Removal of Atomospheric Pollutants

(1)　Removal of NO by Aqueous Alkaline Solutions of KMnO$_4$*

Ichibei KUDO, Tatsuo SUZUKI, Naoyoshi MATSUHIRO
and Takashi KONDO
Eizo SADA and Hidihiro KUMAZAWA**

大気汚染物質除去に関する研究

(1)　KMnO$_4$ アルカリ水溶液による脱硝

工　藤　市兵衛　　鈴　木　達　夫　　松　広　尚　佳

近　藤　高　司　　佐　田　栄　三**　熊　沢　英　博**

The absorption of NO in aqueous solutions of KMnO$_4$ and aqueous mixed solutions of KMnO$_4$ and NaOH was carried out using a batch stirred vessel with a plain gas-liquid interface. The rate of absorption was discussed under the fast-reaction regime. The reaction between NO and aqueous solutions of KMnO$_4$ was found to be first order with respect to NO and first order with respect to KMnO$_4$. The reaction rate constants calculated were given as a function of NaOH concentration.

The removals of sulfur dioxide and nitrogen oxides from exhaust gas as the main pollutants in air have been strongly required in recent years. It is no exaggeration to say that the technical system for the elimination of sulfur dioxide has been almost established. On the other hand, for the removal of nitrogen oxides, several process systems such as dry and wet processes are developed and discussed on the fundamental characteristics, but satisfactory achievement has not yet been obtained in every process. For the time being it is urgent to clarify the physico-chemical mechanism of the removal of nitrogen oxide and to establish its technical system.　Main nitrogen oxides to be removed are considered to be NO and NO$_2$, but the greater part of NO$_X$ generated from combustion processes is NO.

This makes the removal of NO more important. In the removal processes by the use of absorption, furthermore, the solubility of NO in absorbent is much smaller than that of NO_2, which involves great difficulties in the removal of NO. Thus, various absorbents and absorption syatems to remove NO have been presented and some of them are in the improvement stage for practical application. However, the degree of elimination of NO has been considered as a target of intensive investigations. In the present work, the process of simultaneous absorption and oxidation of NO in aqueous solutions of $KMnO_4$ and mixed aqueous solutions of $KMnO_4$ and NaOH was discussed on the standpoint of absorpsion with reaction.

The relevant poblem to be considered here is a process of the gas absorption in which a dissolved gas A reacts with a nonvolatile reactant B in the liquid phase according to the scheme of $A + \nu B \rightarrow$ Products. When it is assumed that the reaction is n-th order with respect to gaseous reactant A and m-th order with respect to liquid reactant B, the gas absorption rate can be expressed by

$$N_A = \sqrt{(2/(n+1)) k C_{B0}^m C_{Ai}^{n+1} D_A} \tag{1}$$

Equation (1) is based on the film theory and clearly valid for $\phi > 3$ and $\sqrt{M} \ll q_B$. If the values of both C_{Ai} and D_A are estimated, then the reaction rate constant k as well as the orders of reaction, n and m, can be determined from the experimental relations of absorption rate N_A to the gas-phase composition of A, that is, C_{Ai} and to the concentration of liquid reactant B, C_{B0}.

In this paper, absorption of NO into aqueous solutions of above-stated oxidizing agent was performed by using a batch stirred vessel with a plain gas-liquid interface. The absorption rates under the fast-reaction regime were analysed by Eq. (1) and the reaction rate expression was given.

