REACTION AND TRANSPORT OF NITROGEN OXIDES IN NITROUS ACID SOLUTIONS

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Depletion of nitrous acid from its aqueous solution is studied over a wide range of experimental conditions. The rate and stoichiometry of this process are determined as a function of mass transfer characteristics of gas-liquid contacting devices. It is found that the depletion of nitrous acid is brought about by three different mechanisms: 1) simultaneous hydration of \( \text{N}_2\text{O}_4 \) and evolution of \( \text{NO} \), both existing in equilibrium with \( \text{HNO}_2 \), 2) desorption of nitrous acid molecules and 3) decomposition of \( \text{HNO}_2 \) into \( \text{NO} \) and \( \text{NO}_2 \) occurring in the vicinity of the liquid surface. A quantitative analysis is made using the various rate and equilibrium constants with the oxides of nitrogen. The relative importance of the three mechanisms and, hence, the rate and stoichiometry of the whole process vary with the mass transfer characteristics of the gas-liquid contactors. The rate constants of the hydration of \( \text{N}_2\text{O}_4 \) and of the decomposition of nitrous acid (\( 2\text{HNO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \)) as well as the solubility of \( \text{N}_2\text{O}_4 \) were established.

Introduction

The interaction of chemical reaction and mass transport is a subject of continuing interest to chemical engineers. In an aqueous solution of nitrous acid, nitrogen oxides are evolved into the gas phase and nitric acid is produced in the liquid phase, resulting in the depletion of nitrous acid. Hence, it is a reverse process of absorption of nitrogen oxides into water. This process has been extensively studied but the rate expressions and the stoichiometric relationships reported in these studies are conflicting. It is supposed that, since the complex interactions of numbers of nitrogen oxides are involved, a single kinetic expression is not applicable over a wide range of experimental conditions. In the light of the importance of systems containing nitrogen oxides for control of atmospheric pollution, a study was undertaken to determine both the rate and the stoichiometry of the decomposition of nitrous acid and to analyze the experimental results considering the interactions of chemical reactions and mass transport.

Decomposition of nitrous acid Abel et al.\(^1\) appears to be the first to report a quantitative study of this system. In their experiments, an agitated aqueous solution of nitrous acid was contacted with nitric oxide gas. The stoichiometry was found to follow

\[
3\text{HNO}_2 \rightarrow \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O} \quad (1)
\]

Since this work, several attempts\(^8,11,12,14 \) were made to examine the validity of Eq. (1). When a solution of nitrous acid was contacted with a stream of nitrogen\(^11,15 \), the molar ratio of nitric acid produced to nitrous acid decomposed varied from one third to about 0.16, depending on experimental conditions. In an attempt to determine the gas phase composition\(^8,14 \), it was found that the molar ratio of \( \text{NO}_3 \) to \( \text{NO} \) varies between zero and unity. These results indicate that the reaction shown by Eq. (2) takes place as well as Eq. (1).

\[
2\text{HNO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \quad (2)
\]

While the dependencies of the stoichiometry on the operating conditions were often noticed, the stoichiometry lies between Eqs. (1) and (2).

Abel et al.\(^1 \) gave a quantitative expression for the rate of depletion in relation to a proposed mechanism of

\[
4\text{HNO}_2 \xrightarrow{k_6} 2\text{NO} + \text{N}_2\text{O}_4 + \text{H}_2\text{O} \quad (3)
\]

\[
\text{N}_2\text{O}_4 + \text{H}_2\text{O} \xrightarrow{k_5} \text{HNO}_3 + \text{HNO}_8 \quad (4)
\]

Assuming that Eq. (4) is rate-determining, the rate was given by

\[
r_{\text{HNO}_2} = k_3 [\text{HNO}_3]^4 [\text{NO}]^6 \quad (5)
\]

which agreed with their experimental results. On the contrary, many experiments showed that the rates are proportional to nitrous acid concentration in the first order or in the order slightly greater than unity\(^7-9,11-15 \). Also, it was generally noticed that the rate increases with agitation speed of the solution, gaseous flow rate or gas-liquid contacting area. It is indicated that mass transfer resistances...
# Mass transfer properties

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## Experiments

### 1. Apparatus and procedure

Experimental equipment is schematically shown in Fig. 1. One of the two gas-liquid contactors was employed (Fig. 2). The bubbling contactor was equipped with one or three fritted-glass balls through which helium was bubbled. Liquid-side volumetric coefficients of mass transfer depended on the gaseous flow rate and the coarseness and number of the fritted-glass balls. In these measurements, sodium nitrate was added to the solution to reduce the difference of its ionic properties from those in the experiments with nitrous acid. The determination of gas-side coefficients was not attempted.

