Oxygenation of Neutral Ferrous Sulfate Solution by Gas Bubbling

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The oxidation of FeSO_4 solution by O_2 gas was studied at pH between 6.0 and 7.7. The oxidation was presumed to be composed of the sequential steps of dissolution of O_2 gas and reaction between Fe^{2+} ion and O_2 , and the rate determining steps were pursued. The rate of oxidation increased with pH. In the region of pH above 6.7 (at 25°C and Re 4000), the overall rate was controlled by the transferring rate of O_2 in the liquid boundary film adjacent to the gas bubbles. The rate of reaction between Fe^{2+} ion and O_2 was revealed to be proportional to the 4/3th power of C_{OH^-} . At the temperature below 15°C, (at pH 6.8 and Re 1000), the overall rate was affected by both rates of mass transfer of O_2 and chemical reaction. From the calculated rate constant of the reaction between Fe^{2+} ion and O_2 , the activation energy of 21 kcal/mol was obtained. The overall rate of oxidation increased with flow rate of gas stream (at 25°C and pH 6.8). At lower Reynolds number, the oxidation was of mass transfer control. When Reynolds number was higher, it was of mixed control of mass transfer O_2 and of chemical reaction.

1 Introduction

The oxidation of ferrous sulfate by O_2 gas in the aqueous solution is composed of the sequential steps of the dissolution of O_2 gas at the surface of rising gas bubbles and the reaction between Fe^{2+} ion and dissolved oxygen.¹⁾

They are represented as

and

or

respectively. The notation $\underline{\text{O}_2}$ represents the dissolved oxygen. It should be noted that the rate of eq. (1) is affected by the hydrodynamic conditions of gas bubbling, whereas the rates of eq. (2) and (3) are not affected because of their homogeneous character.

It was found in the previous study on the air oxidation of ferrous sulfate in an alkaline solution¹⁾ that no catalytic effect of Cu^{2+} ion was observed and the overall rate was not

virtually affected by the temperature, but that the rate increased with the rise of flow rate of air and a zero order rate equation was found to hold. It was concluded that the rate determining step is the oxygen dissolution shown in eq. (1).

It is known^{2)~4)} in the region of pH between 4 and 7.5, on the other hand, that the overall rate of air oxidation of Fe^{2+} ion is proportional to the concentration of Fe^{2+} ion and to the second power of the concentration of OH^- ion in the solution. It is expected in this region of pH that both eq. (1) and (3) may affect the overall rate. From the industrial point of view, the air oxidation of Fe^{2+} ion in this pH region is important to our basic knowledge about the iron removal from the pregnant solution from leaching processes.

Stumm and Lee²⁾ studied the kinetics of the reaction between Fe^{2+} ion and O_2 gas at pH between 6.0 and 7.5. The partial pressure of O_2 gas and pH of the solution were maintained constant during each experimental run by bubbling a mixture of CO_2 and air through the test solution. Various pH values were obtained by using air- CO_2 mixture of different compositions. From the presumption that C_{O_2} is proportional to p_{O_2} in the gas mixture, the follow-

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ing rate equation was proposed.

$$-\frac{dC_{\text{Fe}^{2+}}}{dt} = kC_{\text{Fe}^{2+}} p_{\text{O}_2} C_{\text{OH}^-}^2 \quad (4)$$

The activation energy of 23 kcal was obtained at a constant pH. Furthermore, the catalytic effect of Cu^{2+} ion was found to be considerable for the concentration of 3×10^{-7} M, but it increased only slowly with the concentration. Schenk *et al.*³⁾ and Tamura *et al.*⁴⁾ also studied the catalytic effects of dissolved silica and ferric hydroxide on the rate of air oxidation of Fe^{2+} ion in the neutral solution, respectively.

It was intended in the present work to study the kinetics of oxidation of ferrous sulfate by oxygen in the aqueous solution of pH between 6.0 and 7.7. Not only the reaction (3) but also the reaction (1) were taken into account, and the rate determining steps of the overall reaction were pursued.

2 Experimental

The experimental arrangement in the present work is schematically illustrated in Fig. 1. The pH of the solution was maintained constant during the oxidation by bubbling gas mixture containing CO_2 of a constant partial pressure. Oxygen, nitrogen and CO_2 gases were sent from the gas cylinders, respectively. The flow

Fig. 1 Experimental arrangement
(A) Valve, (B) Manometer, (C) Capillary flowmeter, (D) Humidifier, (E) Nozzle, (F) Reflux condenser, (G) Thermometer, (H) Combined glass electrode, (I) Platinum electrode for measuring CO_2 , (J) Styrofoam floats, (K) Reaction vessel, (L) Thermostat, (M) pH meter, (N) Oxygen meter, (O) Recorder

rate of these gases was separately measured with the capillary flowmeters. After passing through a humidifier, the gas mixture was blown from a glass nozzle into the solution.

