A KINETIC STUDY OF LIQUID-PHASE OXIDATION OF SODIUM SULFIDE WITH OXYGEN CATALYZED BY SULFUR BLACK B DYE

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The waste water from dye-works and black liquor from digestion in the kraft pulp process[1] contain sodium sulfide which is toxic and has a high reducibility. These strongly alkaline solutions cause lowering of the dissolved oxygen in water, an increase in chemical oxygen demand, evolution of hydrogen sulfide as the solution becomes acidic, and corrosion of metals. Therefore, it is preferable that sodium sulfide be converted to sodium thiosulfate by oxidation to decrease chemical oxygen demand of waste water.

For the oxidation of an aqueous solution of soidum sulfide by oxygen, Maeda et al.[3] reported the effects of the presence of some dyes and the treated mud of town sewage on the absorption rate of oxygen. However, there have been few studies of the behavior of liquid compounds and kinetics of this oxidation.

In this investigation, the liquid-phase oxidation of sodium sulfide with oxygen catalyzed by sulfur dye Sulfur Black B* (SBB) has been studied kinetically on the basis of the characteristics of this reaction obtained experimentally.

1. Experimental

The measurement of the rate of oxidation with respect to liquid compounds was carried out with a stirred vessel[4] (volume: 1 l, I.D.: 115 mm, impeller: 6-flat blade turbine) under aeration, while that of the absorption rate of oxygen was performed in a batchwise operation by the usual procedure. Only the outlined experimental procedure using the stirred vessel under aeration will hereinafter be described.

The weighed sodium sulfide and SBB were charged together with distilled water into the stirred vessel under a purified nitrogen atmosphere. After the solution temperature in the vessel reached the desired level with agitation, oxygen gas was introduced to the bottom of the vessel through a ring sparger at the predetermined rate of gas flow.

Liquid samples were then withdrawn at regular intervals and were divided into two fractions. Zinc carbonate powder as a reaction-stopping agent was added immediately to precipitate soluble sulfides, while a large excess of sodium sulfite powder was added to convert disulfide*, one of the products, to thiosulfate in the other fraction. The former solution was termed (A), the latter (B)**. Solution (A) was filtered, and the amount of zinc sulfide, being the precipitate, and the concentrations of sulfite and thiosulfate in the filtrate were determined by iodometry and by high-performance liquid chromatography (Hitachi Model 635, detector: coulometry, column: Bio Rad AG (Hitachi)), respectively. Solution (B) was permitted to stand under a nitrogen atmosphere for at least 20 minutes, and zinc carbonate powder was then added to it. The subsequent analytical procedure for solution (B) was performed by the same as the procedure described above for solution (A).

2. Results and Discussion

2.1 Variation of concentration of liquid compounds with time for sodium sulfide degradation

With regard to the liquid-phase oxidation of sodium sulfide catalyzed by SBB, the time-course of concentrations of liquid compounds was followed. An example of the typical results is shown in **Fig. 1**. It was proved that sodium sulfide was simultaneously changed to sodium sulfite, sodium disulfide, and sodium thiosulfate, and that sodium thiosulfate was also formed by the reaction of sodium sulfite with sodium disulfide.

The preliminary investigations confirmed that the reaction of sodium sulfite with sodium disulfide in the absence of SBB under a nitrogen atmosphere was

* In the previous paper[5], we reported the catalyst activity and the selectivity for the liquid-phase oxidation of sodium sulfide with oxygen by various materials, and that SBB had a high activity as the catalyst for this oxidation reaction.

* Although there is a possibility of the presence of various forms of polysulfides, it was assumed that all polysulfides exist as sodium disulfide.

** As sodium disulfide is converted to sodium sulfide and sodium thiosulfate according to Eq. (5) by addition of excess sodium sulfite, determination of the concentration of sodium disulfide becomes possible.
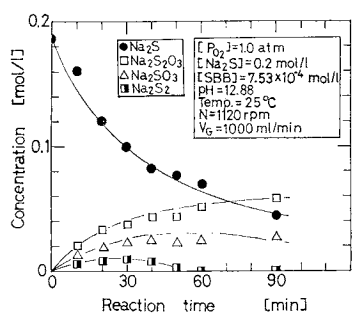
Fig. 1 The course of oxidation of sodium sulfide catalyzed by Sulfur Black B
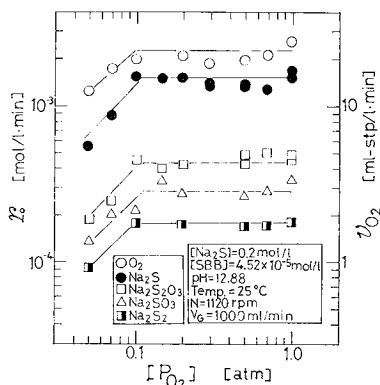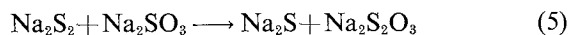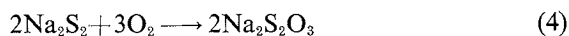