EXPERIMENTAL

All experimental runs were made using a batch stirred tank absorber with a plain gas-liquid interface (Liquid content = 200cc, Gas phase volume = 850cc). The stirred vessel and the impellers in gas and liquid phases were sketched in Fig. 1. The liquid-phase stirrer was a disk turbine impeller with eight flat blades, and was mounted at half of the liquid depth. The gas-phase stirrer was an identical impeller with six flat blades, and placed close to a free liquid surface in the gas phase. Both gas and liquid stirrers were driven by the same shaft. Temperature of the absorber was maintained at 25℃ in the water bath. Solute gas NO was diluted by N_2, saturated with water vapor and fed into the absorber. Liquid absorbent as an ox'dizing agent was aqueo soltions of $KMnO_4$ and aqueous mixed solutions of $KMnO_4$ and NaOH. The concentrations of $KMnO_4$ and NaOH in the absorbent ranged from 0 089 to 0.243 mol/ℓ and from 0.50 to 2.50 mol/ℓ, respectively. The concentration of NO in the feed gas ranged from 1.5 to 20 vol.%.
The composition of NO in the gas phase into and from the absorber was determined by gas chromatography (column packing: molecular sieve 13X) and partially utilized for the calculation of NO absorption rate. For every absorption run, there were several minutes during which the absorption rate was essentially a constant. The initial rate of NO absorption into
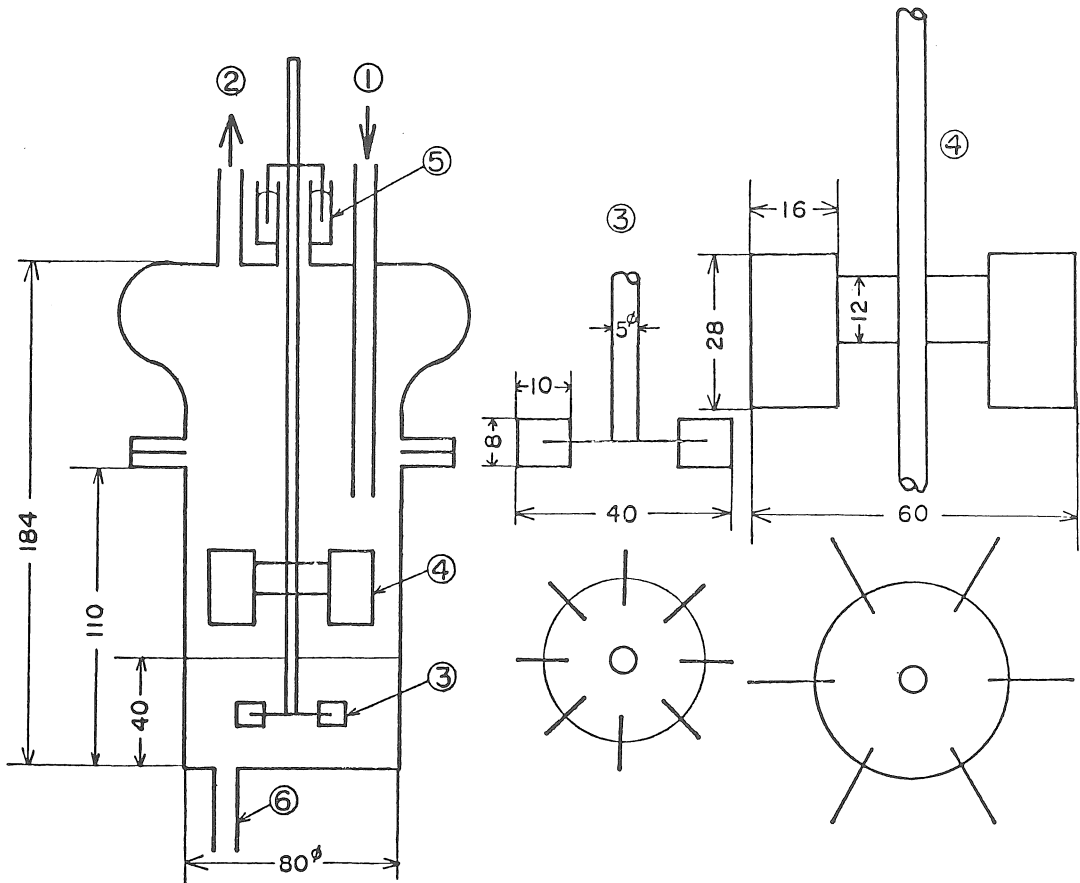
Fig. 1. Stirred vessel and impellers.
① gas inlet ② gas outlet ③ liquid phase stirrer ④ gas phase stirrer ⑤ mercury seal ⑥ drain

each batch of absorbeut was volumetrically determined by using a soap film meter and was taken to be the absorption rate under a pseudo-steady state.   Through all runs absorbent content was maintained 200cc and agitator impeller speed was 130 rpm.