The reaction vessel was a 1000 cm^3 -cylindrical glass flask provided with a glass lid with five holes and was placed in a thermostat. The inner dimension of the flask was 114 mm in inner diameter and 125 mm in height. Through the holes of the glass lid, a glass nozzle, a thermometer, a combined glass electrode, a platinum electrode for measuring CO_2 and a reflux condenser were installed, respectively.

An upward vertical glass nozzle of 0.5 mm in inner diameter was used. Its dimension is shown in Fig. 2. The measurements of pH

Fig. 2 Glass nozzle

and CO_2 were continuously made with a Hitachi-Horiba pH meter of type 42-A and with a Union Giken oxygen meter of type OX-101, respectively. Styrofoam floats were placed on the surface of solution in order to prevent as far as possible the dissolution of oxygen from the surface.

Analytical reagent grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was

dissolved in an aqueous H_2SO_4 solution ($\text{pH} \approx 1$). Electrolytic iron powder was added, and the solution was preserved for a few weeks to reduce the contaminated Fe^{3+} ion. It was filtered, and the aliquot was used for the experiment. On the other hand, a prescribed amount of analytical reagent grade NaHCO_3 was dissolved in the deionized water of 990 cm^3 , and it was transferred into the reaction vessel. After placing the styrofoam floats on the surface of solution, the mixed gas of N_2 and CO_2 of a predetermined composition was bubbled through the glass nozzle at the experimental temperature for about 10 h in order to remove the dissolved oxygen. Then an aliquot of the above FeSO_4 solution was added, and the test solution of 0.01 M FeSO_4 and 0.1 M NaHCO_3 was made up. The concentration of Fe^{2+} ion in the test solution was measured at the start of each experimental run.

After examining that pH of the solution was maintained at the predetermined level, O_2 gas was added to the above gas stream, and the oxidation was started. The partial pressure of O_2 in the mixed gas stream was maintained at 0.2 atm . The flow rate of the mixed gas was represented by the Reynolds number at the glass nozzle. It is possible to correlate this Reynolds number with the size distribution of rising gas bubbles in the solution by applying the experimental results obtained by Leibson⁵⁾ and Tadaki.⁶⁾ At the appropriate time intervals after the start of oxidation, aliquots of the solution were pipetted and placed in $1:4\text{ H}_2\text{SO}_4$ solution to quench the reaction. Colloidal hydroxide was dissolved by heating the solution, and the concentration of Fe^{2+} ion was determined by titrating it against a standard 0.01 M KMnO_4 solution.

In the first place, the effect of pH was studied. By changing the partial pressure of CO_2 in the mixed gas stream, pH was adjusted at a predetermined level between 6.0 and 7.7 . The oxidation was conducted at 25°C . The flow rate of the mixed gas stream was maintained at the Reynolds number of 4000 at the glass nozzle. The results are shown in Fig. 3. As seen in this figure, the overall rate of oxidation increased with pH. It is also seen that CO_2 rose from the start of oxidation and imme-

Fig. 3 Effect of pH on the rate of oxidation (25°C , $\text{Re}=4000$)

$\circ$ — $C_{\text{Fe}^{2+}}$ at pH 6.0, $\cdots \circ$ — $\text{CO}_2/\text{CO}_2^s$ at pH 6.0
 $\bullet$ — 6.5, $\cdots \bullet$ — 6.5
 $\triangle$ — 6.7, $\cdots \triangle$ — 6.7
 $\blacktriangle$ — 7.1, $\cdots \blacktriangle$ — 7.1
 $\square$ — 7.3, $\cdots \square$ — 7.3
 $\blacksquare$ — 7.7, $\cdots \blacksquare$ — 7.7

Fig. 4 Plot of $\log C_{\text{Fe}^{2+}}$ vs. θ

$\circ$ — pH=6.0, $\bullet$ — pH=6.5, $\triangle$ — pH=6.7
 $\blacktriangle$ — pH=7.1, $\square$ — pH=7.3, $\blacksquare$ — pH=7.7

diately reached the saturation at pH of 6.0 and 6.5. At pH higher than 6.7, on the other hand, C_{O_2} was found to be zero until $C_{Fe^{2+}}$ was lowered to about 0.004M due to the progress of oxidation, and thereafter it increased. In order to seek for the experimental rate equation, $\log C_{Fe^{2+}}$ was plotted against θ in Fig. 4. As seen from the plots at pH 6.0 and 6.5, they were linear. This means that the first order rate equation holds at these pH. On the contrary, it was observed in Fig. 3 that $C_{Fe^{2+}}$ linearly decreased in the oxidation at pH above 6.7 during the period in which C_{O_2} was zero. This may suggest that the zero order rate equation holds during this period of oxidation.