The flat surface contactor was a Pyrex cylinder equipped with a cone at the center of the liquid surface to keep it flat. The gas and liquid phases were independently agitated. The liquid side mass transfer coefficients were almost independent of the agitation speed in both phases. The gas-side coefficients were not dependent on the gaseous flow rate but rather on the agitation speed. The mass transfer characteristics for these contactors are summarized in Table 1.

In preparation for a run, helium was introduced through the equipment. The run was started by adding a sulfuric acid solution to the sodium nitrite solution in the contactor to instantaneously generate nitrous acid. The nitrous acid concentration was measured by continuously withdrawing a small stream from the contactor and pumping it through an ultraviolet photometer of 1, 10 or 100 mm optical path length, operating at 372 μ. The flow was returned to the contactor from the photometer. The nitric acid concentration was measured occasionally by the photometer at 303 μ. The nitric oxide concentration in the exit gas stream was measured periodically by gas chromatography.

### 1.2 Bubbling contactor results

Figure 3 shows the data of nitrous acid concentration decay for which initial concentrations were altered for constant mass transfer coefficient, \(k_{La}\). These measurements were repeated for different mass trans-
The depletion rates of nitrous acid were obtained by graphically differentiating the concentration decay curves. Figure 4 shows that the rate is proportional to the nitrous acid concentration in the order of 1.33 and strongly dependent on $k_{L\alpha}$. The rate data at a constant concentration of HNO$_2$ were plotted against $k_{L\alpha}$ in Fig. 5, which shows that the rate is proportional to ($k_{L\alpha}$)$.^2$. It is also shown that the rate at constant concentration is dependent solely on $k_{L\alpha}$, because bubble size, gas-phase holdup and gas flow rate were independently altered in those measurements.

Finally, the experimental rate expression for the depletion of HNO$_2$ was established.

$$r_{\text{HNO}_2} = k (k_{L\alpha})^{2/3} [\text{HNO}_2]^{4/3} \quad (6)$$

The values of $k$ at 25 and 15°C are

- $2.39 \times 10^{-3}$ (sec-mol/l)$^{-1/3}$, (25°C)
- $1.45 \times 10^{-3}$ (sec-mol/l)$^{-1/3}$, (15°C)

* Concentrations are in mol/l unit.

The solid lines in Fig. 3 were predicted from Eq. (6). The evolution rates of NO into the gas phase were about two third of the depletion rate of HNO$_2$ (Fig. 6). This and the ratios of nitric acid formation and nitrous acid depletion (Table 2) show that the stoichiometry follows Eq. (1).

### Flat surface contactor results

Figure 7 shows the data of HNO$_2$ concentration decay, for which the gaseous flow rates were altered for constant mass transfer resistances in both phases and a constant initial concentration of HNO$_2$. Similar data were taken for the initial concentrations of 0.01, 0.004, 0.001 and 0.0004 mol/l. The depletion rate of HNO$_2$ corresponding to its initial concentration was determined from the slope of each ln C vs. time curve.

$$a = \frac{(1/k_{L\alpha})}{(1/k_{a\alpha}) + (V_l/F)} \quad (7)$$

$a$ is the ratio of the mass transfer resistances for the gas and the liquid phases. For comparison with the bubbler results, the depletion rates of HNO$_2$ calculated from Eq. (6) are shown in those figures. The rates agree with Eq. (6) at small values of $a$, but increase remarkably with increasing $a$.

Some typical examples of the ratio of nitric acid formation to nitrous acid depletion are given in Table 3. At large values of $a$ the ratio becomes
smaller than 1/3, which Eq. (1) predicts. This indicates that the process represented by Eq. (2) takes place as well as does that shown by Eq. (1).