In order to compare experimental results for chemical absorption with the theoretical solutions on the basis of film model, the liquid-side mass transfer coefficient under physical conditions which is included in enhancement factor and modulus $\sqrt{M}$ is required. Then, the physical absorption of pure CO$_2$ in to water was preliminarily performed with the same equipment. Agitator impeller speed was varied from 60 to 200 rpm. Absorption rates were determined with a soap film meter as well.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental results for physical absorption of pure CO$_2$ into water at 25℃ were shown in Fig. 2   as a plot of liquid-side mass transfer coefficient k_L^o vs. impeller speed n. From a series of measurements in the range of impeller speed 60 to 160 rpm, it is found that k_L^o is proportional to impeller speed to the power of 0.75.   This dependency is in close agreement with that obtained by previous investigators.   The liquid-side mass transfer coefficient of NO, k_{LA}^o was predicted by

$$k_{LA}^o = k_{LCO_2-H_2O}^o \, (D_A / D_{CO_2-H_2O})^{2/3} \qquad (2)$$

and used in the calculations of enhancement factor ϕ and diffusion-reaction modulus $\sqrt{M}$.

Absorption of NO in aqueous solutions of $KMnO_4$

　　Experimental results were shown in Fig. 3 as a plot of N_A vs. C_{Ai}. According to previous investigation [1] the reaction of NO with neutral aqueous solutions of $KMnO_4$ can be expressed by

$$NO + MnO_4 = NO_3 + MnO_2 \tag{3}$$

In practice the reaction product, MnO_2 was observed on a free liquid surface, and the rate of NO absorption was considerably decreased. Thus the absorption rate for each run was taken before manganese peroxide appeared on the liquid surface.

　　The value of concentration of A at gas-liquid interface, that is, physical solubility of gas A, was estimated from [2]

$$\log (C_{Ai}/C_W) = -KC_{B0} \tag{4}$$
$$K = x_g + x_a + x_c$$

where K is a constant which depends on the ions and gas present and x refers to the contribution of various species. Here the value of x_g was estimated from observed solubilities of NO in aqueous solutions of NaCl and LiCl by Armor [3]. ($x_g = -0.1825$) The value of x_a was not found in any previous paper. Then the value of x_a for MnO_4 was determined to be $x_a = 0.3321$ by measuring the solubility of N_2O in aqueous solutions of $KMnO_4$ with the same apparatus as Onda et al. [2]. The value of x_c was taken to be $x_c = -0.0362$ from the measurement by Onda et al. [3]. The values for the diffusivities of NO in various solutions were evaluated by assuming the relationship $D\mu^{0.85} =$ constant at a constant temperature [4]. When Eq. (1)

Fig. 2. Liquid-side mass transfer coefficient of CO_2 into water at 25℃.
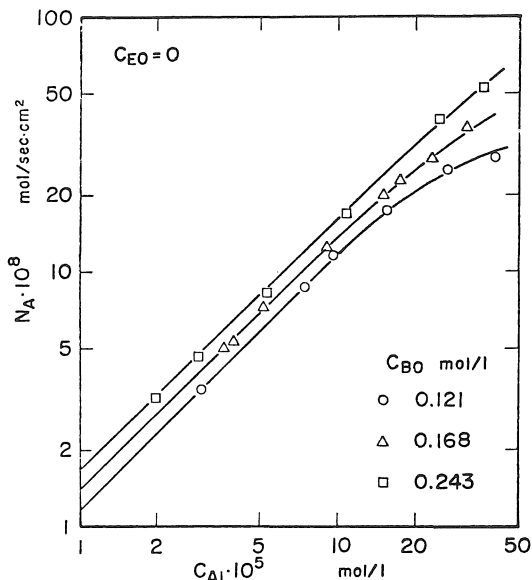
Fig. 3. N_A vs. C_{Ai} as a parameter of C_{B0} for $C_{E0} = 0$.