The effect of temperature was examined. At the temperature of 0°, 10°, 15°, 25° and 35°C, the mixed gas was bubbled at the Reynolds number of 1000, and pH was maintained at 6.8. The experimental results are summarized in Fig. 5. It is seen in this figure that the

Fig. 5 Effect of temperature on the rate of oxidation (pH 6.3, Re=1000)

rate of oxidation increased with the temperature. It is also seen at lower temperature that C_{O_2} rose immediately after the start of oxidation. At higher temperature of 25° and 35°C, on the contrary, the rise of C_{O_2} was retarded, and $C_{Fe^{2+}}$ decreased linearly with the elapsed time during the period of zero C_{O_2} , which implied a zero order reaction. From the examination of the plot of $\log C_{Fe^{2+}}$ versus θ , no linear relationship was found.

In order to pursue the effect of the flow rate of the mixed gas stream, the oxidation was carried out at 25°C at various Reynolds numbers between 500 and 6000. The pH value was maintained at 6.8. The results are summarized in Fig. 6. As seen in this figure, the rate of oxidation increased with the Reynolds number. It is also seen that C_{O_2} remained extremely low during the course of oxidation at the lower Reynolds number. It rose sooner after the start of oxidation at higher Reynolds

Fig. 6 Effect of Reynolds number on the rate of reaction (25°C, pH 6.3)

number. The concentration of Fe^{2+} ion linearly decreased at lower Reynolds number of 500 and 1000 during the period in which C_{O_2} was very low. From the plot of $\log C_{\text{Fe}^{2+}}$ versus θ , however, no linear relationship was found even when the Reynolds number is higher.

3 Discussion

As mentioned earlier, the oxidation of a neutral FeSO_4 solution by O_2 gas is composed of the sequential steps of the dissolution of O_2 gas at the surface of rising gas bubbles and the oxidation of Fe^{2+} ion by O_2 in the solution, which were shown in eq. (1) and (3), respectively. Furthermore, the former step of oxygen dissolution occurring at the gas-liquid interface may be composed of

1. the mass transfer of O_2 gas in the gas boundary film within the bubbles,
2. the dissolution of O_2 gas at the bubble surface, and
3. the mass transfer of O_2 in the liquid boundary film adjacent to the bubbles.

It may be a reasonable presumption that the step 3 determines the overall rate of oxygen dissolution.

Regarding the rate of reaction between Fe^{2+} ion and O_2 , eq. (4) proposed by Stumm *et al.*²⁾ may be rewritten as

$$-\frac{dC_{\text{Fe}^{2+}}}{d\theta} = k_1 C_{\text{Fe}^{2+}} C_{\text{O}_2} C_{\text{OH}^-} \quad (5)$$

On the other hand, Holluta *et al.*⁷⁾ proposed that the oxidation of Fe^{2+} ion is composed of the sequential reactions of

and

and the overall rate is determined by the former reaction (6). They proposed the rate equation of

$$-\frac{dC_{\text{Fe}^{2+}}}{d\theta} = k_2 C_{\text{Fe}^{2+}} C_{\text{O}_2} C_{\text{OH}^-} \quad (8)$$

These rate equations (5) and (8) may be expressed in a generalized form of

$$-\frac{dC_{\text{Fe}^{2+}}}{d\theta} = k_r C_{\text{Fe}^{2+}} C_{\text{O}_2}^\alpha C_{\text{OH}^-} \quad (9)$$

In this equation, the parameter α is between 1

and 2.

The time variation of C_{O_2} is written as

$$\frac{dC_{\text{O}_2}}{d\theta} = \frac{S}{V} k_L (C_{\text{O}_2}^{(s)} - C_{\text{O}_2}) + \frac{1}{4} \frac{dC_{\text{Fe}^{2+}}}{d\theta} \quad (10)$$

The superscript (s) denotes the saturated value. The first term on the right-hand side of this equation represents the dissolving rate of O_2 gas which is determined by the transferring rate of O_2 in the liquid boundary film of gas bubbles, and the second term represents the consuming rate of O_2 due to the reaction with Fe^{2+} ion.

