The Study on Mass Transfer Mechanism for
PbO$_2$-SO$_2$ Reaction System

Yoshishige HAYASHI

ABSTRACT

To estimate precisely an average SO$_2$ concentration in the atmosphere with the lead peroxide method, the actual kinetic expression for SO$_2$-PbO$_2$ reaction system are investigated by regarding the reaction system as a non-catalytic reaction of solid particle with surrounding gas. The reaction models used are progressve-conversion model and unreacted-core model. The experimental research to examine the effect of the atmospheric conditions such as wind velocity, humidity, solute gas concentration, and temperature on the reaction has been performed with the cylindrical PbO$_2$ pellet. The values for the gas film mass transfer coefficient, the effective diffusivity in porous solid, and reaction rate constant are estimated according to the reaction model and experimental data and the rate controlling resistance for the actual kinetic is discussed on the basis of various properties estimated.

Key words: PbO$_2$ method, Reaction mechanism, Unreacted-core-model, Effect of Atmospheric conditions, PbO$_2$-SO$_2$ reaction system.

Introduction

The lead peroxide method[1] for measuring an average pollution by SO$_2$ concentration in the atmosphere has been used in many municipal corporations. This method is inexpensive and convenient to observe the degree of air pullution by sulfur dioxide. The estimated values, however, are not precise due to the environmental conditions[2,3,4] and gaseous substances[5,6,7] coexisting with SO$_2$ such as nitrogen oxide, hydrocarbons.

Although a complete understanding of the reaction mechanism is not necessary for the measurement of SO$_2$ pollution, an understanding of the relative contribution of physical diffusion and of chemical reaction to the overall mass transfer rate is important for a precise estimation of SO$_2$ concentration by this method.

In this study, the basic research on the measurement of the sulfur dioxide with the lead peroxide method was made to obtain the actual kinetic expression for PbO$_2$-SO$_2$ by regarding the mechanism of the reaction system as the mass transfer problem for gas-solid one. The PbO$_2$-SO$_2$ reaction system can be regarded as a noncatalytic reaction of solid particle with the surrounding gas and the chemical reaction is considered to consist of the following steps because no gaseous products are formed and the reaction is irreversible.

1) Diffusion of the gaseous reactant across the gas film surrounding the solid.
2) Diffusion of the gaseous reactant through porous solid layer.
3) Adsorption and desorption of the gaseous reactant at the solid reactant surface.
4) Chemical reaction with the solid surface.

Under the processes described above, the basic equations were derived. As the lead peroxide is a strong oxidizing agent, the gaseous reactant reacts with the solid reactant as soon as both come in contact with and it is assumed that step (3) does not contribute directly to the resistance to reaction. That is, there is no need to considere the application of Langmuir's adsorption isotherm. The processes considered in this study were step (1), (2), and (4).

The reaction model used were two simple idealized models; the progressive-conversion model[8,9] and unreacted-core model[8,10] according to the transfer mechanism in the solid particle.

The experiment was carried out under the

Department of Chemical Engineering, Kanazawa University, 2-40-20 Kodatsuno Kanazawa, 920 Japan

conditions of 20∼1500 ppm (v/v) SO_2-N_2 gas mixture with the cylindrical PbO_2 pellet. The ends of the cylinders were sealed, so that the pellets behaved as infinite cylinders and in addition, the degree of the change of the values for k_f, $\mathcal{D}_{eA}$ and k_s estimated by the reaction models were discussed under the various physical conditions corresponding to meteorology such as wind velocity, humidity, and temperature.

1. Theoretical analysis

Lead peroxide-sulfur dioxide reaction may be represented by the following scheme;

$$aA \ (gas)+B \ (solid) \longrightarrow S \ (solid) \qquad (1)$$
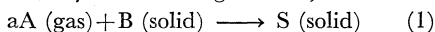
Now, let us consider about the reaction mechanism. As is mentioned above, step (1), (2), and (4) were examined. When two steps (2) and (4) are considered to be series resistances, it is an unreacted-core model and when these resistances are in parallel, it is a progressive-conversion model. In this case, step (1) is a common resistance in both models. Resistances of the different steps usually vary from each other and in the treatment of the actual kinetic, one of the steps is considered as rate controlling. It is, then, important to know which step controls in a given situation. The theoretical discussion to estimate the kinetics was performed by the use of simple geometrical shapes such as infinite cylinders or long cylinders.

To reduce the complexity of the theoretical representation, certain assumptions were made as follows;

1) The reaction system is isothermal and heat transfer due to the heat of reaction is negligible.*

2) Void in the solid is uniform and does not change throughout the reaction.

3) The gaseous reactant diffuses through the porous solid centripetally.

4) The size of solid is unchanging and the gas film mass transfer coefficient, effective diffusivity of gas within the solid, and rate constant are kept constant for all times.

1-1 Unreacted-core model[8, 10]

Figure 1 shows a schematic diagram of concentration profile for the unreacted-core model. The mass balance over a small element of volume in a reactant solid $2\pi r dr L$ is

$$\frac{\partial C_A}{\partial t} = \mathcal{D}_{eA} \frac{1}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C_A}{\partial r}\right) \quad (r_c < r < R) \qquad (2)$$
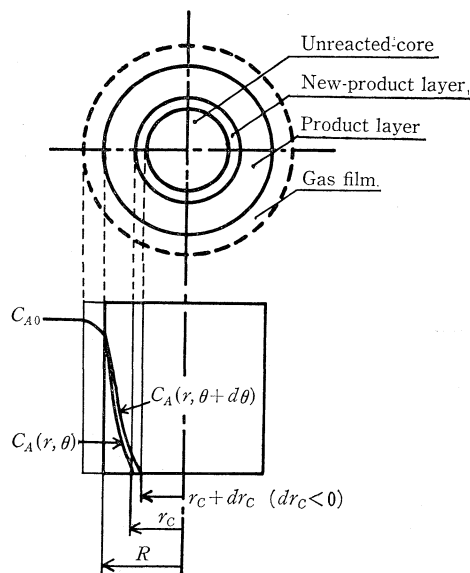