holds, the relationship between log N_A and log C_{Ai} must give a straight line. The slope of the line, $(n+1)/2$, enables one to decide the order of reaction, n, with respect to gas species. In Fig. 3, a linear relationship is obtained for $C_{Ai} < 10^{-4}$ mol/l, and hence basic assumptions that ϕ is greater than 3 and modulus $\sqrt{M}$ is much smaller than q_B are considered to be justified. Slopes of linear portions of these lines give the order of reaction, n, as 1. As C_{Ai} increases, the relationship deviates from the straight line because
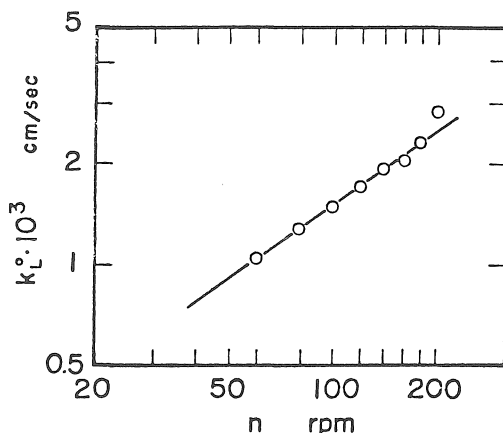
some depletion of the liquid reactant has taken in the vicinity of the interface. The relationships between N_A and C_{B0} for $C_{Ai}=2 \cdot 10^{-5}$ and $5 \cdot 10^{-5}$ mol/1, which are obtained by interpolating experimental values, give essentially straight lines as shown in Fig. 4. The linearity is attributed to the fact that there is not very much change in diffusivity of A, D_A, within the range of the investigated concentration of B. The slopes of these straight lines give $m=1$.

Thus, the rate of chemical reaction between NO and an aqueous solution of KMnO₄ can be expressed in terms of 1st-order with respect to NO and 1st-order with respect to KMnO₄. Equation (1) in this case reduces to

$$N_A = \sqrt{kC_{B0}D_A}\ C_{Ai} \qquad (5)$$

Averaged value of reaction rate constant, k, is determined $7.00 \cdot 10^5$ 1/mol·sec from experimental points falling on linear portions of lines in Fig. 2.

Figure 5 shows observed relations of ϕ vs. $\sqrt{M}$. A basic assumption of $\phi=\sqrt{M}$ is found to be essentially valid when $C_{B0}>0.1$ mol/ℓ and the concentration of A at the gas-liquid interface is low.

Absorption of NO in aqueous mixed solutions of KMnO₄ and NaOH

Representative results for absorption of NO into aqueous mixed solutions of KMnO₄ and NaOH are given in Figs. 6 and 7 as a plot of N_A vs. C_{Ai}. The reaction between NO and KMnO₄ in an aqueous strong alkaline solution is considered to be

$$NO+MnO_4^- +2OH^- = NO_2^- +MnO_2^- +H_2O \qquad (6)$$
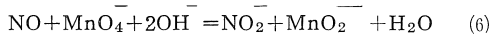
and, on the other hand, the corresponding reaction in an aqueous weak alkaline solution can be expressed by

$$NO_2^- +2MnO_4^- +2OH^- = NO_3^- +2MnO_4^{--} +H_2O \qquad (7)$$

$$3NO_2^- +MnO_4^- +H_2O = 3NO_3^- +2MnO_2 +2OH^- \qquad (8)$$
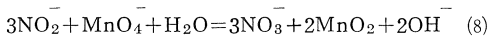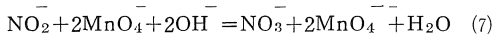
as well as reaction (6) as reported by Obuchi et al. [1]. There was no floating materials such as the reaction product, MnO₂, observed
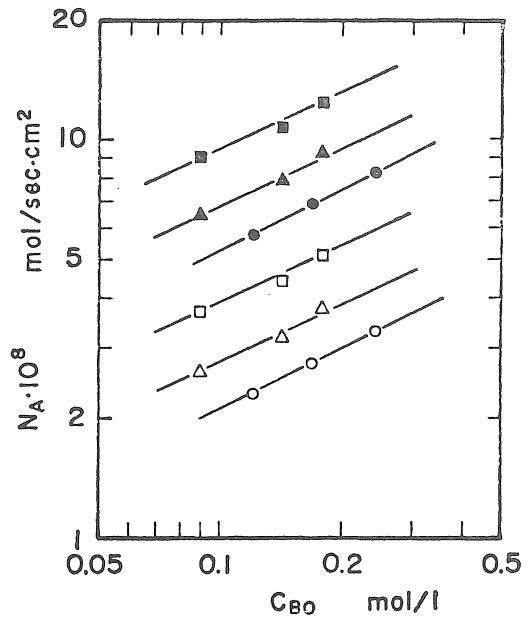

