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REVIEW

KINETICS OF ABSORPTION OF HYDROGEN SULFIDE INTO AQUEOUS Fe(III) SOLUTIONS

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Abstract – In our recent studies, absorption of H_2S into the aqueous $Fe_2(SO_4)_3$ and $FeCl_3$ solutions with various values of ionic strength and pH was investigated in an agitated vessel with a flat interface. The experimental results for both systems revealed that the species which reacts with H_2S is $FeOH^{2+}$. The absorption rates were explained by the theory of gas absorption with an irreversible (1,1)-th order reaction between H_2S and $FeOH^{2+}$. The reaction rate constants were independent of the ionic strength of the solution and correlated as a function of temperature. In this paper, kinetics and mechanism of these absorption reactions are reviewed and the identity for both systems is emphasized.

Key words: Gas Absorption, Hydrogen Sulfide, Fe(III) Solutions, Reaction Kinetics, Reaction Mechanism

INTRODUCTION

Removal of H_2S from gas streams is a familiar industrial requirement, and economical removal will increase an importance in connection with the utilization of fuels with a higher sulfur content in the near future. Among many removal processes of H_2S proposed, conversion to elemental sulfur is advantageous, because it can be used for treatment in an environmentally permissible procedure and can be applied even to the treatment of gases with relatively low concentrations of H_2S in the presence of CO_2 in substantial concentration. However, the established procedures often have some drawbacks [Asai et al., 1990].

Recently Dowa Mining Co. and Idemitsu Kosan Co. in Japan developed unique new processes of H_2S removal using $Fe_2(SO_4)_3$ and $FeCl_3$ as absorbents, which are regenerated biologically and electrochemically, respectively. These processes are made in environmentally favorable closed system, as follows.

Dowa Process [Imaizumi, 1986]:

$$H_2S+Fe_2(SO_4)_3 \rightarrow S\downarrow +2FeSO_4+H_2SO_4 \qquad \text{(absorption)} \quad \text{(a)}$$

$$2FeSO_4+H_2SO_4+1/2O_2 \xrightarrow[T.\ ferrooxidans]{\text{biological}} Fe_2(SO_4)_3+H_2O \qquad \text{(regeneration)} \quad \text{(b)}$$

$$H_2S+1/2O_2 \rightarrow S\downarrow + H_2O \qquad \text{(overall reaction)} \quad \text{(c)}$$

Idemitzu Process [Kikuchi et al., 1991]:

$$H_2S+2FeCl_3 \rightarrow S\downarrow +2FeCl_2+2HCl \qquad \text{(absorption)} \quad \text{(d)}$$

$$2FeCl_2+2HCl \xrightarrow{\text{electrochemical}} 2FeCl_3+H_2 \qquad \text{(regeneration)} \quad \text{(e)}$$

$$H_2S \rightarrow S\downarrow +H_2 \qquad \text{(overall reaction)} \quad \text{(f)}$$

This paper reviews our previous studies [Asai et al., 1990, 1997], which clarified the kinetics of the above absorption reactions in these processes.

ABSORPTION RATES OF H_2S

An agitated vessel with a flat interface (13.2 cm i.d. and 23.0 cm high) and the experimental conditions used are shown in Fig. 1 and Table 1, respectively. The effects of $Fe_2(SO_4)_3$ and $FeCl_3$ concentrations on the measured initial absorption rates N_A of H_2S are shown in Fig. 2. It may be seen in the region of low concentrations of absorbents that the absorption rates N_A without adjustment of the pH increase with $Fe_2(SO_4)_3$ or $FeCl_3$ concentrations, and that the concentration

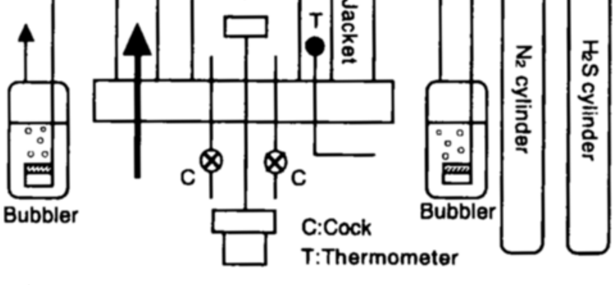

Fig. 1. Agitated vessel with a flat interface.