Fig. 1. Schematic diagram of concentration profile for the unreacted-core model

The boundary conditions for a cylindrical pellet are:

at the pellet surface R,

$$k_f(C_{A0}-C_A) = \mathcal{D}_{eA} \frac{\partial C_A}{\partial r}\bigg|_R \qquad (3)$$

at the moving interface r_c,

$$\mathcal{D}_{eA} \frac{\partial C_A}{\partial r}\bigg|_{r_c} = ak_s C_{s0} C_A \qquad (4)**$$

and

$$\mathcal{D}_{eA} \frac{\partial C_A}{\partial r}\bigg|_{r_c} = -aC_{s0} \frac{dr_c}{dt} \qquad (5)$$

and initial conditions are

$$\text{at } t=0, \quad C_A=0 \quad \text{and} \quad r_c=R \qquad (6)$$

For most of solid-gas reaction systems, the psudo-steady approximation is valid except for systems with extremely high pressure and very low solid reactant concentration.[10] These conditions are satisfied in the PbO_2-SO_2 reaction system in the atmosphere and this approximation is reasonably accurate.

Rearrangement of Eq. (2) by the use of the pseudo-steady state approximation gives

$$\frac{\partial}{\partial r}\left(r \frac{\partial C_A}{\partial r}\right)=0 \quad (r_c < r < R) \qquad (7)$$

Eq. (7) is solved with boundary conditions given by Eqs. (3) and (4), and the concentration profile of A is represented by

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* In this reaction, the heat of reaction is 895 J·mol⁻¹ and the maximum amount of product is about 10⁻⁴ mol.

** It is assumed that the rate of reaction is a linear function with respect to both the gas and the solid, and all of the gaseous reactant across the reaction interface reacts with solid.

$$\frac{C_A}{C_{A0}}=\frac{\ln(r/r_c)+(\mathscr{D}_{eA}/ak_sC_{S0}r_c)}{(\mathscr{D}_{eA}/k_fR)+\ln(R/r_c)+(\mathscr{D}_{eA}/ak_sC_{S0}r_c)} \tag{8}$$

and from Eqs. (5) and (8)

$$-\frac{dr_c}{dt}=\frac{C_{A0}}{aC_{S0}}\times$$

$$\frac{1}{(r_c/k_fR)+\{r_c\ln(R/r_c)/\mathscr{D}_{eA}\}+(1/ak_sC_{S0})} \tag{9}$$

While the fractional conversion in unreacted-core model is giveb ny

$$f=\frac{\pi R^2LC_{S0}-\pi r_c^2LC_{S0}}{\pi R^2LC_{S0}}=1-\left(\frac{r_c}{R}\right)^2 \tag{10}$$

and from Eqs. (9) and (10), overall reaction rate equation is

$$\frac{df}{dt}=\frac{2C_{A0}}{RaC_{S0}}\times$$

$$\frac{1}{(1/k_f)+\{R\ln(1-f)^{-1/2}/\mathscr{D}_{eA}\}+(1/ak_sC_{S0}\sqrt{1-f})} \tag{11}$$

The initial condition for Eq. (11) is as follows;

at $t=0$, $f=0$ (12)

and from Eqs. (11) and (12)

$$t=C_1f+C_2\{f+(1-f)\mathfrak{l}_n(1-f)\}+C_3(1-\sqrt{1-f}) \tag{13}$$

where

$$C_1=(RaC_{S0}/4C_{A0})\cdot(2/k_f) \tag{14}$$
$$C_1=(R^2aC_{S0}/4C_{A0})\cdot(1/\mathscr{D}_{eA}) \tag{15}$$
$$C_3=(R/C_{A0})\cdot(1/k_s) \tag{16}$$

In addition, the relationship between the total amount of products W and f is

$$W=\pi R^2LC_{S0}f \tag{17}$$

Now, let us discuss the resistance of this reaction by the use of following parameters;

$$P_1=1/k_f \tag{18}$$
$$P_2=\{R\ln(1-f)^{-1/2}/\mathscr{D}_{eA}\} \tag{19}$$
$$P_3=1/ak_sC_{S0}\sqrt{1-f} \tag{20}$$

When the resistance for chemical reaction is negligible, k_s approaches infinity and consequently P_3 tends to zero except for the complete conversion. On the other hand, when the reaction takes place only on the surface of pellet, the resistance of effective diffusivity of gaseous reactant does not need to be considered and further f is regarded as very small. It is, then, clear that $\mathscr{D}_{eA}\to\infty$ and $f\doteqdot0$, that is, P_2 tends to zero.

1-2 Progressive-conversion model[8,9]

1-2-1 Unsteady state solution with linear approximation

Figure 2 shows a schematic diagram of concentration profile for the progressive-conversion model. The material balance equation is

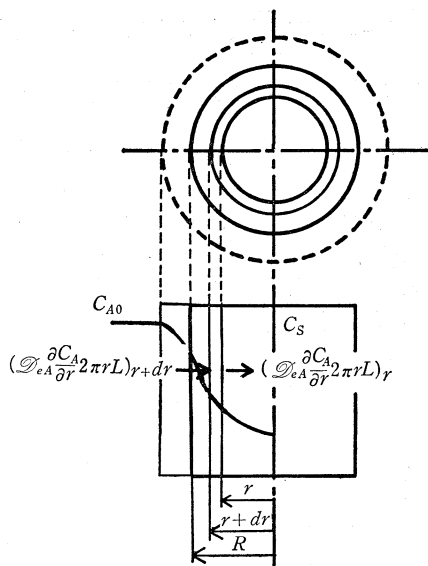

Fig. 2. Schematic diagram of concentration profile for the progressive-conversion model

$$\frac{\partial C_A}{\partial t}=\mathscr{D}_{eA}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_A}{\partial r}\right)-R_A \quad (0<r<R) \tag{21}$$

In general, the rate equation is not determined easily like as in homogeneous reaction as the pore structure within the solid is very complicated and moreover as the reaction system is in heterogeneous noncatalytic one. By considering the sufficiently thin cylindrical element in the solid, however, it is assumed that the molecule of gaseous reactant is moved about freely in its element and so the treatment like as in homogeneous reaction is able to be considered for the analysis of the reaction system discussed.