Fig. 4. N_A vs. C_{B0} as a parameter of C_{Ai} for $C_{E0}=0$, 1.0 and 2.5 mol/1.
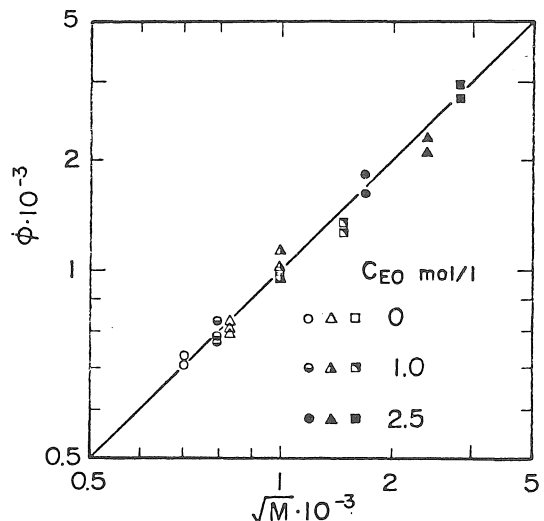
Fig. 5. ϕ vs. $\sqrt{M}$ for $C_{E0}=0$, 1.0 and 2.5 mol/1.

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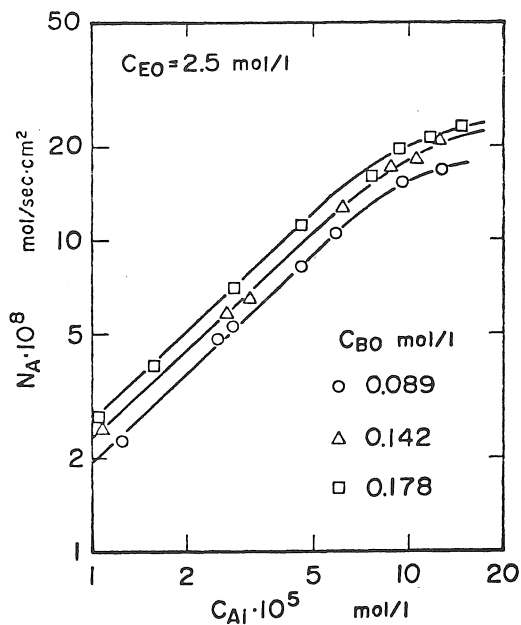
Fig. 6. N_A vs. C_{Ai} for $C_{E0}=2.5$ mol/1.
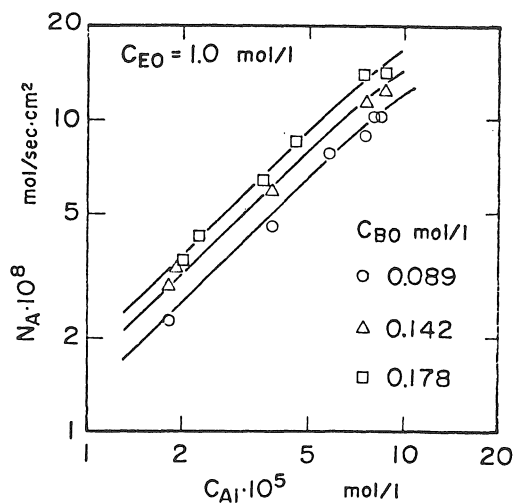
Fig. 7. N_A vs. C_{Ai} for $C_{E0}=1.0$ mol/1.