When the overall rate of the oxidation is controlled solely by the dissolving rate of O_2 gas, C_{O_2} is presumed to be $C_{\text{O}_2}^{(e)}$ which is the equilibrium concentration of O_2 of eq. (3). It is unvaried at a constant temperature.

Then

$$\frac{dC_{\text{O}_2}}{d\theta} = 0 \quad (11)$$

Furthermore, presuming that $C_{\text{O}_2}^{(e)}$ is far lower than $C_{\text{O}_2}^{(s)}$, eq. (10) is rewritten as

$$\frac{dC_{\text{Fe}^{2+}}}{d\theta} = -\frac{4S}{V} k_L C_{\text{O}_2}^{(s)} \quad (12)$$

which is the zero order rate equation.

When the overall rate is solely controlled by the rate of reaction between Fe^{2+} ion and O_2 , on the other hand, C_{O_2} is presumed to be equal to $C_{\text{O}_2}^{(s)}$.

Then eq. (9) is rewritten as

$$-\frac{dC_{\text{Fe}^{2+}}}{d\theta} = k_r C_{\text{Fe}^{2+}} C_{\text{O}_2}^{(s)} C_{\text{OH}^-} \quad (13)$$

It is the first order rate equation with regard to $C_{\text{Fe}^{2+}}$ when pH is maintained constant.

When the overall rate of the oxidation is affected by both rates of the dissolution of O_2 gas and the reaction Fe^{2+} ion and O_2 , C_{O_2} does not remain constant but increases along with the progress of the oxidation. By eliminating C_{O_2} from the simultaneous rate equations (9) and (10), we have

$$\begin{aligned} k_r' &= k_r C_{\text{OH}^-}^\alpha \\ &= \frac{1}{C_{\text{Fe}^{2+}}} \left(\frac{dC_{\text{Fe}^{2+}}}{d\theta} \right)^2 - \frac{S}{V} k_L \frac{dC_{\text{Fe}^{2+}}}{d\theta} - \frac{d^2 C_{\text{Fe}^{2+}}}{d\theta^2} \\ &= \frac{C_{\text{Fe}^{2+}} \left(-\frac{S}{V} k_L C_{\text{O}_2}^{(s)} + \frac{1}{4} \frac{dC_{\text{Fe}^{2+}}}{d\theta} \right)}{C_{\text{Fe}^{2+}} \left(-\frac{S}{V} k_L C_{\text{O}_2}^{(s)} + \frac{1}{4} \frac{dC_{\text{Fe}^{2+}}}{d\theta} \right)} \end{aligned} \quad (14)$$

From this equation, the rate constant k_r' ($=k_r C_{\text{OH}}^\alpha$) was calculated. The mixed gas stream of O_2 , N_2 and CO_2 was blown through the same glass nozzle shown in Fig. 2 into the reaction vessel filled with deionized water, and the dissolving rate of O_2 gas was measured. The obtained $(S/V)k_L$ values were used in the calculation. The value of $C_{\text{O}_2}^{(s)}$ was referred to a literature⁸⁾ presuming that $C_{\text{O}_2}^{(s)}$ in water and in aqueous FeSO_4 solution are virtually equal. Furthermore, $(dC_{\text{Fe}^{2+}}/d\theta)$ and $(d^2C_{\text{Fe}^{2+}}/d\theta^2)$ values were obtained graphically from the plot of $C_{\text{Fe}^{2+}}$ versus θ .

The calculation was carried out with the experimental results of Fig. 3, and the logarithm of the obtained k_r' value was plotted against pH. It is shown in Fig. 7. It is seen

Fig. 7 Plot of $\log k_r'$ vs. pH (25°C, $\text{Re}=4000$)

that a linear relationship holds between them. From the slope of this straight line, the parameter α was calculated to be 1.33 by the least squares method. It may be written that

$$k_r = k_r' / C_{\text{OH}}^{1.33} \quad (15)$$

Under the experimental conditions that the temperature is 0°, 10° and 15°C and the Reynolds number is maintained at 1000 shown in Fig. 5 and that the temperature is maintained at 25°C and the Reynolds number is 2000, 3000, 4000 and 6000 shown in Fig. 6, respectively, it is thought that the oxidation is

Fig. 8 Plot of $\log k_r$ vs. $C_{\text{Fe}^{2+}}$

- at 0°C and $\text{Re}=1000$, -●- at 25°C and $\text{Re}=2000$
 -△- 10°C $\text{Re}=1000$, -▲- 25°C $\text{Re}=3000$
 -□- 15°C $\text{Re}=1000$, -■- 25°C $\text{Re}=4000$
 -◆- 25°C $\text{Re}=6000$

of mixed control of the mass transfer of O_2 and the chemical reaction. The rate constant k_r was calculated from these experimental results, and $\log k_r$ was plotted against $C_{\text{Fe}^{2+}}$ in Fig. 8. In this figure, no systematic time variation of k_r is observed along the progress of the oxidation. The temperature variation of the mean value of k_r is evident, while it is virtually unvaried at different Reynolds numbers. From this behavior of k_r value, the calculated k_r is thought to satisfy the condition that the reaction