Now the reaction rate equation is assumed to be 2-molecular reaction with regard to gaseous and solid reactants and R_A in Eq. (21) is represented by

$$R_A=a(\partial C_A/\partial t)=ak_vC_A(C_{S0}-C_S) \tag{22}$$

The boundary and initial conditions are:

at $r=R$, $\quad k_f(C_{A0}-C_A)=\mathscr{D}_{eA}\dfrac{\partial C_A}{\partial r}\Big|_R$ (23)

at $r=0$, $\quad \dfrac{\partial C_A}{\partial r}=\dfrac{\partial C_S}{\partial r}=0$ (24)

at $t=0$, $\quad C_A=0$ and $C_S=0$ (25)

Applying the similar way of thinking proposed by Fujishige[9] to Eq. (22), one obtains

$$\partial C_S/\partial t=k_vC_{S0}C_A-k_vC_{A0}C_S \tag{26}$$

By using boundary conditions and initial condition; Eqs. (23) to (25), the solutions of the simultaneous partial differential equation; Eqs. (21), (26) are

$$C_A^* = 1 - 2\eta\delta \sum_{n=1}^{\infty} (A_n C_n / B_n) e^{-S_n t^*} \quad (27)$$

$$C_S^* = 1 - e^{-\zeta t^*} - 2\eta\zeta\delta \sum_{n=1}^{\infty} (A_n C_n / B_n)(e^{-S_n t^*} - e^{-\zeta t^*})$$
$$(28)$$

$$\left.\begin{array}{l} C_A^* = C_A / C_{A0}, \qquad C_S^* = C_S / C_{S0} \\ \eta = k_f R / \mathcal{D}_{eA}, \qquad \delta = C_{A0} / a C_{S0} \\ \zeta = R^2 k_v C_{A0} / \mathcal{D}_{eA}, \; t^* = \mathcal{D}_{eA} t / R^2 \\ r^* = r/R, \qquad A_n = \beta_n (\zeta - S_n)^2 \\ B_n = S_n (\beta_n^2 + \eta^2) \{(\zeta - S_n)^2 \delta + \zeta^2\} \\ C_n = J_0 (\beta_n r^*) / J_0 (\beta_n) \end{array}\right\} \quad (29)$$

where β_n is possitive root of the following equation;

$$\eta J_0 (\beta_n) - \beta_n J_1 (\beta_n) = 0 \quad (30)$$

and S_n is expressed by

$$S_n = \frac{1}{2} \left\{ \zeta + \frac{\zeta}{\delta} + \beta_n^2 + \right.$$
$$\left. \left(\zeta^2 + \frac{2\zeta^2}{\delta} + \frac{\zeta^2}{\delta^2} + 2\zeta\beta_n^2 + \frac{2\zeta\beta_n^2}{\delta} + \beta_n^4 \right)^{1/2} \right\} \quad (31)$$

The fractional conversion for progressive-conversion model is defined by

$$f = \left(\int_0^R 2\pi r L C_S dr \right) / \pi R^2 L C_{S0} = 2 \int_0^1 r^* C_S^* dr^* \quad (32)$$

and from Eqs. (28) and (32)

$$f = 1 - e^{-\zeta t^*} - 4\eta^2 \zeta\delta \sum_{n=1}^{\infty} (\zeta - S_n)(e^{-S_n t^*} - e^{-\zeta t^*}) / B_n \quad (33)$$

1-2-2 The solution for semi-infinite treatment

Provided that the reaction occures only near the surface of solid, the curvature in diffusion equation by cylindrical coordinates is negligible and this problem is reduced to one-dimensional treatment by rectangular coordinates. In this case, it can be considered that the diffusion resistance in the porous solid or ash layer is regarded as very large and that the chemical resistance is very small as compared with the ash diffusion resistance.

The basic equations, initial and boundary conditions are as follows;

$$\partial C_s^* / \partial t = \mathcal{D}'_{eA} \partial^2 C_s^* / \partial x^2 \quad (0 < x < \infty) \quad (34)$$
$$\text{at } x = 0, \qquad \partial C_s^* / \partial x + h(1 - C_s^*) = 0 \quad (35)$$
$$\text{at } x = \infty, \qquad C_s^* = 0 \quad (36)$$
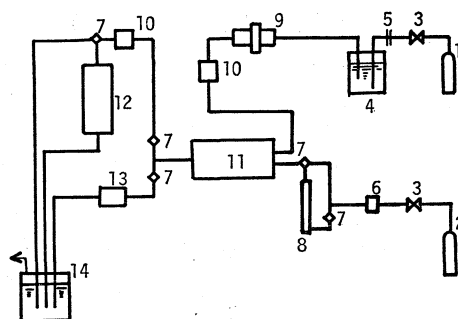$$\text{at } t = 0, \qquad C_s = 0 \quad (37)$$

where

$$\mathcal{D}'_{eA} = C_{A0} \mathcal{D}_{eA} / a C_{S0}, \quad h = k_f / \mathcal{D}_{eA} \quad (38)$$

the solution of this equation is

$$C_s^* = \text{erfc}(x/2\sqrt{\mathcal{D}'_{eA}t}) - \exp(hx^2 + h^2 \mathcal{D}'_{eA}t)$$
$$\times \text{erfc}(x/2\sqrt{\mathcal{D}'_{eA}t} + h\sqrt{\mathcal{D}'_{eA}t}) \quad (39)$$

and the fractional conversion is expressed by

$$f = (2/R)[(1/h) \times$$
$$\{\exp(h^2 \mathcal{D}'_{eA}t) \cdot \text{erfc}(h\sqrt{\mathcal{D}'_{eA}t}) - 1\}$$
$$+ 2\sqrt{\mathcal{D}'_{eA}t/\pi}] \quad (40)$$

