C_{H_2O}) - (k_2 + k_4)\,(C_{HNO_2})\,(C_{HNO_5}) \qquad (13)$$

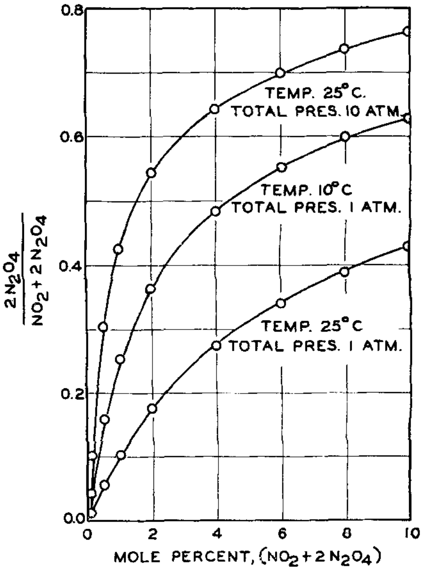

FIG. 1. EFFECT OF eNO_2 CONCENTRATION OF TOTAL OXIDE PRESENT AS N_2O_4.

Only three assumptions have been made in the derivation of Equation (13). They are (1) NO_2 and N_2O_4 are in continuous equilibrium, (2) the reactions as indicated represent the important chemical process, and (3) a stationary state is rapidly obtained. All these assumptions appear to be justified on the basis of results obtained in this work and by other investigators. It should be noted that Equation (13) could also have been derived from Equations (*a*), (*b*), (*e*), (*f*), and (*g*) on the basis of rate of change in HNO_3 concentration.

SIMPLIFICATION AND INTEGRATION OF RATE EQUATIONS

If the net chemical reactions (*f*) and (*g*) are essentially irreversible, the last term in Equation (13) may be neglected. If the irreversible reaction occurs in the gas film, the concentration of HNO_3 will be very small since it diffuses rapidly into the liquid phase. Under any conditions if the reactions are irreversible the concentration of HNO_2 will be very small. The concentration of H_2O may be assumed as constant at any given temperature. If the reactions occur in the gas film, the H_2O concentration will be directly proportional to the H_2O vapor pressure, and if the reactions occur in the liquid film the H_2O concentration (or activity) will be essentially constant unless there is a large change in the acid concentration. With these two simplifications Equation (13) may be written as follows:

$$-\left(\frac{dC_{N_2O_4}}{dt}\right)_{net} - \frac{1}{4\sqrt{K_c C_{N_2O_4}}}\left(\frac{dC_{N_2O_4}}{dt}\right)_{net} = A\,(C_{N_2O_4}) \qquad (14)$$

where

$$A = \frac{3}{4}\left(k_1 + \frac{k_3}{2K_c}\right)(C_{H_2O})$$

For gas concentrations less than about 10% eNO_2, the volumetric flow rate remains essentially constant, and under this condition Equation (14) may be integrated directly. The equation may be rearranged and integrated between the limits of zero time (corresponding to an original N_2O_4 concentration of $C_{o_{N_2O_4}}$) and the time (*t*) any portion of the gas is in contact with the liquid (corresponding to a final N_2O_4 concentration of $C_{f_{N_2O_4}}$).