2. Analysis

Of the several oxides of nitrogen, NO, NO₂, N₂O₃ and N₂O₄ play important roles in reaction and transfer processes at around atmospheric pressure and temperature. The following reactions are important in the presence of water.

\[
2\text{HNO}_2 \xrightleftharpoons[k_1]{k_{-1}} \text{NO} + \text{NO}_2 + \text{H}_2\text{O} \quad (8)
\]

\[
2\text{NO}_2 \xrightarrow[k_2]{k_{-2}} \text{N}_2\text{O}_4 \quad (9)
\]

\[
\text{N}_2\text{O}_4 + \text{H}_2\text{O} \xrightarrow[k_3]{k_{-3}} \text{HNO}_2 + \text{HNO}_3 \quad (10)
\]

\[
\text{NO} + \text{NO}_2 \xrightarrow[k_4]{k_{-4}} \text{N}_2\text{O}_3 \quad (11)
\]

Due to the low concentrations of HNO₂, the reverse reaction of Eq. (10) is negligible in the present system.

2.1 Simplified model

First, an attempt was made to interpret the bubbling contactor results by supposing a model based upon the following assumptions.

1. Desorption of the components other than NO, from liquid to gas, can be neglected. This is valid when the stoichiometry follows Eq. (1), as in the present bubbler results.

2. The reactions in the liquid film can be neglected so that the transport rate of NO is given by \( k_l a \).

3. Equilibria represented by Eqs. (8), (9) and (11) are set up in bulk liquid.

4. Rates of accumulation of NO, NO₂, N₂O₃ and N₂O₄ in the bulk liquid can be neglected compared with depletion rate of HNO₂ (steady-state hypothesis).

Noting assumptions (1), (2) and (4), the depletion rate of HNO₂ can be related to the desorption rate of NO or to the formation rate of HNO₃ by

\[
r_{\text{HNO}_2} = 3 k_4 [\text{N}_2\text{O}_3] \quad (12)
\]

\[
r_{\text{HNO}_2} = \frac{3}{2} k_4 a [\text{NO}] - [\text{NO}_3] \quad (13)
\]

The third assumption gives

\[
[\text{NO}][\text{NO}_3]/[\text{HNO}_2]^3 = K_1 \quad (14)
\]

\[
[\text{N}_2\text{O}_3][\text{NO}_3]^2 = K_2 \quad (15)
\]

Combining Eqs. (12), (14) and (15) shows that \( r_{\text{HNO}_2} \) is related to \( [\text{HNO}_2] \) and \( [\text{NO}] \) by

\[
r_{\text{HNO}_2} = 3 k_4 K_1 [\text{HNO}_2]^3 [\text{NO}] \quad (16)
\]

The relation of \([\text{NO}]\) to \([\text{HNO}_2]\) depends on the experimental conditions. In the present bubbler experiments, \([\text{NO}]_s\) in Eq. (13) is negligibly small compared with \([\text{NO}]\) (Appendix 1). Then, combining Eqs. (13) and (16) gives

\[
[\text{NO}] = 4^{1/3} (k_4 K_1 a)^{1/3} [\text{HNO}_2]^{1/3} \quad (17)
\]

Substituting Eq. (17) into Eq. (16) gives

\[
r_{\text{HNO}_2} = (3/2)^{1/3} (k_4 K_1 a)^{1/3} [\text{HNO}_2]^{1/3} \quad (18)
\]

A result identical with the experiments (Eq. (6)) was obtained and their comparison gives

\[
V_a s = \left\{ \begin{array}{ll}
2.02 \times 10^{-8} & \text{mol} \cdot \text{sec} \quad (25\text{°C}) \\
4.50 \times 10^{-7} & \text{mol} \cdot \text{sec} \quad (15\text{°C})
\end{array} \right.
\]

According to the procedures shown in Appendix 2, the rate constant of the hydration of \( \text{N}_2\text{O}_4 \), \( k_s \) is determined as

\[
k_s = \left\{ \begin{array}{ll}
194 \text{ sec}^{-1} & \text{(25°C)} \\
82.8 \text{ sec}^{-1} & \text{(15°C)}
\end{array} \right.
\]

Abel et al.¹ obtained the rate expression of Eq. (21) as well as the stoichiometry of Eq. (1).

\[
r_{\text{HNO}_2} = 3.93 \times 10^{-6} [\text{HNO}_2]^3 [\text{NO}] \quad (21)
\]

It might be assumed that \([\text{NO}]\) is equal to \([\text{NO}_3]\), because in Eq. (13) \( r_{\text{HNO}_2} \) was relatively small due to
the considerable pressures of NO introduced in the gas phase, and \( k_L \alpha \) was large due to strong agitation of the solution. Then, comparing Eqs. (16) and (21) gives

\[
K_1^2 K_2 k_3 = 1.31 \times 10^{-6} \text{ l/mol·sec (25°C)}
\]  

(22)

The slightly smaller value than Eq. (19) probably comes from the fact that [NO] was actually a little larger than \([\text{NO}]_0\). It is noted that the two different experiments of ours and those of Abel et al., which give the same stoichiometry, have been interpreted by the same model. The different rate forms resulted from the different dependencies of [NO] on [HNO₂].