1	N_2 gas holder	8	Soap film flow meter
2	SO_2 gas holder	9	Mist separater
3	Valve	10	Assmann's aspiration psychrometer
4	Humidifier		
5	Orifice meter	11	Homogenizing chamber
6	Mass flow controller	12	Reaction chamber
7	Cock	13	SO_2 analyzer
		14	Absorber

Fig. 3. Experimental apparutus

2. Experimental equipment and procedures

Figure 3 shows the schematic diagram of the experimental apparatus. The reaction chamber was a cylinder with a length of 71 cm and a diameter of 24 cm and was covered with black paper. Solute gas used in this experiment was nitrogen-sulfur dioxide gas mixture. Both nitrogen and sulfur dioxide gases from cylinders were fed to the reaction chamber after the humidity of nitrogen gas was regulated to the desired value by the humidifier and further both gases were well mixed in a homogenizing chamber. The SO_2 content in the nitrogen gas was controlled by reducing valves installed on the cylinders and mass flow controller and was measured by SO_2 analyzer. The flow rates of SO_2 and N_2 were measured by soap film flow meter and orifice meter, respectively. The relative humidity was measured by the Assmann aspiration psychrometer.

The gas compositions were 500, 1000, and 1500 ppm. The gas velocity were 0.087, 0.17 and 0.29 cm/s and the relative humidity were 50, 70, and 90 %.

On the other hand, the fractional coversion was checked under the condition of the gas velocity more than 27 cm/s. In this case, the regulation of the humidity was difficult due to the large amount of gas† and only the effect of gas velocity on the reaction was examined. The gas mixture was composed by air and SO_2. The gas velocity
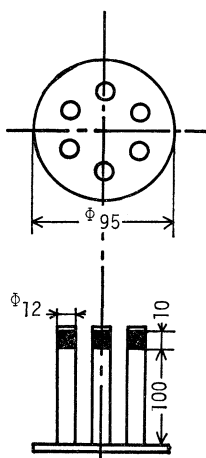
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† The humidity was about 60%.

Fig. 4. Arrangement of pellets

were 27, 55, and 93 cm/s and the SO_2 contents in the air were 20, 50, and 100 ppm.

In the beginning, the three way cock was regulated in order to flow the gas mixture through bypass and various conditions such as humidity, gas concentration, and gas velocity were adjusted

to the desired values.

When it was confirmed that the operating conditions were kept constant, the PbO_2 pellets were arranged in the reaction chamber as in **Fig. 4** and then the gas mixture was sent to the reaction chamber by the three way cock. The PbO_2 pellets were formed into a cylindrical shape with a length of 1.0 cm and a diameter of 1.2 cm with a manual pressurizing machine and its mass was 3×10^{-3} kg. The voidage of the pellet was almost 72 %. The PbO_2 sample used was standard one for use in determination of sulfur in the atmosphere checked by British Standards Institution, Investigation of Atmospheric Pollution.

The reaction times fixed were 30, 60, 100, 210, and 300 min. At the time when the desired time from the start of the experiment lapsed, the gas mixture was sent to the bypass by the cock and a sample was taken out rapidly.

Analysis of the sample was done by the colorimetric method with a Beckman spectrophotometer. The experiment was carried out under the atmospheric temperature; $291 \sim 316$ K. The operating conditions are summarized in **Table 1**.

Table 1. Operating conditions

| Run	u [m/s] $\times 10^2$	C_{A0} [ppm]	H [%]	T [K]	Run	u [m/s] $\times 10^2$	C_{A0} [ppm]	H [%]	T [K]
1	0.087	1500	50	293	24	0.29	1000	90	293
2	0.17	1500	50	293	25	0.087	500	90	293
3	0.29	1500	50	292	26	0.17	500	90	292
4	0.087	1000	50	291	27	0.29	500	90	293
5	0.17	1000	50	293	28	93	100	62	304
6	0.29	1000	50	293	29	93	50	62	316
7	0.087	500	50	292	30	93	20	62	304
8	0.17	500	50	292	31	55	100	78	304
9	0.29	500	50	293	32	55	50	73	313
10	0.087	1500	70	293	33	55	20	74	314
11	0.17	1500	70	292	34	27	100	55	312
12	0.29	1500	70	293	35	27	50	52	309
13	0.087	1000	70	292	36	27	20	54	312
14	0.17	1000	70	292	37	93	100	61	303
15	0.29	1000	70	293	38	93	50	61	303
16	0.087	500	70	293	39	93	20	61	304
17	0.17	500	70	292	40	55	100	58	304
18	0.29	500	70	292	41	55	50	58	305
19	0.087	1500	90	292	42	55	20	60	305
20	0.17	1500	90	293	43	27	100	67	305
21	0.29	1500	90	292	44	27	50	67	303
22	0.087	1000	90	292	45	27	20	68	304
23	0.17	1000	90	293					
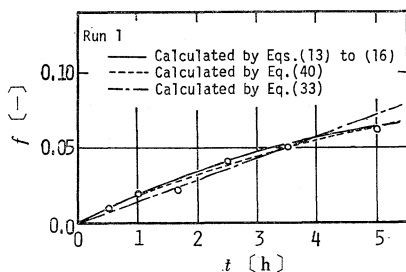
Fig. 5. Comparison of the experimental results for Run 1 with the calculated results