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Table 1. Experimental conditions

$Fe_2(SO_4)_3$	0.01-1.00 kmol/m^3
$FeCl_3$	0.01-0.50 kmol/m^3
K_2SO_4	0-0.319 kmol/m^3
H_2SO_4	0-0.137 kmol/m^3
KOH	0-0.002 kmol/m^3
KCl	0-0.521 kmol/m^3
HCl	0-0.03 kmol/m^3
H_2S	0.00189-0.0204 mole fraction
Temperature	293-313 K
pH	0.88-2.60
Ionic strength	0.06-3.00 kmol/m^3

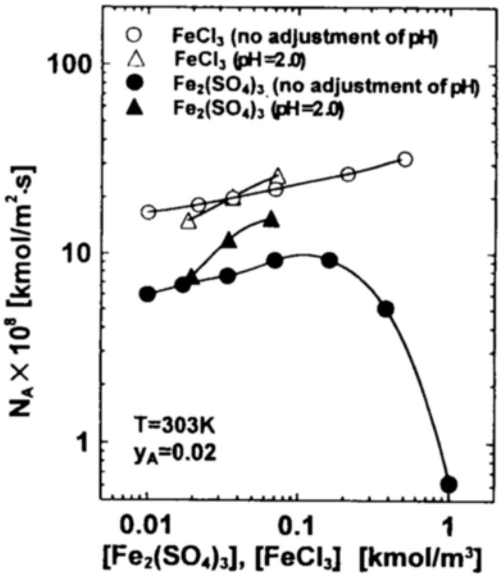

Fig. 2. Effects of $Fe_2(SO_4)_3$ and $FeCl_3$ concentrations on absorption rates of H_2S.

dependency of the absorption rates for both systems using absorbents adjusted to pH=2 with KOH becomes larger than that without adjustment of pH. On the other hand, in the region of relatively high concentrations of absorbents, the absorption rates for $Fe_2(SO_4)_3$ solutions decrease remarkably with an increase in $Fe_2(SO_4)_3$ concentration. The absorption rates into the aqueous $FeCl_3$ solutions may be noted to be much larger than those into the aqueous $Fe_2(SO_4)_3$ solutions, especially in the region of their higher concentrations. Fig. 3 represents the effect of pH on the absorption rates. It can be seen that the absorption rates for both solutions increase significantly with pH.

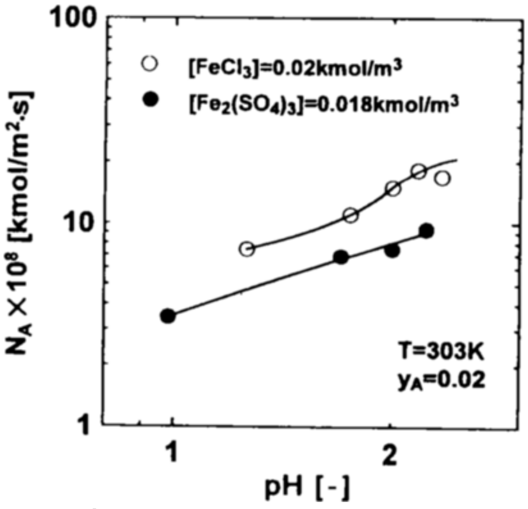

Fig. 3. Effect of pH on absorption rates of H_2S.