2.2 General model

The first assumption in the simplified model (NO alone desorbs) is not valid in the flat surface contactor experiments, because the stoichiometry differs from Eq. (1). When a liquid phase component desorbs into a well-mixed gas stream, the rate of desorption is given by Appendix 1 as

\[
r_{\text{des}} = \frac{\alpha}{H + \alpha} k_L \alpha C
\]

(23)

Supposing the simplified model, the concentration of each component may be given by Eq. (17) and

\[
[\text{NO}] = K[H\text{NO}_2]^p[\text{NO}]
\]

\[
= 4^{-1/3} k_3(K_2^2 K_3) \left( k_L \alpha \right)^{1/3} [\text{HNO}_2]^{2/3}
\]

(24)

\[
\]

\[
= 4^{-1/3} k_3^2(K_2 K_3)^{3/5} \left( k_L \alpha \right)^{2/3} [\text{HNO}_2]^{2/3}
\]

(25)

\[
[N_2\text{O}_3] = K_4[\text{N}_2\text{O}_3][\text{NO}] = K_1 K_4[H\text{NO}_2]^p
\]

(26)

The concentrations from these equations and the various constants listed in Appendix 2 were used to estimate the desorption rate of each component from Eq. (23). The results, as shown in Table 4, show that NO alone significantly desorbs at small values of \( \alpha \) and that desorption of HNO₂ becomes significant with increasing \( \alpha \). In Figs. 8 and 9, \( r_{\text{des}, \text{HNO}_2} \) calculated from Eq. (23) was added to Eq. (6). The curve fits the data points rather well at lower concentrations of HNO₂ (Fig. 8). For higher concentration (Fig. 9), the curve becomes significantly lower than the data points. This indicates the existence of another mechanism which results in the depletion of HNO₂.

So far, the reactions in the liquid film have been neglected by the second assumption. But the composition in the film, in particular near the liquid surface, may deviate from equilibrium due to the decrease in NO and NO₂ concentrations. Hence, the net reaction of Eq. (8) might take place to yield NO and NO₂. This effect can be taken into account by solving a set of differential equations representing the film processes as

\[
D \frac{d^2[H\text{NO}_2]}{dl^2} = 2k_3[H\text{NO}_2]^p - 2k_1[\text{NO}][\text{NO}_2] - k_3 K_1^2 K_2 [\text{NO}_2]^3
\]

(27)

\[
D \frac{d^2[\text{NO}] }{dl^2} = -k_1[\text{NO}]^2 - k_{-1}[\text{NO}][\text{NO}_2] + 2k_3 K_1^2 K_2 [\text{NO}_2]^3
\]

\[
D \frac{d^2[\text{HNO}_2]}{dl^2} = -k_3 K_2 K_3 [\text{NO}_2]^4
\]

(28)

\[
D \frac{d^2[\text{N}_2\text{O}_4]}{dl^2} = -k_2 K_1 [\text{N}_2\text{O}_4]^p + k_{-2}[\text{NO}][\text{NO}_2]
\]

\[
+ 2k_1 K_1 K_2 [\text{NO}_2]^3
\]

at \( l = 0 \)

\[
[\text{HNO}_2] = [\text{HNO}_2]_0, \quad [\text{NO}] = (2K_1 K_3 K_0 [\text{HNO}_2]^p / k_L \alpha)^{1/3}
\]

and \([\text{NO}_2] = K_4 [\text{HNO}_2]^p / [\text{NO}]_0\)

(29)

at \( l = L \)

\[
D \frac{d^2[\text{HNO}_2]}{dl^2} = -k_L \alpha [\text{HNO}_2]_s
\]

\[
D \frac{d^2[\text{NO}]}{dl^2} = -k_L \alpha [\text{NO}]_s
\]

\[
D \frac{d^2[\text{N}_2\text{O}_4]}{dl^2} = -k_L \alpha [\text{N}_2\text{O}_4]_s
\]

(30)