3. Experimental results and Discussion

3-1 Selection of reaction model

Figure 5 shows the comparison of the experimental results with the calculated ones which were estimated under such a condition as the deviation between data and results calculated by the solutions in this paper was minimized by assuming the values for k_f, $\mathcal{D}_{eA}$ and k_s. As is evident from this figure, the calculated results by unreacted-core model and semi-infinite solid model represent more suitable relation with the data and the solution with the linear approximation is not so good. The solution by semi-infinite solid treatment in progressive-conversion model was derived under the assumption that the chemical reaction resistance was smaller than the diffusion resistance in porous solid and that the reaction occurred only near the surface of solid. While in progressive-conversion model, the reaction rate equation was represented by Eq. (22). When the chemical reaction resistance is negligible, $k_v \to \infty$ and by paying attention $\partial C_s/\partial t$ has a finite value at all times, it is, then, found that the following relations must be satisfied.

$$C_A = 0 \tag{41}$$
$$C_S = C_{S0} \tag{42}$$

On the other hand, the relation as shown in Eqs. (41) and (42) are valid in unreacted-core model. That is, Eqs. (41) and (42) are satisfied in the region of $0 \sim r_c$ and $r_c \sim R$, respectively. As a result, it is found that this model is very similar to the unreacted-core model. The values of effective diffusivity in porous solid estimated by the solution of linear approximation lay in the region of $1.1 \sim 1.4 \times 10^{-4}$ m^2/s and those by the unreacted-core model were in the region of $0.002 \sim 0.008 \times 10^{-4}$ m^2/s. The molecular diffusivity of SO_2, however, was about 0.13×10^{-4} m^2/s which was estimated by the Gilland,[11] Arnold[12], and Fujita[13] equations. In this case, such a contradiction that the effective diffusivity in porous solid by the

linear approximation is about ten times molecular diffusivity is not able to explain for the PbO$_2$-SO$_2$ reaction system.

After 6 hours from the start of the experiment, the surface of the pellet was observed and it was found that the layer like as the product one existed at the outside part of the cylindrical pellet, and then the samples of the outer part and the inner one separated were analyzed with the spectrophotometer. It became clear that the outer skin of the pellet was lead sulphate layer and the inner part was unreacted core of lead peroxide.

As a result of this discussion, it is assumed that the unreacted-core model corresponds closely to what really takes place in lead peroxide pellet.

3-2 Estimation of the predominant resistance

Now, let us discuss about the parameter P_1, P_2, and P_3 which represent the resistances on the basis of the values for k_f, $\mathcal{D}_{eA}$ and k_s estimated. As a typical example, the experimental results for Run 14 is dealed with. In this case the values for k_f, $\mathcal{D}_{eA}$ and k_s estimated by Eqs. (13) to (16) were as follows; $k_f = 0.609 \times 10^{-2}$ m/s, $\mathcal{D}_{eA} = 0.00386 \times 10^{-4}$ m^2/s, $k_s = 4.6 \times 10^{-5}$ m^4/(mol·s). The resistances P_1, P_2, and P_3 were calculated from Eqs. (18) to (20). The results are shown in **Table 2**. As is evident from Table 2, the chemical reaction resistance P_3 is considerably small as compared with P_1 and P_2 and it can be considered that the chemical reaction resistance is negligible for the PbO$_2$-SO$_2$ reaction system used in this experiment.

In **Figs. 6** and **7**, P_1 and P_2 are plotted against f with a parameter of k_f and $\mathcal{D}_{eA}$ for the fractional conversion in the region of $0 \sim 0.1$. As the values of P_3 calculated were less than 5 s/m, the relation between P_3 and f is not described in the figures. As is evident from the figures, the gas film diffusion resistance P_1 is predominant at the beginning of the reaction and the ash layer resistance P_2 increases with proceeding the reaction. Finally P_2 becomes the dominant resistance because P_1 is

Table 2. Estimated values for gas film diffusion, ash layer diffusion and chemical reaction resistances

f [—]	P_1 [s/m]	P_2 [s/m]	P_3 [s/m]
0.005	164.2	40.0	2.10
0.05	164.2	388.9	2.23

kept constant throughout the reaction and in general, it will be concluded $P_2 > P_1 \gg P_3$ for the PbO₂-SO₂ reaction system.

3-3 Effect of weather conditions on chemical reaction

3-3-1 Gas velocity **Figures 8** and **9** show the relation between gas velocity and fractional conversion. From Fig. 8, the total amount of product tends to increase with increasing gas velocity. In this case, the gas velocity is less than 0.29 cm/s and the gas flow pattern in the reaction chamber is considered to be closer to stagnant state. The effect of gas velocity on the reaction is not, then, concluded from this figure even though it is slightly observed. On the other hand, from the results in Fig. 9 which show the experimental data obtained at gas velocities above 27 cm/s, its tendency is observed clearly. In actual, the average wind velocity in the atmosphere is more than 2~3 m/s. Further, the gas concentration used in this experiment lies in the region of 20~100 ppm. The air pollution restriction for SO₂ is less than 0.1 ppm and it can be assumed that the results in Fig. 9 is more likely to those under the atmospheric conditions. It can be then concluded that the total amount of product for PbO₂-SO₂ system increases with increasing the gas velocity and this tendency is applied to the atmospheric conditions.
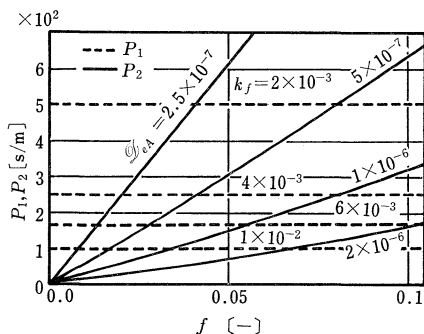