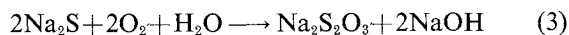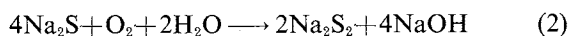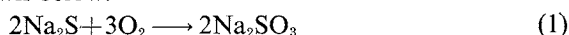Fig. 2 Effect of oxygen partial pressure on initial rate of disappearance of sodium sulfide, $r_{0(Na_2S)}$, and initial rates of formation of sodium disulfide, $r_{0(Na_2S_2)}$, sodium sulfite, $r_{0(Na_2SO_3)}$, and sodium thiosulfate, $r_{0(Na_2S_2O_3)}$, and absorption rate of oxygen, v_{O_2}

Fig. 3 Effect of sodium sulfide concentration on $r_{0(Na_2S)}$, $r_{0(Na_2S_2)}$, $r_{0(Na_2SO_3)}$, $r_{0(Na_2S_2O_3)}$, and v_{O_2}

Fig. 4 Effect of Sulfur Black B concentration on $r_{0(Na_2S)}$, $r_{0(Na_2S_2)}$, $r_{0(Na_2SO_3)}$, $r_{0(Na_2S_2O_3)}$, and v_{O_2}

very rapid and was almost irreversible (equilibrium constant: 3×10^8) to form sodium sulfide and sodium thiosulfate, and that sodium disulfide was directly oxidized to sodium thiosulfate. The overall chemical reaction equations associated with this oxidation are shown below.

$$2Na_2S + 3O_2 \longrightarrow 2Na_2SO_3 \qquad (1)$$

$$4Na_2S + O_2 + 2H_2O \longrightarrow 2Na_2S_2 + 4NaOH \qquad (2)$$

$$2Na_2S + 2O_2 + H_2O \longrightarrow Na_2S_2O_3 + 2NaOH \qquad (3)$$

$$2Na_2S_2 + 3O_2 \longrightarrow 2Na_2S_2O_3 \qquad (4)$$

$$Na_2S_2 + Na_2SO_3 \longrightarrow Na_2S + Na_2S_2O_3 \qquad (5)$$

Since in the absence of SBB the rates of oxidation of Eqs. (1) to (3) had a very low value, that is, a magnitude of about 10^{-5} mol/l·min as the disappearance rate of sodium sulfide, they were neglected in the measurement of the oxidation rate of sodium sulfide in the presence of SBB.

2. 2 Effects of reaction factors on initial rates of oxidation

1) Effects of concentrations of reactants   Under the condition that chemical reaction was rate-controlling (No effects of mass transfer were observed in the region above 800 rpm stirring speed and 800 ml/min gas
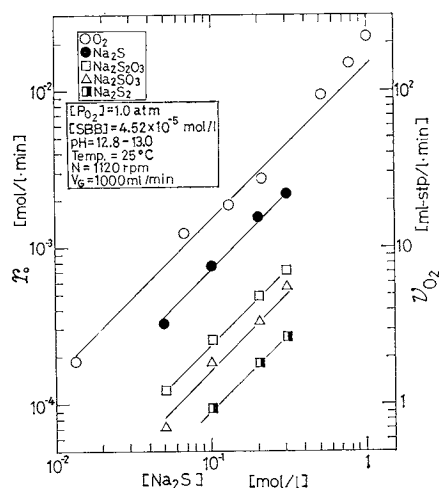
flow rate), effects of the partial pressure of oxygen and the concentrations of sodium sulfide and SBB on the initial rates of this oxidation were measured. The results obtained are shown in **Figs. 2** to **4**. As shown in Fig. 2, the rate was first-order with respect to oxygen in the region lower than 0.1 atm, while it was independent of oxygen in the upper region. Figures 3 and 4 show that the rate of oxidation was first- and half-order with respect to sodium sulfide and SBB, respectively.