CHEMICAL SPECIES REACTING WITH H_2S

The observed effects of the $Fe_2(SO_4)_3$ and $FeCl_3$ concentrations and pH on the absorption rates of H_2S cannot be expected from the weak variation in the values of the relevant physical properties. Therefore, an attempt was made to identify the species likely to react with H_2S by allowing for the equilibria of the relevant reactions in the solution. The concentrations of the individual species were evaluated from the chemical equilibrium constants of the relevant reactions, mass balance for iron, chloride, sulfate and potassium, and the measured values of pH. The chemical equilibrium constants were evaluated as a function of the ionic strength of the solution and temperature from the literature [Dean, 1985; Smith and Martell, 1976]. Among the calculated concentrations of the relevant species, the concentrations of $FeOH^{2+}$ for $Fe_2(SO_4)_3$ and $FeCl_3$ solutions systems are illustrated as functions of the $Fe_2(SO_4)_3$ and $FeCl_3$ concentrations in Fig. 4, respectively. The calculations were limited to the concentrations of $Fe_2(SO_4)_3$ and $FeCl_3$ less than 0.2 kmol/m^3, because the ionic strength dependency of the relevant chemical equilibrium constants for the larger values of the ionic strength was unknown. The behavior of $FeOH^{2+}$ is consistent with that of the absorption rates of H_2S, while the tendency of any other species, which was not shown here, was not in line with that expected from the observed absorption rates. Fig. 5 shows the variation in concentrations of $FeOH^{2+}$ for both systems with pH of the solu-

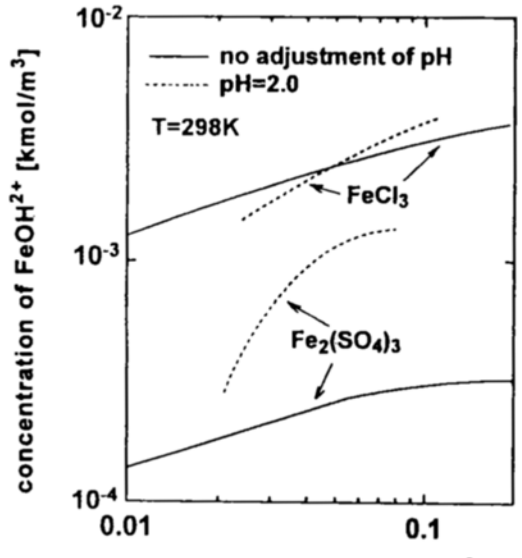

Fig. 4. Variation in $FeOH^{2+}$ concentration with $Fe_2(SO_4)_3$ and $FeCl_3$ concentrations.

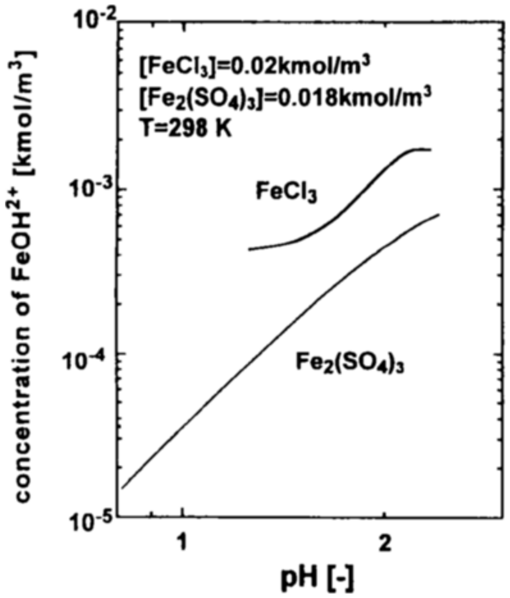

Fig. 5. Variation in FeOH^{2+} concentration with pH.

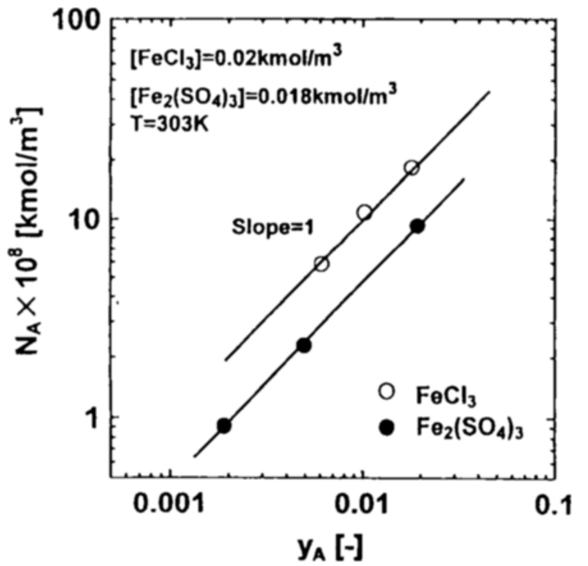

Fig. 6. Effect of gas-phase concentration on absorption rates of H$_2$S.

tion. The behavior is also consistent with that of the absorption rates of H_2S. Thus, the chemical species reacting with H_2S was inferred to be $FeOH^{2+}$.

