KINETICS OF THE OXIDATION OF AQUEOUS SODIUM SULFITE SOLUTIONS WITH AIR

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The catalytic oxidation of aqueous sodium sulfite solutions by dissolved oxygen has been applied to the evaluation of mass transfer characteristics in gas-liquid contactors. Therefore, the kinetics of this reaction has been studied by many workers. There are, however, some differences in the rate expressions in those studies.

In this work, the absorption rate of oxygen from air into aqueous sodium sulfite solutions was measured in the regime of the fast second-order reaction, with cobaltous sulfate as a catalyst, in a stirred cell. Effects of such variables as cobalt concentration, pH of the solution and temperature on the rate constant were investigated and the rate constant was expressed as a function of these variables.

1. Experimental

According to the review by Linek *et al.*⁽⁶⁾, when air at atmospheric pressure is used and the sulfite concentration is larger than its critical value⁽¹⁰⁾, the reaction rate of sulfite oxidation is second-order with respect to dissolved oxygen and zero-order with respect to sulfite. As a result, oxygen absorption into sulfite solutions can be considered as an absorption enhanced by this irreversible fast second-order reaction when the Hatta number⁽²⁾ is a fully large value.

A Pyrex glass stirred cell with four baffle plates was used and set up in a water bath. The experimental conditions are shown in Table 1. The pH of the solution was adjusted by adding a proper amount of 1N sulfuric acid and was measured by a pH meter. Sampling the liquid phase from the cell at fifteen-minute intervals during the course of the absorption run, sulfite concentration and cobalt concentration were determined by iodometry and EDTA chelate titration, respectively.

From the mass balance, a relation between variation of the sulfite concentration in the cell and time was derived as follows.

$$\Delta C = C_{\text{SO}_3^{2-}}^0 - C_{\text{SO}_3^{2-}} = \left\{ 2\sqrt{\frac{2}{3}} k D_{\text{O}_2} \left(\frac{A}{V} \right) \left(\frac{p_{\text{O}_2}}{H} \right)^{3/2} \right\} t \quad (1)$$

A plot of ΔC against t gave a good linear relationship in each run. The rate constant k was calculated from the slope of each straight line by using Eq. (1).

2. Results and Discussion

2.1 Effect of cobalt

Log-log plots of rate constant k against cobalt concentration C_{Co} are shown in Fig. 1 for various pH, including the results* presented by other workers^(9,11).

Table 1 Experimental conditions

$C_{\text{SO}_3^{2-}}^0$	$= 0.8 \text{ kmol} \cdot \text{m}^{-3}$
C_{Co}	$= 1.69 \times 10^{-5} - 1.69 \times 10^{-3} \text{ kmol} \cdot \text{m}^{-3}$
pH	$= 7.7-9.3$
T	$= 298 \text{ K}$
$D_{\text{O}_2}^{(3)}$	$= 1.85 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ at 298 K
$H^{(6)}$	$= 1.522 \times 10^8 \text{ Pa} \cdot \text{m}^3 \cdot \text{kmol}^{-1}$
$k_L^{(4)}$	$= 1.1 \times 10^{-5} - 2.7 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}$
r	$= 13.5-102.7$
A	$= 1.205 \times 10^{-2} \text{ m}^2$
V	$= 1.0 \times 10^{-3} \text{ m}^3$
Q_A	$= 2.0 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$

Fig. 1 Effect of cobalt concentration on second-order rate constant

* All values of rate constants quoted from the literature were corrected by using the solubilities recommended by Linek *et al.*⁽⁶⁾.

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Fig. 2 Effect of pH of solutions on second-order rate constant

It is found from Fig. 1 that k is first-order with respect to C_{O_2} for each pH. This agrees with the results already reported by other workers⁵⁻¹¹.

2.2 Effect of pH on the rate constant

Several workers^{1,5-13} have pointed out that the rate constant is strongly dependent on pH. However, there are some differences in its dependency. In this work, the effect of pH on k was investigated in the range of $7.7 \leq \text{pH} \leq 9.3$. The plots of k/C_{O_2} against pH are shown in Fig. 2 for various temperatures.

In Fig. 2, the dependency of k on C_{H^+} estimated from the slope of each straight line was found to be independent of C_{O_2} , but it was affected by temperature even in a narrow range.

Furthermore, Figure 2 shows that k has a maximum at a high value of pH in the case of a large value of C_{O_2} . In the first-order regime with respect to dissolved oxygen, Onda *et al.*⁷) and Yasunishi¹²) reported the same tendency as this work. Onda *et al.*⁷) explained that the presence of the maximum of k was due to the formation of precipitates. In this work, however, no precipitates were found at pH slightly higher than the pH giving the maximum, which was the same as the result reported by Yasunishi¹²).