In writing these equations, \( N_2O_4 \) was assumed to be in equilibrium with \( NO_5 \). It was further assumed that the bulk liquid composition which specifies the boundary conditions at \( l = 0 \) is that previously calculated from the simplified model. The validity of these boundary conditions is examined later. Equations (27) to (31), with the boundary conditions, may be solved numerically to determine the concentration profiles. Since the transport of NO₃ and HNO₂ at \( l = 0 \) was found to be negligible, the overall depletion rate of HNO₂, \( r_{\text{HNO}_2,\text{ov}} \), was obtained according to

\[
r_{\text{HNO}_2,\text{ov}} = -\frac{3}{2} a D \frac{d^2[\text{NO}]}{dl^2} = -a D \frac{d^2[\text{N}_2\text{O}_4]}{dl^2}
\]

(32)

The predicted \( r_{\text{HNO}_2,\text{ov}} \) vs. \( \alpha \) curves can then be compared with the experimental points in Figs. 8 and 9 to establish the most appropriate value of \( k_1 \) which is solely unknown in Eqs. (27) to (31). The curves in Figs. 8 and 9 show that the general model fits the data well over the entire range of \( \alpha \) and \([\text{HNO}_2]_0\). The values of \( k_1 \) and \( k_{-1}(=k_3/K_1) \) corresponding to the curves are

\[
\{k_1 = 45.6 \text{ l/mol·sec (15°C)}
\]

\[
k_{-1} = 6.9 \times 10^8 \text{ l/mol·sec}
\]

(33)

The same procedures were repeated for the data at 25°C. The values of \( k_1 \) and \( k_{-1} \) were

\[
\{k_1 = 1.36 \times 10^8 \text{ l/mol·sec (25°C)}
\]

\[
k_{-1} = 1.12 \times 10^8 \text{ l/mol·sec (25°C)}
\]

(34)

Figure 10 and Table 5 show, respectively, examples of the concentration profiles in the film and the corre-
responding material balance of each component. The fluxes at \( l=0 \) show that the composition of the bulk liquid can be well approximated by the simplified model, because the fluxes of NO and HNO3 are negligibly small and the flux of NO is almost equal to \( k_L[NO] \). Hence, the boundary conditions of Eq. (30) can be applied. Also, since the flux of HNO3 at \( l=L \) is compared well with that calculated by \( \{a/(H+a)\} \times k_{La}[HNO3] \) (Eq. (23)), as shown in Table 5, Eq. (32) can be written in the approximate form

\[ r_{HNO3,o} = r_{\text{film}} + r_{\text{des}} \]  

(35)

\( r_{\text{film}}, \) represents 1.5\( k_{La}[NO] \), which can be evaluated according to Eq. (18) independently of \( \alpha \), and \( r_{\text{des}} \), is given by \( \{a/(H+a)\} \times k_{La}[HNO3] \). \( r_{\text{film}} \) represents the net reaction rate of Eq. (8) in the film to produce NO and NO2. The relative importance of these three contributions are shown by the solid lines in Figs. 8 and 9. At large values of \( \alpha \), the composition near the liquid surface significantly deviates from equilibrium. Hence, the contribution of \( r_{\text{film}} \) is important. With decreasing \( \alpha \), the composition approaches equilibrium even in the vicinity of the liquid surface, mainly due to the increased NO3 concentration. Hence, the contribution of \( r_{\text{film}} \) appears as well as that of \( r_{\text{des}} \). Under such conditions, the simplified model can be applied.

Since \( k_{La} \) in the bubbler experiments were not determined, \( \alpha \) cannot be calculated accurately. But it can be supposed that \( V_{Li}/F \) is much greater than \( 1/k_{La} \) in the experiments. The calculated approximate values of \( \alpha \) according to \( 1/(V_{Li}/F) \) were around unity. Hence, the simplified model can be applied.

The depletion rate data, such as shown in Figs. 8 and 9, were re-plotted as \( r_{HNO3,o} vs. [HNO3] \) for various values of \( \alpha \) as well as the predicted results (solid lines in Fig. 11). It is shown that the depletion rate dependency on \([HNO3]\) changes from the 4/3rd to the first order with increasing \( \alpha \). Hence, it is concluded that the previously reported rate dependencies ranging from first to fourth order might be caused by different operating conditions. Since nitric acid is not formed through nitrous acid depletion mechanism represented by \( r_{\text{des}} \) or \( r_{\text{film}} \), the stoichiometry of this whole process changes from Eq. (1) to Eq. (2) with increasing \( \alpha \). This also agrees with the experimental findings as shown in Table 3 as well as those found by other investigators.