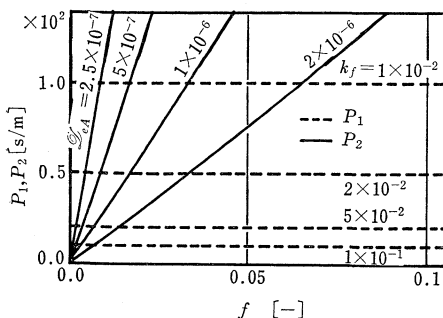Fig. 6. Estimation of values of individual resistances P_1, P_2

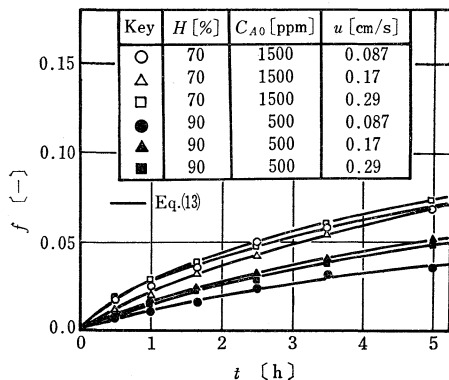Fig. 7. Estimation of values of individual resistances P_1, P_2

Key	H [%]	C_{A0} [ppm]	u [cm/s]
○	62	100	93
△	78	100	55
□	55	100	27
●	62	20	93
▲	74	20	55
■	54	20	27
— Eq.(13)			

Fig. 9. Effect of gas velocity on total amount of solid product

Key	H [%]	C_{A0} [ppm]	u [cm/s]
○	70	1500	0.087
△	70	1500	0.17
□	70	1500	0.29
●	90	500	0.087
▲	90	500	0.17
■	90	500	0.29
— Eq.(13)			

Fig. 8. Effect of gas velocity on total amount of solid product

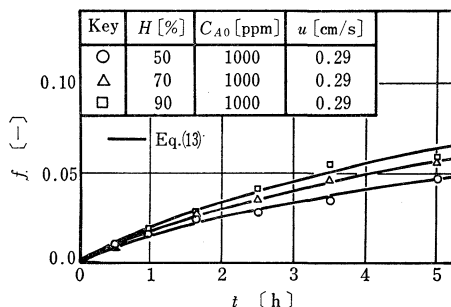| Key	H [%]	C_{A0} [ppm]	u [cm/s]
○	50	1000	0.29
△	70	1000	0.29
□	90	1000	0.29
— Eq.(13)			
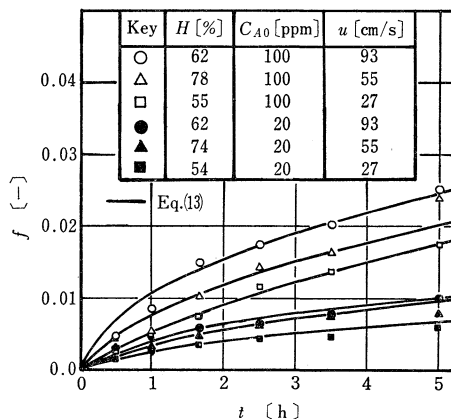
Fig. 10. Effect of humidity of gas on total amount of solid product

3-3-2 Humidity **Figure 10** shows the relationship between f and t as a parameter of humidity. As is evident from this figure, the fractional conversion increases with increasing the relative humidity. As the experiment is performed in a dark room and the inert gas is nitrogen, the effect of sunray and oxidation by oxigen need not to be considered and this tendency is mainly caused by the following reasons; When the relative humidity is high, it is assumed that SO_2 molecule is combined with the mist of water vapor in the gas phase and the mist of sulfurous acid reacts with PbO_2 pellet, or that the water vapor sticks to the surface of PbO_2 pellet and the adsorption of SO_2 molecule to the surface of PbO_2 pellet is promoted.

3-3-3 Gas concentration **Figures 11** and **12** show the effect of gas concentration on the amount of product. The amount of product increases with increasing gas concentrations as might be expected. As mentioned above, however, the region of SO_2 concentrations in the experiment is different from that in the atmosphere and from the results 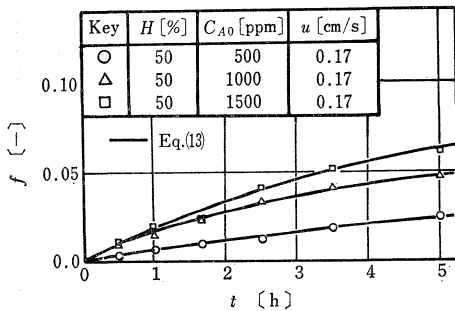shown in Figs. 11 and 12, the relationship between SO_2 concentration in the atmosphere and the values measured with the lead peroxide method is not determined immediately.
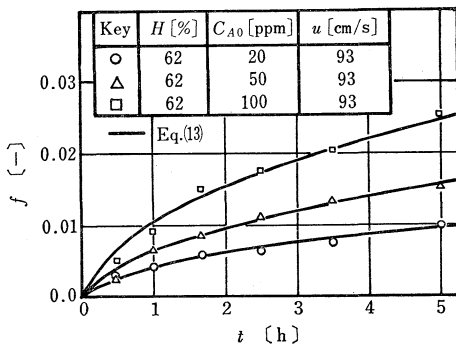
3-3-4 Atmospheric temperature The effect of the atmospheric temperature on PbO_2-SO_2 reaction was not recognized and it can be concluded the reaction velocity for PbO_2-SO_2 reaction is not affected by the change of the atmospheric temperature.[6]

3-4 The effect of atmospheric conditions on k_f and $\mathcal{D}_{eA}$

3-4-1 Gas film mass transfer coefficient The gas concentration in the experiment is relatively low and the physical properties such as density and viscosity do not change, that is, almost all have a constant value. The effect of gas concentration on the gas film mass transfer coefficient is, then, not considered.