during a series of present experiments. The values of C_{Ai} on the abscissa of Figs. 6 and 7 were estimated using a correlation of solubility of gases in aqueous solutions of mixed salts presented by Onda et al. [5]. The slopes of these lines allow one to predict $n=1$. The relationships between log N_A and log C_{Bo} for $C_{Ai}=2\cdot10^{-5}$ and $5\cdot10^{-5}$ mol/ℓ also give essentially straight lines with the slope of $1/2$, which are shown as triangular and square points in Fig. 4, respectively. The linearity is partially attributed to the fact that the value of D_A is apparently controlled by NaOH concentration in absorbent and is almost independent of $KMnO_4$ concentration. So the order of reaction with respect to $KMnO_4$, m, can be determined as $m=1$. Thus, the rate of chemical reaction of NO with aqueous alkaline solutions of $KMnO_4$ can be expressed in terms of 1st-order with respect to $KMnO_4$. Averaged values of reaction rate constants can be determined from xperimental points falling on the linear portions of lines in Figs. 6 and 7, and plotted as a function of NaOH concentration, C_{E0}, in Fig. 8. In order to show that a basic assumption, $\phi=\sqrt{\overline{M}}$, is

signnificantly justified, typical examples of the relations of ϕ vs. $\sqrt{\overline{M}}$ were plotted in Fig. 5. Figure 8 shows that the reaction rate constant, k, increases with an increase in alkaline concentration and hence the absorpt-ion rate can be enhanced. However, the values of C_{Ai} and D_A are decreased by increasing alkaline concentration. That is, the decreases in C_{Ai} and D_A with an increase in alkaline concentration exert a negative effect on the rate of NO absorption. Therefore, the increase in alkaline concentration does not
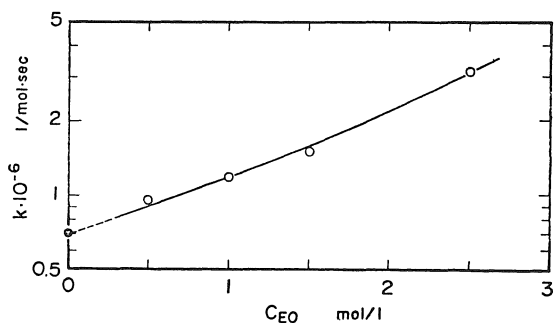

Fig. 8. Effect of NaOH concentration on reaction rate constant.

always enhance the absorption rate when it is compared with each other with keeping partial pressure of NO in gas phase constant.

CONCLUSION

The absorption rate of NO in aqueous solutions of KMnO₄ and aqueous mixed solutions of KMnO₄ and NaOH was performed with a batch stirred vessel with a plain gas–liquid interface. The rate of NO absorption was discussed under the fast-reaction regime. It was found that the reaction between NO and aqueous solutions of KMnO₄ can be expressed in terms of the first-order with respect to NO and the first order with respect to KMnO₄. The rate constants of second-order reaction as a function of NaOH concentration in liquid phase were obtained as in Fig. 8.

NOTATION

C   concentration in liquid phase. mol/ℓ

C_W solubility of NO in water, mol/ℓ

D   diffusivity in liquid phase, cm^2/sec

K   salting-out parameter

k   rate constant of (n, m) -th order reaction, l^{m+n-1}/mol^{m+n-1}. sec

k_L liquid-side mass transfer coefficient, cm/sec

M $= \dfrac{2}{n+1} k C_{Bo}^m \, C_{Ai}^{n-1} D_A / (k_{LA}^o)^2$

m, n   order of reaction

q_B $= C_{Bo}/\nu C_{Ai}$

x_g, x_a, x_c contributions of gas, anion and cation to K, respectively

Greek symbols

ϕ enhancement factor

ν stoichiometric coefficient $(A + \nu B \rightarrow Products)$

Subscripts

A   dissolved gas A (NO)

B   liquid reactant B (KMnO₄)

E   liquid reactant E (NaOH)

i   gas-liquid interface

0   initial value

Supercript

o   without reaction

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