Fig. 9 Arrhenius plot of k_r

(3) is of homogeneous character. From the Arrhenius plot of the mean k_r values shown in Fig. 9, the activation energy of 21 kcal/mol was obtained. This value is in good agreement with 23 kcal/mol reported by Stumm *et al.*²⁾

The temperature variation of the liquid-film mass transfer coefficient of O_2 in the form of Sk_L was also investigated: Sk_L values were calculated from the slope of the straight lines at 15°, 25° and 35°C shown in Fig. 5, and $\ln(Sk_L)$ was plotted against $1/T$. The obtained apparent activation energy was 7 kcal/mol. This value is thought to be appropriate as a measure of temperature variation of the mass transfer coefficient in liquid phase.

Furthermore, the variation of Sk_L due to the flow rate of the mixed gas flow was investigated. It was presumed from Fig. 6 that the mass transfer of O_2 in the liquid boundary film is the rate determining step below the Reynolds number of 1000 and that the oxidation is of mixed control of mass transfer and chemical reaction above the Reynolds number of 2000. The Sk_L value was calculated from the linear portion of $C_{Fe^{2+}}$ versus θ curves obtained in the former stage of the oxidation shown in Fig. 6 where C_{O_2} is maintained at zero. They were plotted against the Reynolds number in Fig. 10. As seen in this diagram, Sk_L value

Fig. 10 Plot of Sk_L vs. Re (25°C, pH 6.8)

linearly increases with the Reynolds number. The increase of Sk_L value may be mainly attributed to the increased surface area of the rising gas bubbles at higher Reynolds number.

4 Summary

The oxidation of neutral $FeSO_4$ solution by O_2 gas was studied in the present work. The mixed gas of nitrogen, oxygen and CO_2 was blown from an upward vertical glass nozzle of 0.5 mm in inner diameter into the solution. The pH of the solution was maintained at the predetermined level between 6.0 and 7.7 by changing the partial pressure of CO_2 in the mixed gas stream. The concentrations of Fe^{2+} ion and the dissolved oxygen were measured during the progress of the oxidation.

The overall rate of oxidation increased with the rise of pH. At pH above 6.7, the concentration of dissolved oxygen was maintained at zero in the former part of the oxidation, and the overall rate was controlled by the transferring rate of dissolved oxygen in the liquid boundary film adjacent to the gas bubbles. The rate of reaction between Fe^{2+} ion and dissolved oxygen was revealed to be proportional to the 4/3 th power of C_{OH^-} .

The temperature variation of the overall rate of oxidation was pursued with the aqueous solution of pH 6.8 and at the Reynolds number of 1000. At higher temperature above 25°C, the concentration of dissolved oxygen was virtually zero during the progress of oxidation, and the reaction was of mass transfer control of dissolved oxygen. At lower temperature, on the other hand, the overall rate was affected by both rates of mass transfer and chemical reaction. The rate constant of the reaction between Fe^{2+} ion and dissolved oxygen was calculated, and the activation energy of 21 kcal/mol was obtained.

The overall rate of the oxidation increased with the Reynolds number of the mixed gas stream under the experimental conditions of 25°C and pH 6.8. In the region below the Reynolds number of 1000, the concentration of dissolved oxygen remained extremely low, and the oxidation was of mass transfer control. The transferring rate of dissolved oxygen in the liquid boundary film increased with the Reynolds number mainly due to the increase of the surface area of rising gas bubbles. In the region of the Reynolds number above 2000, the oxidation was of mixed control of mass transfer and chemical reaction.

Nomenclature

C : Concentration	[mol/l]
k : Rate constant	[l ² /mol ² ·atm·s]
k_1 : Rate constant	[l ³ /mol ³ ·s]
k_2 : Rate constant	[l ² /mol ² ·s]
k_L : Liquid-film mass transfer coefficient	[cm/s]
k_r : Rate constant	[l ² ·s ³ /mol ² ·s]
p_{O_2} : Partial pressure of oxygen	[atm]
S : Total surface area of gas bubbles	[cm ²]
t : Temperature	[°C]
T : Absolute temperature	[K]
V : Volume of solution	[cm ³]

Greek letters

α : Parameter	[—]
θ : Time	[s]

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