Here the effect of gas velocity and relative himidity on k_f is studied. Arranging the results in the experiment in J-factor, one obtains the following experimental equations

$$J_D = (k_f/u) \cdot Sc^{2/3} = 0.20H^{0.74}Re^{-0.83} \quad (43)$$

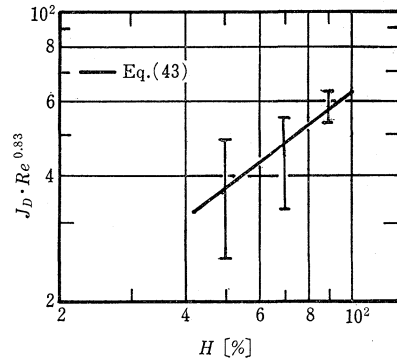where $50 \leqq H \leqq 90\%$, $0.64 \leqq Re \leqq 2.10$

Key	H [%]	C_{A0} [ppm]	u [cm/s]
○	50	500	0.17
△	50	1000	0.17
□	50	1500	0.17

Fig. 11. Effect of gas concentration on total amount of solid product

Fig. 13. Relationship between $J_D \cdot Re^{0.83}$ and H

Key	H [%]	C_{A0} [ppm]	u [cm/s]
○	62	20	93
△	62	50	93
□	62	100	93

Fig. 12. Effect of gas concentration on total amount of solid product

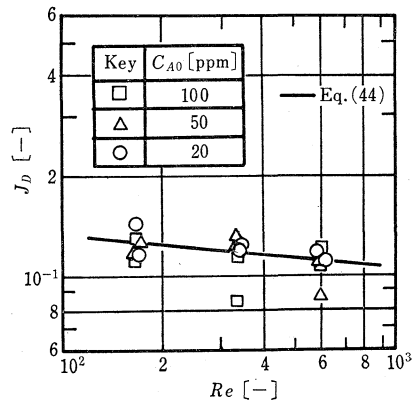| Key	C_{A0} [ppm]
□	100
△	50
○	20

Fig. 14. Relationship between J_D and Re

and

$$J_D = 0.21Re^{-0.10} \quad (150 \leqq Re \leqq 610) \quad (44)$$

The experimental results arranged by Eqs. (43) and (44) are shown in **Figs. 13** and **14**, respectively. In Fig. 13, vertical lines show the range of plotted data. As is evident from Eq. (43), k_f is proportional to the 0.74 power of humidity. In the theoretical analysis, the concentration of gaseous reactant at the gas-solid interface was assumed to change continuously. In actual, however, there are interfacial resistance at the gas-solid interface and it is considered that the concentration profile of gaseous reactant at the interface is discontinuous as is shown in **Fig. 15**. In this case, the following relationship may be established;

$$k_g(C_{A0}-C_{Ag}) = \gamma(C_{Ag}-C_{AS}) = k_f(C_{A0}-C_{AS}) \quad (45)$$

where γ indicates the reciprocal of interfacial resistance. Now let us assume the concentration profile of gaseous reactant in the gas film changes linearly. From Eq. (45), then, the following relationship is deriven;

$$1/k_f = 1/k_g + 1/\gamma \quad (46)$$

Provided that k_g is the gas film mass transfer coefficient being irrelevant to the humidity and depending on the gas velocity, and that γ is affected by humidity alone, then the effect of humidity on k_f is interpreted as follows; When the relative humidity is high, the interfacial resistance becomes small and the overall gas film mass transfer coefficient k_f has a large value. That is, under the conditions of high humidity, it can be considered that the water vapor attaches to the solid surface at the gas-solid interface and thin liquid film promoting the mass transfer velocity of gaseous reactant are formed at the gas-solid interface.
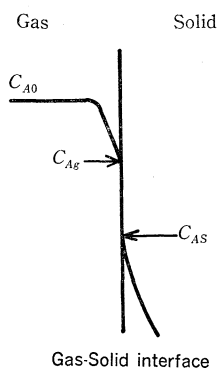
3-4-2 Effective diffusivity in porous solid   It is very difficult to study the physical characteristics in porous solids because of the mass transfer phenomena in the porous solid are affected by various physical factors. In this experiment, the structure in the PbO_2 pellets was not searched in details and the voidage of the pellets was held constant at about $\varepsilon = 72$ by mannual technique, and then the degree of the effects of gas velocity and humidity on $\mathcal{D}_{eA}$ was discussed quantitatively. The result obtained is as follows;

$$Sc' = (\nu/\mathcal{D}_{eA}) = 2.9 \times 10^3 H^{-1.0} \quad (47)$$

where $50 \leqq H \leqq 90\%$, $0.64 \leqq Re \leqq 610$

The effect of gas velocity on $\mathcal{D}_{eA}$ assums to be negligible because its effects was scarecely recognized in this experiment. The results are shown in **Fig. 16**. Vertical lines show the range of plotted data.

Conclusion

To evaluate precisely the SO_2 concentration in the atmosphere measured with the lead peroxide method, the reaction mechanism for PbO_2-SO_2 reaction system was studied theoretically and the effect of atmospheric conditions such as gas velocity, humidity and gaseous reactant concentration on the reaction was discussed experimentally. The followings are concluded in this study.