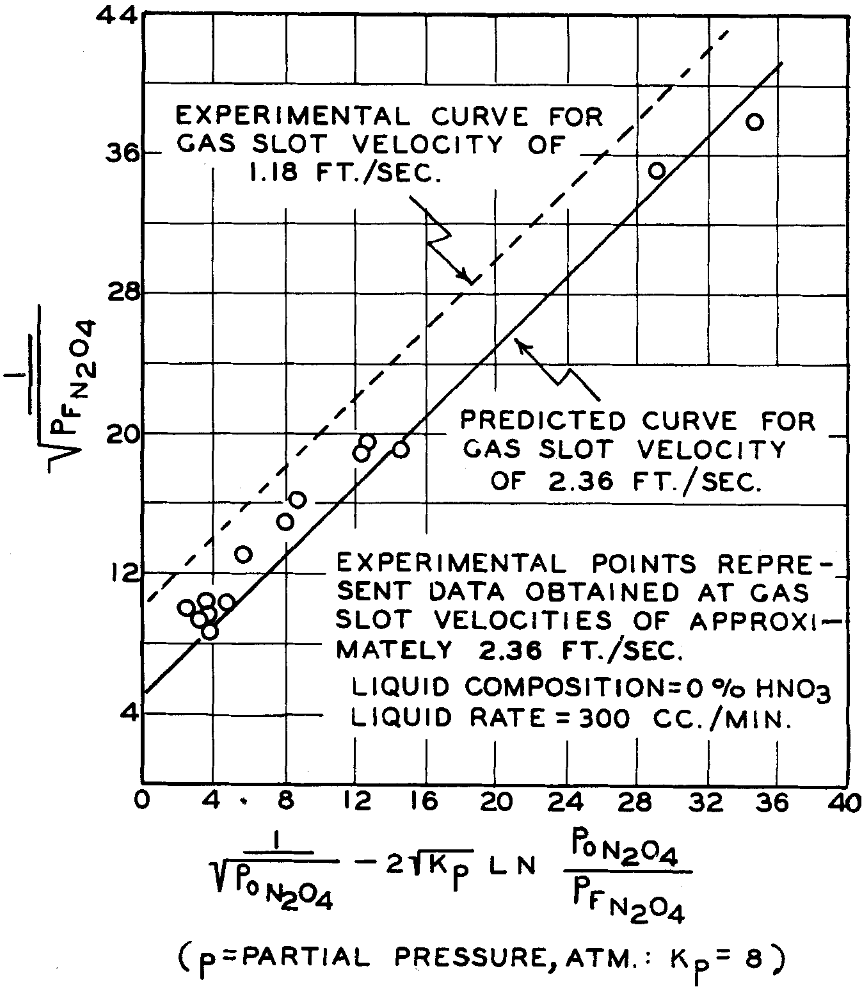

FIG. 2. EXPERIMENTAL TEST FOR VALIDITY OF INTEGRATED RATE EQUATION ASSUMING PROCESS CONTROLLED BY CHEMICAL REACTION RATES.

$$-\int_{C_{o_{N_2O_4}}}^{C_{f_{N_2O_4}}} \frac{dC_{N_2O_4}}{C_{N_2O_4}} - \frac{1}{4\sqrt{K_c}}\int_{C_{o_{N_2O_4}}}^{C_{f_{N_2O_4}}} \frac{dC_{N_2O_4}}{(C_{N_2O_4})^{3/2}} = A\int_0^t dt \qquad (15)$$

Integration, substitution of the limits and rearrangement give

$$\frac{1}{(C_{f_{N_2O_4}})^{1/2}} = \frac{1}{(C_{o_{N_2O_4}})^{1/2}} - 2\sqrt{K_c}\,\ln\frac{C_{o_{N_2O_4}}}{C_{f_{N_2O_4}}} + 2A\sqrt{K_c}\,t \qquad (16)$$

At partial pressures of eNO_2 less than 0.1 atm. perfect-gas deviations are small and the concentration terms in Equation (16) can be expressed in more convenient units of partial pressure to give the following simplified equation:

$$\frac{1}{(P_{f_{N_2O_4}})^{1/2}} = \frac{1}{(P_{o_{N_2O_4}})^{1/2}} - 2\sqrt{K_p}\,\ln\frac{P_{o_{N_2O_4}}}{P_{f_{N_2O_4}}} + B\,t \qquad (17)$$

where

P = partial pressure, atm.
K_p = equilibrium constant = $\frac{P_{N2O4}}{P_{NO2}}$, atm.$^{-1}$
B = a constant at any temperature

Equation (17) shows that a plot of

$$\frac{1}{(P_{f_{N_2O_4}})^{1/2}} \text{ vs. } \left[\frac{1}{(P_{o_{N_2O_4}})^{1/2}} - 2\sqrt{K_p}\,\ln\frac{P_{o_{N_2O_4}}}{P_{f_{N_2O_4}}}\right]$$

TABLE 1.—EXPERIMENTAL DATA

Bubble-cap-plate Column

Total pressure = 1 atm.