COMPARISON OF OBSERVED ABSORPTION RATES WITH THEORETICAL PREDICTIONS

The measured absorption rates were compared with the theoretical predictions, in which a reactant with H_2S was taken as $FeOH^{2+}$. Under the present experimental conditions, the gas-phase mass transfer resistance was always negligible and the interfacial concentrations A_i of H_2S were much less than the $Fe_2(SO_4)_3$ and $FeCl_3$ concentrations. Therefore, the experimental data were analyzed on the basis of the theory of absorption accompanied by an irreversible pseudo-mth order reaction.

When this reaction is fast, the absorption rate is given by the Hikita-Asai equation [Hikita and Asai, 1963].

$$N_A = \sqrt{\frac{2}{m+1} k_{m,n} D_A A_i^{m+1} B_o^n} \tag{1}$$

Fig. 6 represents the effect of the gas-phase mole fraction y_A of H_2S on the absorption rates. The absorption rates for $Fe_2(SO_4)_3$ and $FeCl_3$ solutions systems may be seen to be proportional to the mole fractions, that is, the physical solubilities A_i. This suggests that the reaction order m with respect to H_2S may be taken as unity. Substituting m=1 in Eq. (1), one obtain the following equation.

$$N_A / A_i \sqrt{D_A} = \sqrt{k_{1,n} B_o^n} \tag{2}$$

Based on Eq. (2), the experimental data are plotted in Fig. 7. B_O refers to the bulk concentration of the reactant $FeOH^{2+}$. The slope of the representative line of experimental data for both systems is 1/2. This corresponds to n=1, if the dependeny of the reaction rate constant $k_{1,n}$ on the ionic strength of the solution is negligible. Substitution of n=1 into Eq. (2) yields:

$$N_A/A_i \sqrt{D_A B_O} = \sqrt{k_{1,1}} \tag{3}$$

According to Eq. (3), Fig. 8 shows the dependency of $N_A/A_i\sqrt{D_A B_O}$, i.e. the reaction rate constant $k_{1,1}$ on the ionic strength I, which was varied with the addition of K_2SO_4 and KCl to aqueous $Fe_2(SO_4)_3$ and $FeCl_3$ solutions, respectively. It may be seen from this figure that the reaction rate constant $k_{1,1}$, which is identical to the square of the values of the ordinate, is independent of the ionic strength. The value of $k_{1,1}$ was evaluated to be 4,100 m^3/kmol·s at 303 K. Thus, the rate-determining reaction for this system may be regarded as second order, that is, first order in both H_2S and $FeOH^{2+}$.

Using the measured reaction rate constant $k_{1,1}$=4,100 m^3/kmol·s at 303 K, the reaction factors β were evaluated from all the observed absorption rates N_A, including those used in the analysis of the kinetics. Then, the reaction factors β were compared with the theoretical solution (Lévêque model) of absorption accompanied by an irreversible pseudo-first order reaction [Hikita et al., 1973, 1975]:

$$N_A = \beta k^{\bullet}_{lA} A_i \tag{4}$$

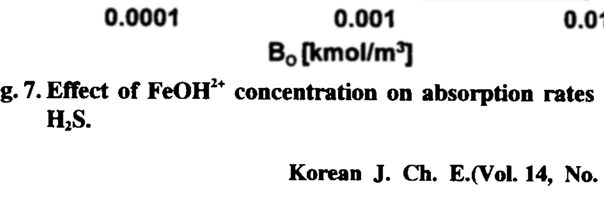

Fig. 7. Effect of FeOH^{2+} concentration on absorption rates of H$_2$S.