The value of pH at the maximum of k varied with C_{O_2} . The condition where k has its maximum value is approximately correlated as follows.

$$C_{O_2} \cdot C_{H^+}^{-2} = 3.4 \times 10^{14} \quad (2)$$

2.3 The relation between the activation energy and pH

Reith *et al.*⁹) reported that the activation energy E for the second-order rate constant varied with pH. However, no equation to express the relation between the values of E and pH has yet been proposed.

The fact that the dependency of k on pH varies with temperature, suggests that E will be expressed as a function of pH. Therefore, the Arrhenius plot

Fig. 3 Arrhenius plot of second-order rate constant

Fig. 4 Relationship between activation energy and pH

is shown in Fig. 3, including the results obtained by other workers^{6,8,9,11}), where the values at pH=7.7, 8.1, 8.4, and 8.8 were estimated by extrapolation of the straight lines in Fig. 2. Since the slope in Fig. 3 varies with pH, the activation energy E is obviously dependent on pH. Thus, the value of E is plotted against pH in Fig. 4 and the following linear relationship between E and pH was obtained.

$$E = 350 - 32.5 \text{ pH} \quad (3)$$

2.4 A correlation of the rate constant

Based on the effects of C_{O_2} and pH on k , the value of k at 298 K denoted by k^* was correlated as follows.

$$k^* = 3.28 \times 10^4 C_{O_2} C_{H^+}^{-0.69} \quad (4)$$

where

$$1.69 \times 10^{-5} \leq C_{O_2} \leq 1.69 \times 10^{-3}, 7.7 \leq \text{pH} \leq 8.8 \quad (5)$$

The value of k at another temperature can be expressed by using Eqs. (3) and (4). As a result, we have the relation

$$\frac{k}{k^*} = \exp \left\{ -\frac{350 - 32.5 \text{ pH}}{R} \left(\frac{1}{T} - \frac{1}{298} \right) \right\} \quad (6)$$

Fig. 5 Comparison of second-order rate constants calculated from Eqs. (4) and (6) with those observed experimentally

The expressions by Eqs. (4) and (6) were similar to those presented by Onda *et al.*⁷⁾ in the first-order regime with respect to dissolved oxygen.

A comparison of the calculated values k_{cal} from Eqs. (4) and (6) with the observed ones k_{obs} is shown in Fig. 4. The values of k_{cal} are in good agreement with those of k_{obs} for various conditions. Consequently, Eqs. (4) and (6) are found to be valid.

Nomenclature

A	= interfacial area in the cell	[m ²]
C_{Co}	= cobalt concentration	[kmol·m ⁻³]
C_{H^+}	= hydrogen ion concentration	[kmol·m ⁻³]
$C_{SO_3^{2-}}$	= sulfite concentration	[kmol·m ⁻³]
$C_{SO_3^{2-}}^0$	= initial sulfite concentration at $t=0$	[kmol·m ⁻³]

D_{O_2}	= diffusivity of oxygen	[m ² ·s ⁻¹]
E	= activation energy	[kJ·mol ⁻¹]
H	= Henry constant	[Pa·m ³ ·kmol ⁻¹]
k	= second-order rate constant	[kmol ⁻¹ ·m ³ ·s ⁻¹]
k^*	= value of k at 298K	[kmol ⁻¹ ·m ³ ·s ⁻¹]
k_L	= liquid-phase mass transfer coefficient in the cell	[m·s ⁻¹]
p_{O_2}	= oxygen partial pressure	[Pa]
Q_A	= air flow rate	[m ³ ·s ⁻¹]
R	= gas constant	[kJ·K ⁻¹ ·mol ⁻¹]
T	= temperature	[K]
t	= time	[s]
V	= liquid volume	[m ³]
γ	= Hatta number $\left(= \sqrt{\frac{2}{3}} \frac{k D_{O_2} \left(\frac{p_{O_2}}{H} \right)}{k_L} \right)$	[—]

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EFFECT OF WATER ON BENDING STRENGTH OF GLASS

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In the previous papers¹⁻³⁾, the authors discussed the difference between dry and wet grinding of nine kinds of materials using a small ball mill, from a kinetic point of view.

It has been considered that the difference in grindability in different atmospheres may arise from the change of surface energy, the degree of dispersion

of particles, the consumption of kinetic energy by water, the chemical reaction between water and material and some other reasons⁴⁻⁷⁾. However, there has been no satisfactory explanation because the quantitative effects of the above causes were not understood.

In this work, bending tests were carried out on glass material in order to investigate the quantitative effect of water on bending strength and crack prop-

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