Run	Plate temp., °C	Ent. liq. comp., wt. % HNO_3	Exit liq. rate, cc./min.	Exit liq. comp., wt. % HNO_3 $\times 10^2$	Ent. gas rate, cu. ft./min.	Entering-gas composition, mole %			Exit-gas composition, mole %		
						$NO_2 + 2N_2O_4$	NO_2	N_2O_4	$NO_2 + 2N_2O_4$	NO_2	N_2O_4
1	19.8	0	292	0.615	1.22	0.454	0.420	0.0171	0.422	0.392	0.0150
2	23.0	0	301	0.845	1.18	0.534	0.497	0.0185	0.491	0.459	0.0159
3	18.2	0	298	0.900	1.21	0.622	0.554	0.0340	0.578	0.518	0.0298
4	23.6	0	302	2.08	1.18	0.685	0.628	0.0286	0.576	0.534	0.0206
5	19.4	0	286	1.84	1.21	0.699	0.622	0.0388	0.611	0.550	0.0306
6	23.0	0	311	1.61	1.18	0.741	0.672	0.0344	0.656	0.602	0.0272
7	21.1	0	304	1.81	1.21	0.794	0.707	0.0435	0.696	0.627	0.0347
8	18.8	0	306	2.23	1.21	0.800	0.697	0.0515	0.686	0.608	0.0393
9	18.4	0	306	2.16	1.21	0.821	0.710	0.0554	0.714	0.628	0.0430
10	24.0	0	288	3.12	1.20	0.831	0.752	0.0394	0.681	0.626	0.0276

based on experimental data should be a straight line with a slope equal to 1.0 if the reactions occur irreversibly and all concentration values are determined at approximately the same temperature and a constant value of t. Experimental conditions in which the reactions occur essentially irreversibly may be obtained by contacting gases containing only NO_2 and N_2O_4 (plus air or nitrogen as a diluent) with dilute nitric acid or with pure water. Experimental data at various N_2O_4 concentrations have been obtained under these conditions maintaining constant gas rates (i.e., constant t) and constant temperature (i.e., constant values of A, B, and K_p). These data are plotted as

$$\frac{1}{(P_{f_{N_2O_4}})^{1/2}} \text{ vs. }$$

$$\left[\frac{1}{(P_{o_{N_2O_4}})^{1/2}} - 2\sqrt{K_p}\ln\frac{P_{o_{N_2O_4}}}{P_{f_{N_2O_4}}}\right]$$

in Figure 2. It can be seen that a straight line with a slope of 1.0 is obtained in agreement with Equation (17).

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A bubble-cap-plate column containing one plate was used for obtaining the experimental data. The bubble-cap plate was made of Lucite and was equipped with seven Lucite bubble caps. One bubble cap was located in the center of the plate, and the other six caps were arranged peripheral to the center cap. Eight equally spaced circular slots of 5/16-*in. diam.* were drilled in the center cap, and four slots in each of the peripheral caps, these slots being directed toward the center to reduce wall effects. The total slot area was 2.46 sq. in. The total depth of liquid on the plate was 1 in., and the tops of the slots were 1/2 in. below the liquid surface. A stainless steel cooling coil was also immersed in the liquid on the plate. The inside diameter of the glass column was 7 1/2 in., and the bubble-cap plate was 12 in. from both the top and bottom plates.

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

Gaseous nitrogen oxides, obtained from cylinders containing NO_2 and N_2O_4, were diluted with nitrogen or air and admitted at a steady rate to the lower section of the column. The inlet and exit gases were sampled by means of evacuated Gaillard bulbs. The gas-flow rates were measured by calibrated Venturi meters. Pressures at the top and bottom of the column were measured by open-tube manometers containing α-bromonaphthalene. The indicating fluid in the Venturi manometers was also α-bromonaphthalene, which is not strongly reactive with NO_2. Temperatures at the following points were measured by means of copper-constantan thermocouples: (1) liquid on bubble-cap plate, (2) entering liquid, (3) exit liquid, (4) entering gas, (5) exit gas.

Runs were made at liquid-flow rates of 300 and 600 cc/min., gas-slot velocities of 1.18 and 2.36 ft./sec., entering liquid compositions of 0 and 15 wt. % HNO_3, and gas compositions of 0.45 to 11.6 vol. % eNO_2. All runs were carried out at atmospheric pressure. Nitrogen was used as the diluent for the first series of runs, which was checked by use of air at the same flow conditions, and no significant difference in results was found; consequently, air was used for the remainder of the runs. If more than one bubble-cap plate had been used or if NO had been admitted to the column with the NO_2, there would have been a significant difference in the nitrogen and air results because air would have supplied oxygen for the oxidation of NO to NO_2.