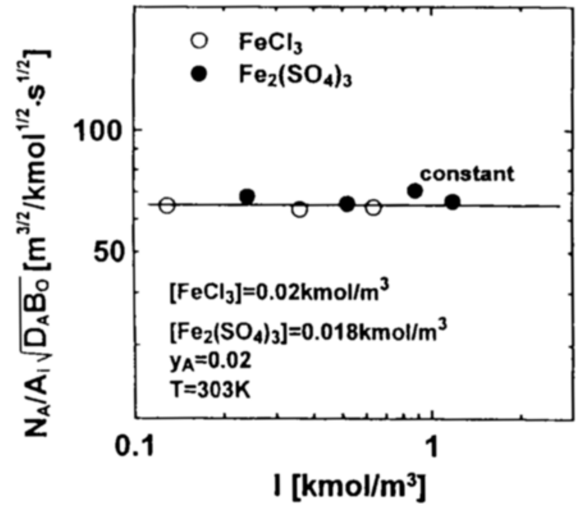

Fig. 8. Effect of ionic strength on absorption rates of H_2S.

$$\beta=\gamma+0.474715/\gamma \quad (\gamma \geqq 2.4) \tag{5}$$

$$\beta=1+\sum_p b_p \gamma^{2p} \quad (\gamma<2.4) \tag{6}$$

$$\gamma=\sqrt{kB_O D_A}/k^*_{LA} \tag{7}$$

where b_p are constants, D_A is the diffusivity of H_2S and k^*_{LA} is the liquid phase mass transfer coefficient of H_2S. Fig. 9 illustrates the comparison of observed reaction factors β for both systems with the theoretical predictions. The agreement between them for the various compositions of gas and liquid is remarkable. Thus, the validity of identification of a species reacting with H_2S and the analytical procedure was confirmed.

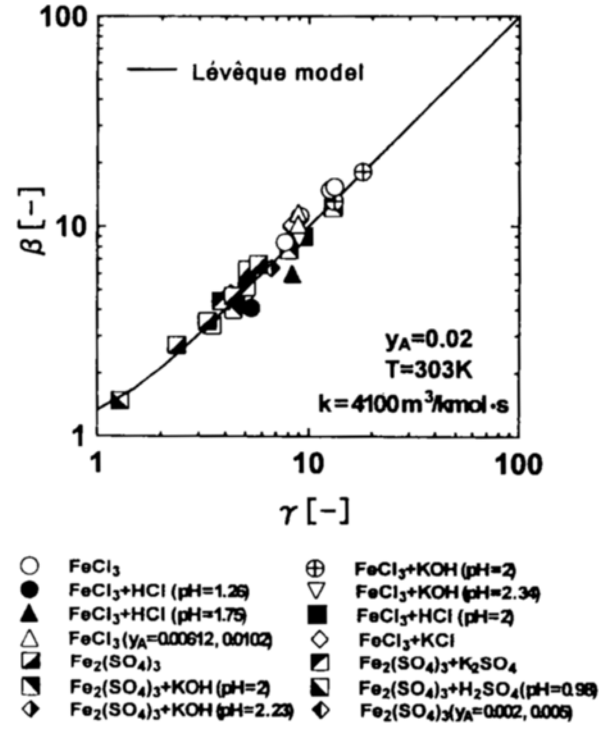

Fig. 9. Comparison of observed reaction factors with theoretical prediction for irreversible (1,1)-th order reaction.

REACTION RATE CONSTANT AND REACTION MECHANISM

The experimental data measured at 283, 293 and 313 K were also analyzed in the same manner. The Arrhenius plot of the reaction rate constant k is shown in Fig. 10. The data for both systems are represented by a single straight line, and the reaction rate constants can be correlated by:

$$\ln k=32.98-7520/T \tag{8}$$

independent of the ionic strength.