### 3. Discussion

The validity of the steady state and equilibrium assumptions Of the four assumptions made in the simplified model, the first and second have been removed in the general model. The last assumption, of “steady state hypothesis”, is found to be a good approximation for the system, since the concentrations of NO, NO2, N2O4 as well as N2O3 are small with respect to that of HNO3 (Table 5). Also, Appendix 3 shows the third assumption of “equilibrium in the bulk liquid”, to be a good approximation. Role of N2O3 It may be possible that N2O3 is involved as an intermediate in Eq. (8). That is, instead of
Eq. (8), it may be
\[
2\text{HNO}_2 \xrightarrow{k_{-2}} \text{N}_2\text{O}_3 + \text{H}_2\text{O} \tag{36}
\]
\[
\text{N}_2\text{O}_3 \xrightarrow{k_{-4}} \text{NO} + \text{NO}_2 \tag{11}
\]
Even if this is the case, the processes proceeding in the bulk liquid phase are not affected since equilibria are set up there. But in the film processes represented by Eqs. (27)-(29), the rate constants of Eq. (8) are replaced by those of Eqs. (36) and (11). Two extreme cases with rate-controlling step might be considered. It is very unlikely that Eq. (36) is rate-controlling. For equilibrium is set up for Eq. (11) so that \( k_i \) needs to be still bigger than the previously calculated value of \( k_{-4} \) (6.9 \times 10^7 \text{l/mol} \cdot \text{sec})

Conclusion

The depletion of nitrous acid is brought about by three different mechanisms: 1) simultaneous hydration of \( \text{N}_2\text{O}_4 \) and evolution of NO, both existing in equilibrium with \( \text{HNO}_2 \), 2) desorption of nitrous acid molecules and 3) decomposition of \( \text{HNO}_2 \) into NO and \( \text{NO}_2 \), occurring in the vicinity of the liquid surface. The most important parameter which governs the relative importance of each mechanism is the ratio of the mass transfer resistances, \( \alpha \), defined by Eq. (7). When \( \alpha \) is small, that is, when the gas-phase resistance is big, NO alone desorbs. The stoichiometry follows Eq. (1) and the rate follows Eq. (5) or (6), depending on the relation of \([\text{NO}]\) to \([\text{HNO}_2]\). When \( \alpha \) is large, the second mechanism is dominant. The nitric acid molecules which escape from the liquid are considered to rapidly decompose into NO and \( \text{NO}_2 \) because of dilution in the gas phase. Hence, the total stoichiometry follows Eq. (2) and the rate follows the first-order law. When \( \alpha \) is intermediate, each of the three mechanisms is important. Hence, the stoichiometry and the rate are transient.

This process has been studied extensively but the conclusion varied with the authors. This is because each author made experiments in limited conditions with respect to mass transfer characteristics.

The rate constants \( (k_iand k_{-i}) \) and the solubilities \( (\text{N}_2\text{O}_4 and \text{HNO}_2) \) have been established.

Appendix 1

Desorption of a liquid-phase component into a gas stream is considered. It is assumed that both gas and liquid phases are well-mixed and that the gas stream is originally free from the component. The rate at steady state may be expressed in three ways:
\[
r_{des} = \frac{F}{V_L} C_0 = -k_0 a \frac{dC}{dx} \tag{A-1}
\]
Noting that \( C_{GS} \) is equal to \( C_0/H \), \( C_0 \) may be written as
\[
C_0 = \frac{k_0 a}{k_{ad} + F/V_L} C_0 \tag{A-2}
\]
Substituting Eq. (A-2) into Eq. (A-1) gives
\[
r_{des} = k_0 a \frac{dC}{dx} \tag{A-3}
\]
The boundary conditions of Eq. (31) may be obtained from Eq. (A-3).

When diffusion is rapid with respect to reaction so that the concentration profile is linear, \( (-dC/dx)_S \) becomes \( C - C_S \). Then Eq. (A-3) gives
\[
C_S = \frac{1}{1 + \alpha (H + a) \cdot C} \tag{A-4}
\]
Equation (23) has been obtained.

In the bubbling experiments, the values of \( \alpha \) are around 1. Then, applying Eq. (A-4) to the concentration of NO shows that \([\text{NO}]_S \) is not greater than 0.04 \times [NO] in Eq. (13).