At the start of a run the liquid- and air-flow rates were set and blank samples of each taken. Then the NO_2 was admitted at the desired flow rate and the equipment was run until steady-state conditions were attained. The liquid flow from the column was then diverted to the collecting bottle, and liquid was collected for 10 to 20 min. while the flow rates were carefully held constant. The pressures and temperatures were read, and entering- and exit-gas samples, as well as liquid samples, were taken near the beginning and near the end of the timing period. The liquid samples were analyzed for HNO_3 by titrating a known volume with standard $NaOH$ solution.

The gas samples were taken in evacuated bulbs containing hydrogen peroxide. The amount of sample was found by weighing, and the amount of nitrogen oxides present was determined by titrating the HNO_3 formed by the reaction between H_2O_2 and NO_2, N_2O_4, or NO. In order to analyze the exit gases for the NO content, a second sampling bulb containing potassium permanganate in sulfuric acid was used. The excess permanganate was back titrated with ferrous sulfate, and the results obtained from the hydrogen peroxide bulb and the permanganate bulb were used to determine the NO content in the exit gases. The observed exit-gas analyses differed considerably from the calculated values based on the liquid analysis. Collection of liquid sampes in H_2O_2 determined that a slight discrepancy was caused by NO being given up by the liquid; however, a large error in the exit-gas analyses was due to the admittance of a significant amount of mist to the sampling bulbs. It was not possible to determine the amount of mist to make the necessary corrections. The mist also obviated the possibility of analyzing the exit gases by photometric methods because it would have critically interfered with the cell readings. All results consequently were reported on the basis of the liquid-flow rate, the entering- and exit-liquid analyses, the air-flow rate, and the entering-gas analysis.

The fraction of the oxides which theoretically could be converted to HNO_3 according to the over-all reaction

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO$$

was calculated by the method of Sherwood and Pigford(*6*) by use of extrapolated values of the equilibrium constant. When water (0% HNO_3) was used as the absorbent and the entering gases contained only NO_2 (with N_2O_4) and nitrogen or air, the calculated theoretical conversion was practically 66 2/3% based on the total gaseous oxides. This indicates that the reaction is essentially irreversible under these conditions because 1 mole of NO theoretically can be liberated for every 3 moles of equivalent NO_2 entering the system.

The relative amounts of NO_2 and N_2O_4 in the entering and exit gases were determined from the equilibrium constants for the reaction(*6*)

$$2\,NO_2 \rightleftharpoons N_2O_4 .$$

INTERPRETATION OF RESULTS*

Table 1 presents a sample of the experimental results. The runs were all carried out under conditions in which the chemical reactions involved were essentially irreversible. All the runs at a slot velocity of 1.18 ft./sec. were at approximately the same temperature. Under these conditions, if the chemical reaction rate is the controlling mechanism in the over-all process, Equation (17) should apply, and a plot of

$$\frac{1}{(P_{f_{N_2O_4}})^{1/2}} \text{ vs. } \left[\frac{1}{(P_{o_{N_2O_4}})^{1/2}} - 2\sqrt{K_p}\ln\frac{P_{o_{N_2O_4}}}{P_{f_{N_2O_4}}}\right]$$

should be a straight line with a slope of 1.0. Figure 2 indicates that Equation (17) agrees with the experimental data. This plot covers a 150-fold change in N_2O_4 concentration in the entering gases and gives strong support to the theory that the rates of the chemical reactions involving N_2O_4 and NO_2 control the over-all removal process. The sensitivity of the correlation was checked by making calculations for conversions other than the reported values, and it was found that the correlation was quite sensitive to changes in the experimental results, especially at high eNO_2 concentrations.