(1) The transport phenomena for PbO_2-SO_2 reaction system is represented adequately by the unreacted-core model disregarded the chemical reaction resistance.

(2) The effect of gas temperatures on the chemical reaction is not recognized at the atmospheric conditions.

(3) The gas film mass transfer coefficient is in proportion to 0.74 powers of relative humidity in the region of $50 \sim 90\%$ and increases proportionally to 0.17 powers of the gas velocity in the region of $0.09 \sim 0.29$ cm/s and 0.9 powers in the

Gas   Solid

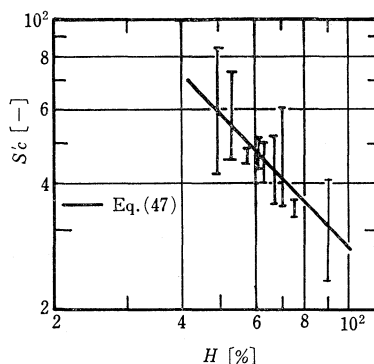Fig. 15. Concentration profile of gaseous reactant at gas-solid interface

Fig. 16 Relationship between $S'c$ and H

region of 27.5~93.4 cm/s.

(4) The effective diffusivity of SO$_2$ in the PbO$_2$ pellet increases with increasing the relative humidity in the region of 50~90% and the effect of gas velocities on $\mathscr{D}_{eA}$ is scarecely recognized.

Acknoewldgment

The author would like to thank Dr. E. Hirai for his helpful advice, The author also wish to thank Messrs. T. Hirota, S. Kawaguchi and K. Suzuki for their helpful experimental skill.

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Nomenclature

A_n, B_n, C_n = dimensionless variable defined by Eq. (29) [—]

a = stoichiometric coefficient [—]

C_A = concentration of gaseous reactant in solid [mol/m^3]

$C_A{}^*$ = dimensionless concentration of gaseous reactant in solid defined by Eq. (29)

C_{A0} = concentration of gaseous reactant in bulk phase [mol/m^3], [ppm(v/v)]

C_{Ag} = concentration of gaseous reactant in gas phase at gas-solid interface [mol/m^3]

C_{AS} = concentration of gaseous reactant in solid phase at gas-solid interface [mol/m^3]

C_S = concentration of solid reactant [mol/m^3]

$C_S{}^*$ = dimensionless concentration of solid reactant defined by Eq. (29)

C_{S0} = initial concentration of solid reactant [mol/m^3]

C_1, C_2, C_3 = variables defined by Eqs. (14), (15), and (16) respectively [s]

$\mathscr{D}_{eA}$ = effective difficivity of gaseous reactant in porous solid [m^2/s]

$\mathscr{D}'_{eA}$ = modified effective diffusivity of gaseous reactant in porous solid defined by Eq. (38) [m^2/s]

f = fractional conversion [—]

H = relative humidity [%]

h = parameter defined by Eq. (38) [1/m]

J_0, J_1 = Bessel functions of zero order and first kind, respectively [—]

J_D = Chilton-Colburn J-factor for mass transfer [—]

k_f = overall gas film mass transfer coefficient [m/s]

k_g = individual gas film mass transfer coefficient [m/s]

k_s = reaction rate constant of gaseous reactant based on unit surface [m^4/(mol·s)]

k_v = reaction rate constant of gaseous reactant based on unit volume [m^3/(mol·s)]

L = height of sample [m]

P_1 = resistance of gas film diffusion defined by Eq. (18) [s/m]

P_2 = resistance of ash layer diffusion defined by Eq. (19) [s/m]

P_3 = resistance of chemical reaction defined by Eq. (20) [s/m]

R = radius of sample [m]

R_A = Chmeical reaction rate [mol/(m^3·s)]

Re = Reynolds number $(=2Ru\rho/\mu)$ [—]

r = distance from the axis of pellet [m]

r_c = distance from the axis of pellet to unreacted-core surface [m]

r^* = dimensionless distance defined by Eq. (29) [—]

S_c = Schmidt number [—]

S_c' = dimensionless parameter defined by Eq. (47) [—]

S_n = parameter expressed by Eq. (31) [—]

T = temperature of gas [K]

t = contact time or reaction time [h], [s]

t^* = dimensionless contact time defined by Eq. (29) [—]

u = mean gas velocity [m/s]

W	=total amount of solid product	[mol]
β_n	=positive roots of Eq. (30)	[—]
γ	=parameter defined by reciprocal of resistance at gas-solid interface	[m/s]
δ	=dimensionless parameter defined by Eq. (29)	[—]
ε	=voidage	[—]
ζ	=dimensionless parameter defined by Eq. (29)	[—]
η	=dimensionless parameter defined by Eq. (29)	[—]
μ	=viscosity of gas	[kg/(m·s)]
ν	=kinematic viscosity of gas	[m²/s]
ρ	=density of gas	[kg/m³]

PbO₂-SO₂ 反応系の物質移動機構の検討

林　良　茂

金沢大学工学部化学工学科

920　金沢市小立野2-40-20

抄　録

　二酸化鉛法で求めた大気中の平均亜硫酸ガス濃度を精度良く評価するために，PbO-SO₂ 系反応を固体粒子とそれをとりまくガス間の非触媒反応とみなして，その反応機構を検討した。使用した反応モデルは均一反応モデルと未反応殻モデルである。この反応に及ぼす風速，湿度，溶質ガス濃度，温度などの大気条件の影響を調べるために，円柱状の PbO₂ ペレットを用いて実験を行った。ガス境膜物質移動係数，固体内有効拡散係数および反応速度定数を実験データと反応モデルに基づいて推定した。そして，これらの値を用いてこの反応の速度支配抵抗について検討した。