Appendix 2

Following quantities are known for the system including \( \text{NO}, \text{NO}_2, \text{N}_2\text{O}_4, \text{N}_2\text{O}_3, \text{HNO}_2 \) and \( \text{H}_2\text{O} \).

\begin{align*}
\text{<Equilibrium>} & \quad \text{<Solubility>} & \quad \text{<Others>}
\text{K}_{G1} & = \frac{[\text{NO}]_g[\text{NO}_2][\text{H}_2\text{O}]_g}{[\text{HNO}_2]_g^2} & H_{\text{NO}2} & \quad H_{\text{NO}2 \cdot \sqrt{D_{\text{NO}2} \cdot K_{G1}}} \tag{10}
\text{K}_{G1} & = \frac{[\text{NO}]_g[\text{NO}_2][\text{H}_2\text{O}]_g}{[\text{HNO}_3]_g^2} & H_{\text{NO}_3} & \quad k_5 K_2 K_6 \tag{this work}
\text{K}_{G2} & = \frac{[\text{N}_2\text{O}_4]_g}{[\text{NO}_2]_g H_{\text{NO}_2}} & \text{H}_2\text{O}_2 & \tag{9}
\text{K}_{G3} & = \frac{[\text{N}_2\text{O}_3]_g}{[\text{NO}_2]_g [\text{H}_2\text{O}]_g} & \text{H}_2\text{O} & \tag{8}
\text{K}_1 & = \frac{[\text{NO}]_g [\text{H}_2\text{O}]_g}{[\text{HNO}_2]_g^2} & \text{K}_1 = \frac{K_{G4}}{K_{G1} \cdot K_{G2}} \tag{10}
\end{align*}

(* \( a_w \) is the activity of water defined by the vapor pressure on the solution divided by that on pure water.)

\[
k_5 K_2 K_6 K_7 = k_5 H_{\text{NO}_2} H_{\text{NO}_4} K_6 K_2 \tag{A-6}
\]
Rearranging Eq. (A-6) gives
\[
k_5 H_{\text{NO}_2} = \frac{(k_5 K_2 K_6)}{H_{\text{NO}_2} K_6 K_2} \tag{A-7}
\]
Combining \( k_5 H_{\text{NO}_2} \) and \( \sqrt{k_5 H_{\text{NO}_4}} \) separates \( k_5 \) and \( H_{\text{NO}_2} \).

\[
K_{G3} = K_{G2} K_{G1} = \frac{[\text{NO}_2]_g [\text{H}_2\text{O}]_g}{[\text{HNO}_2]_g^2} \tag{A-8}
\]
Combining \( K_{G3} \) and \( K_3 \) yields
\[
H_{\text{NO}_3} = \frac{[\text{NO}_2]_g}{[\text{N}_2\text{O}_3]_g} = K_3 H_{\text{NO}_2} [\text{H}_2\text{O}]_g \tag{A-9}
\]

\[
K_1, K_2, K_3, K_4
\]

\begin{align*}
K_1 & = \frac{H_{\text{NO}_2} H_{\text{NO}_4} K_6}{(H_{\text{NO}_2})^2 [\text{H}_2\text{O}]_g} \tag{A-10}
K_2 & = \frac{H_{\text{NO}_2} K_{G2} K_6}{H_{\text{NO}_4}^2} \tag{A-11}
K_4 & = K_1/K_2 \tag{A-12}
\end{align*}
$k_1$ and $k_{-1}$

These have been determined in the present study.

The numerical results can be summarized as follows.

<table>
<thead>
<tr>
<th>Reaction rate</th>
<th>Solubility</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1 = 1.23 \times 10^{-3}$</td>
<td>$H_{NO} = 0.0473$</td>
<td>$k_1 = 136$</td>
</tr>
<tr>
<td>$K_2 = 8.73 \times 10^6$</td>
<td>$H_{NO_2} = 1$</td>
<td>$k_{-1} = 11.2 \times 10^6$</td>
</tr>
<tr>
<td>$K_3 = 6.04 \times 10^9$</td>
<td>$H_{NO_2} = 609$</td>
<td>$k_2 = 194$</td>
</tr>
<tr>
<td>$K_4 = 0.743$</td>
<td>$H_{NO_2} = 40.4$</td>
<td>$k_3 = 82.8\text{ (sec}^{-1})$</td>
</tr>
<tr>
<td>$K_5 = 0.743$</td>
<td>$H_{NO_2} = 58.5$</td>
<td>$k_4 = 907$</td>
</tr>
<tr>
<td>$K_6 = 2500$</td>
<td>$H_{NO_2} = 2500$</td>
<td>$k_5 = 2500$</td>
</tr>
</tbody>
</table>

(* extrapolated from the value at 25°C assuming the same temperature dependency as NO.)