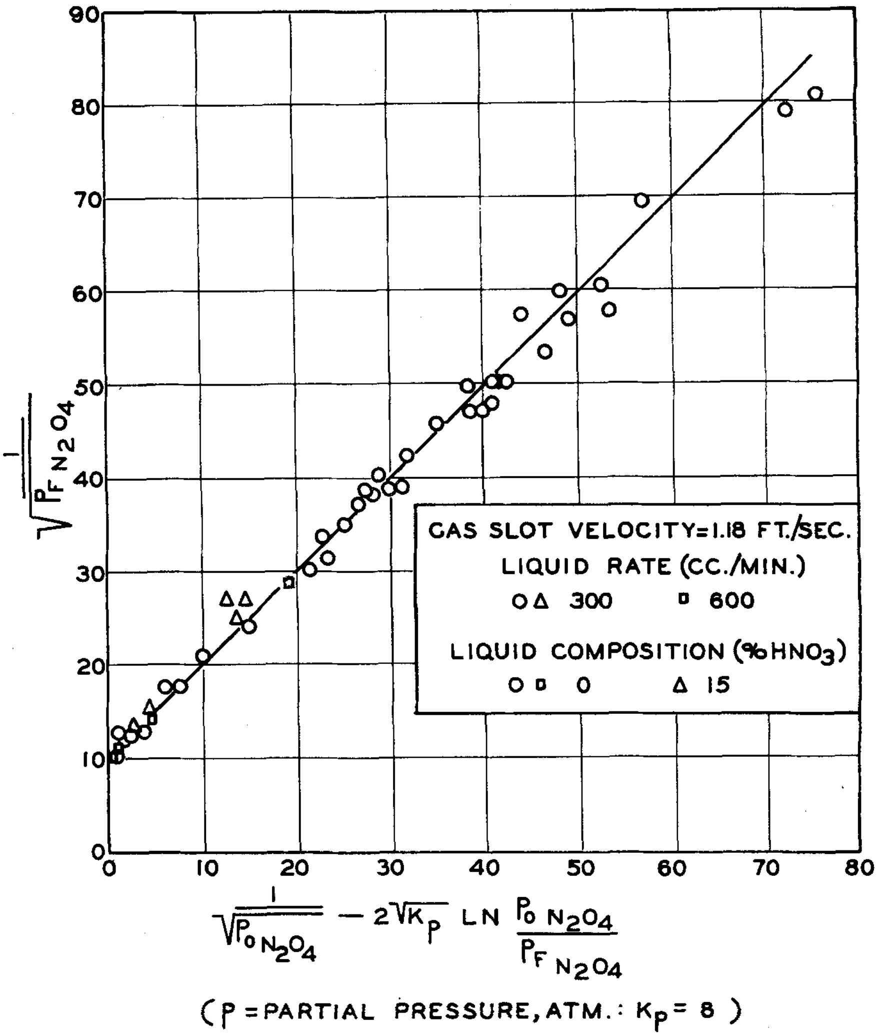

FIG. 3. PREDICTED CURVE FOR RELATIONSHIP BETWEEN ENTERING AND EXIT N_2O_4 CONCENTRATIONS.

The intercept of the straight line at

$$\left[\frac{1}{(P_{o_{N_2O_4}})^{1/2}} - 2\sqrt{K_p}\ln\frac{P_{o_{N_2O_4}}}{P_{f_{N_2O_4}}}\right]$$

equal to zero is Bt. The numerical value of the intercept can be used to predict the line for a similar plot at the same temperature with a different contact time, assuming the effective gas-liquid interfacial area does not change appreciably. This was done for a contact time equivalent to a gas-slot velocity of 2.36 ft./sec., and the predicted curve is shown in Figure 3. The experimental data fall slightly above the predicted curve probably because the effective contact area between the gas and liquid varies somewhat with gas rate.

The individual plate efficiency for the removal process may be expressed as the actual amount of nitrogen oxides removed from the gases divided by the amount of oxides which would have been removed if the plate were theoretically perfect. A plot of plate efficiency vs. percentage of eNO_2 in the entering gases at constant gas rate is shown in Figure 4. The plate efficiency decreases as the percentage of eNO_2 in the entering gases decreases. This effect would be expected if the factor which controls the over-all mechanism is the rate of the chemical reactions since the fraction of total oxides present as N_2O_4 decreases with reduced eNO_2 concentrations.

The change in removal efficiency with change in total gaseous oxides concentration must be recognized when systems for the aqueous absorption of nitrogen oxides are designed. As is indicated in Figure 1, an increase in pressure at any given composition of the gases causes a larger fraction of the total

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*Complete tabulations of the experimental data are on file with the Photoduplication Service, American Documentation Institute, Library of Congress, Washington 25, D. C., as Document 4423, which may be ordered for $1.25 for microfilm or photoprints.

nitrogen oxides to be present in the form of N_2O_4. Consequently, higher plate efficiencies may be obtained by increasing the total pressure of the gases.