From the above-mentioned results, the absorption reactions (a) and (d) for the present reaction systems may be presumed to consist of the following four step reactions, respectively:

H_2S-aqueous $Fe_2(SO_4)_3$ solutions system

$$Fe_2(SO_4)_3+2H_2O \longrightarrow 2FeOH^{2+}+3SO_4^{2-}+2H^+ \tag{g}$$

$$H_2S+FeOH^{2+} \longrightarrow H_2S \cdot FeOH^{2+} \tag{h}$$

$$H_2S \cdot FeOH^{2+}+FeOH^{2+} \longrightarrow S\downarrow +2Fe^{2+}+2H_2O \tag{i}$$

$$2Fe^{2+}+3SO_4^{2} +2H^+ \longrightarrow 2FeSO_4+H_2SO_4 \tag{j}$$

$$H_2S+Fe_2(SO_4)_3 \longrightarrow S\downarrow +2FeSO_4+H_2SO_4 \tag{a}$$

H_2S-aqueous $FeCl_3$ solutions system

$$2FeCl_3+2H_2O \longrightarrow 2FeOH^{2+}+6Cl^-+2H^+ \tag{k}$$

$$H_2S+FeOH^{2+} \longrightarrow H_2S \cdot FeOH^{2+} \tag{h}$$

$$H_2S \cdot FeOH^{2+}+FeOH^{2+} \longrightarrow S\downarrow +2Fe^{2+}+2H_2O \tag{i}$$

$$2Fe^{2+}+6Cl^-+2H^+ \longrightarrow 2FeCl_2+2HCl \tag{l}$$

$$H_2S+2FeCl_3 \longrightarrow S\downarrow +2FeCl_2+2HCl \tag{d}$$

The second step irreversible reaction (h), which is first-order in both H_2S and $FeOH^{2+}$, is rate-controlling.

Apart from the hydrolysis reactions (g) and (k), and terminal reactions (j) and (*l*), therefore, the reaction mechanism Eqs. (h) and (i) and the kinetics for the absorption of H_2S may be inferred to be identical for any aqueous Fe(III) solutions with

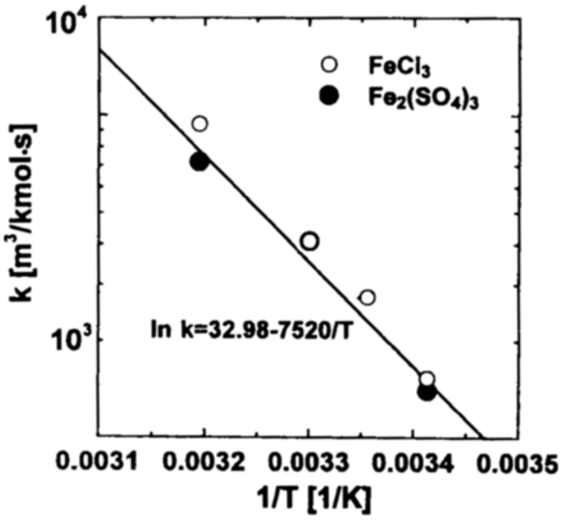

Fig. 10. Arrhenius plot of measured reaction rate constants.

different anions.

CONCLUSIONS

Absorption of H_2S into aqueous $Fe_2(SO_4)_3$ and $FeCl_3$ solutions is accompanied by the irreversible (1,1)-th order reaction between H_2S and $FeOH^{2+}$. The relevant reaction rate constants are correlated by Eq. (8) independent of the ionic strength of the solutions. The reaction kinetics and skeleton of reaction mechanism for the absorption of H_2S may be inferred to be identical for any aqueous Fe(III) solutions with different anions.

NOMENCLATURE

A : concentration of dissolved gas, H_2S [kmol/m^3]
B : concentration of reactant, $FeOH^{2+}$ [kmol/m^3]
b_p : coefficient in Eq. (6) (refer to Hikita et al., 1975) [-]
D : liquid-phase diffusivity [m^2/s]
I : ionic strength [kmol/m^3]
k_L^* : liquid-phase mass transfer coefficient [m/s]
$k_{m,n}$: (m,n)-th order reaction rate constant $[(m^3/kmol)^{m+n-1}/s]$
m : reaction order with respect to dissolved gas, H_2S [-]
N_A : absorption rate of H_2S [kmol/$m^2 \cdot$ s]
n : reaction order with respect to reactant, $FeOH^{2+}$ [-]
T : thermodynamic temperature [K]
y : mole fraction in gas phase [-]

Greek Letters

β : reaction factor [-]
γ : dimensionless number defined by Eq. (7) [-]

Subscripts

A : dissolved gas, H_2S
i : gas-liquid interface
O : bulk

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