The upper and the lower values refer respectively to 25 and 15°C.

Appendix 3

Since it has been shown that the steady state assumption is a good approximation, the material balance equations in the bulk liquid phase may be written as

$$d[N_2O_4]/dt = k_1 [NO][NO_2] - k_{-1} [N_2O_3]$$

$$d[N_2O_3]/dt = k_2 [NO_2] - k_3 [N_2O_4]$$

$$d[N_2O_2]/dt = k_4 [NO] + k_5 [N_2O]$$

The last terms in Eqs. (A-15) and (A-16) have been incorporated to account approximately for the bulk-to-film diffusion. The diffusion rate of NO is given by $k_4 [NO]$ and the rate of NO is negligible. Since $k_2$ is ordinarily much smaller than $k_3$ ($\sim 100 \text{ sec}^{-1}$), Eq. (A-15) becomes

$$[N_2O_4] = k_2 \left( k_{-1} + k_3 \right) [N_2O_3]^2$$

It is likely that the dissociation of $N_2O_3$ ($k_{-2}$) is more rapid than its hydration ($k_2$). $N_2O_3$ may be in equilibrium with NO and NO$_2$. Similarly, $N_2O_2$ may be in equilibrium with NO and NO$_2$. Substituting $[N_2O_2] = k_2 [N_2O_4]$ into Eq. (A-14) gives

$$k_1 [HNO_2]^3 = k_{-2} [NO][NO_2]^2$$

The equilibrium between HNO$_2$, NO and NO$_2$ is set up under the condition of

$$k_{-2} [NO] > 2k_2 [KNO_4]$$

Substituting [NO] and [N$_2$O$_4$] (Eqs. (17) and (24)) yields

$$[HNO_2]^3/k [NO] > (2k_2/k_1)^{1/3}$$

The minimum value for the left side in the present experiments is $5.6 \times 10^{-8}$. Hence, the condition for equilibrium is satisfied.

Nomenclature

- $A$ = concentration of a component A in liquid (Subscript G refers to that in gas. Subscripts 0 and S refer respectively to bulk liquid and liquid surface. Subscript f refers to the start of an experimental run.) [mol/l]
- $a$ = gas-liquid interfacial area per unit volume of liquid [cm$^{-2}$]
- $C$ = concentration of an arbitrary substance in liquid (Subscripts G and S refer respectively to gas and surface.) [mol/l]
- $D$ = diffusion coefficient [cm$^2$/sec]
- $F$ = volumetric flow rate of gas [cm$^3$/sec]
- $H$ = gas-liquid absorption equilibrium constant defined by $[A] = H[A]_0$ [l/mol]
- $K$ = equilibrium constants. (Subscript G refers to gas phase. $K_1$ is defined by Eq. (5). $K_2$, $K_3$, $K_4$ and $K_5$ are defined by Eqs. (9), (11), (38) and (3), respectively.) [sec$^{-1}$]
- $k$ = reaction rate constant defined by Eq. (6) [l/mol$^{1/2}$sec$^{-1/3}$]
- $k_1$ = second order reaction rate constant defined by Eq. (6), $k_1$, $k_2$ and $k_3$ are those defined by Eqs. (9), (11) and (38) [mol/-sec]
- $k_2$ = first-order reaction rate constant defined by Eq. (10) [sec$^{-1}$]
- $k_3$ = fourth-order reaction rate constant defined by Eq. (3) [l$^2$/mol$^3$sec]
- $k_{-4}$ = rate constant of a reverse reaction corresponding to $k_4$
- $k_L$ = liquid-phase mass transfer coefficient ($k_L$ is that for gas phase.) [cm/sec]
- $L$ = thickness of liquid film [cm]
- $l$ = length measured from bulk-film interface toward liquid surface
- $r$ = rate per unit volume of liquid ($r_{gas}$ is defined by Eq. (23)) [mol/l-sec]
- $V_L$ = volume of liquid [cm$^3$]
- $x = l/L$ [--]
- $\alpha$ = ratio of mass transfer resistances in liquid and gas phases, Eq. (7) [--]

Literature Cited

9) Komuro, Y.: ibid., 74, 979 (1953).