The experimental data obtained with the bubble-cap column showed that an increase in the gas rate caused a decrease in the fraction of entering oxides converted to nitric acid, but a twofold change in the liquid-flow rate had no appreciable effect on the fractional conversion.

SUMMARY

The factor which controls the over-all mechanism in the removal of nitrogen oxides from gaseous mixtures by contact with water is the rate of the chemical reactions involved. The rate of removal of the nitrogen oxides is proportional to the concentration of N_2O_4 in the gases. As the fraction of total oxides present as N_2O_4 is low when the concentration of gaseous oxides is low, the individual plate efficiencies for removal of nitrogen oxides from dilute gases are poor; however improved plate efficiencies can result with high total pressure.

The chemical reactions between nitrogen oxides and water occur partially in the gas phase or in the gas film, as evinced by the formation of a mist when NO_2 and N_2O_4 are in vapor.

The fraction of the entering oxides which are converted to nitric acid decreases as the contact time between the gas and liquid decreases. If experimental data for the equipment are available at one gas rate, the integrated kinetic equations can be used for an estimation of the effect of change in gas-liquid contact time.

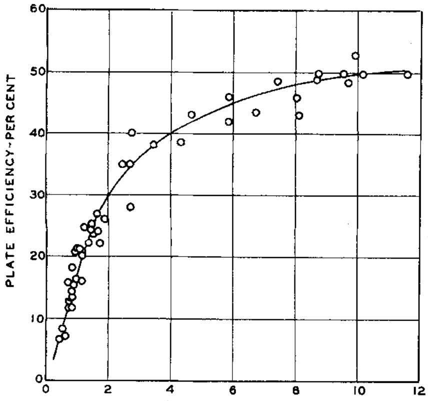

FIG. 4. EFFECT OF eNO_2 CONCENTRATION IN ENTERING GASES ON ABSORPTION EFFICIENCY (BUBBLE-CAP COLUMN AT 1 ATM. TOTAL PRESSURE; GAS-SLOT VELOCITY OF 1.18 FT./SEC.)

ACKNOWLEDGMENT

This work has been conducted in the Engineering Experiment Station of the University of Illinois as part of Contract AT(30-3)-28, United States Atomic Energy Commission, H. F. Johnstone, technical director. Detailed information concerning the theory and experimental results are available as Technical Report 10, COO-1011, Technical Information Service, United States Atomic Energy Commission, Oak Ridge, Tennessee.

NOTATION

A = constant at any temperature
B = constant at any temperature
C = concentration, gram moles/cc.
C_f = final concentration, gram moles/cc.
C_o = original concentration, gram moles/cc.
D = diffusivity, sq. cm./sec.
eNO_2 = equivalent $NO_2 = NO_2 + 2\ N_2O_4$
k = reaction-rate constant, units depending on reaction involved
K = equilibrium constant for the reaction, $2\ NO_2 = N_2O_4$
N_{eNO_2} = rate of nitrogen oxides removal based on equivalent NO_2 removal, gram moles/(sec.) (sq. cm.)
P = partial pressure, atm.
P_f = final partial pressure, atm.
P_o = original partial pressure, atm.
t = time, sec.
x_f = effective film thickness, cm.
ΔC = differences in concentration between main body of gas and gas-liquid interface, gram moles/cc.

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APPROXIMATE EQUATIONS FOR TIME OF BATCH FRACTIONATION

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Analytical expressions are obtained for the calculation of the time required for batch rectification of binary feeds which may be treated by assuming constant relative volatility and no column holdup. The equations cover constant reflux operations and varying reflux constant product operations for the two cases involving either a large or a small number of theoretical stages. The latter type of calculation has hitherto been possible only by tedious graphical methods. This paper introduces novel pseudo-equilibrium curves which lead to simple equations of considerable accuracy. The equations obtained may be rearranged or modified so that other factors such as sharpness of fractionation may be represented analytically.

An accurate method for the design of equipment for the batch distillation and fractionation of binary liquid mixtures of constant overhead product composition with varying reflux ratio was presented by Bogart(*1*). However, the method covered only the case of constant distillate composition with varying reflux ratio and involved a rather tedious graphical integration. Many subsequent papers have dealt with modifications of assumptions made by Bogart, notably the inclusion of the effect of holdup.