Therefore, the empirical initial rate for all reactions was expressed as follows:

$$r_0 = k \, [\text{SBB}]^{1/2} \, [\text{Na}_2\text{S}] \, [\text{P}_{O_2}]^a \qquad (6)$$

where $a=1$ for $P_{O_2} < 0.1$ atm and $a=0$ for $P_{O_2} > 0.1$ atm. The values of rate constants, k, in Eq. (6) are shown in **Fig. 5**. The activation energies of all rates were found to be 16 Kcal/mol from the Arrhenius' plot of the rate constants.

That the apparent rates of formation for products are expressed in an identical equation, Eq. (6), may be

explanable by assuming that a common intermediate occurs in the course of the process in which sodium sulfide is converted to products, that the formation process of the common intermediate is the rate-determining step, and that the reaction process by which the common intermediate is converted to products is very rapid. The degradation rate of sodium sulfide is also expressed in Eq. (6), and accordingly it could be presumed that this oxidation reaction had a complicated mechanism involving chain reactions in the same manner as the liquid-phase oxidation of sulfite to form sulfate in the presence of metal-ion catalysts[2,6]. The detailed functions of SBB and oxygen in the liquid-phase oxidation of sodium sulfide couldn't be clarified, but it can be claimed that SBB, having the polysulfide bond and the part of indophenol in the ring structure, acted as the initiator of chain reactions and that oxygen reoxidized SBB reduced by sodium sulfide to produce its original form.

2) Effect of pH   Sodium sulfide dissociates in aqueous solution as shown below.

$$S^{2-}+H_2O \rightleftharpoons HS^-+OH^- \qquad (7)$$

$$HS^-+H_2O \rightleftharpoons H_2S+OH^- \qquad (8)$$
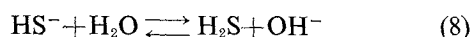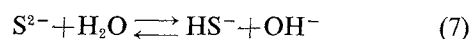
Effects of the pH of reaction solution on the initial rates of this oxidation are shown in **Fig. 6**. As hydrogen sulfide is evolved in solutions of pH less than 9, this oxidation was carried out in a pH range greater than 10.   In pH range 10–13.5, the rates of this oxidation increased in proportion to the apparently 0.15th-order with respect to the hydrogen ion concentration. Therefore, it was found that the increase in concentration of HS anion accelerated the rate of oxidation.

The oxidation of aqueous solution of ammonium sulfide, pH value 10.9, with oxygen catalyzed by SBB has also been carried out and the results obtained are shown in Fig. 6.   The results indicated agreement with those of oxidation of aqueous solution of sodium sulfide adjusted to pH 10.9.   Accordingly, under the same reaction conditions including pH of solution, it was found that the oxidation rate of an aqueous solution of ammonium sulfide would be equivalent to that of an aqueous solution of sodium sulfide.

2. 3   Correlation between absorption rate of oxygen and oxidation rates for liquid compounds

According to the oxidation reactions of Eqs. (1) to (3), the absorption rate of oxygen expressed with molar concentration is related to the initial rates of oxidation for liquid compounds as shown below.

$$r_{O_2}=(P_{O_2}/RT)(dV_{O_2}/dt)=P_{O_2}\cdot v_{O_2}/RT$$

$$=-d[Na_2S]/dt+d[Na_2SO_3]/2dt-3d[Na_2S_2]/2dt$$

$$=r_{0(Na_2S)}+r_{0(Na_2SO_3)}/2-3r_{0(Na_2S_2)}/2 \qquad (9)$$

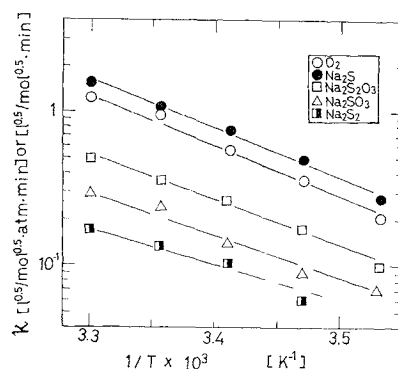In Eq. (9), the observed values of the second term and the third term on the right-hand side were about

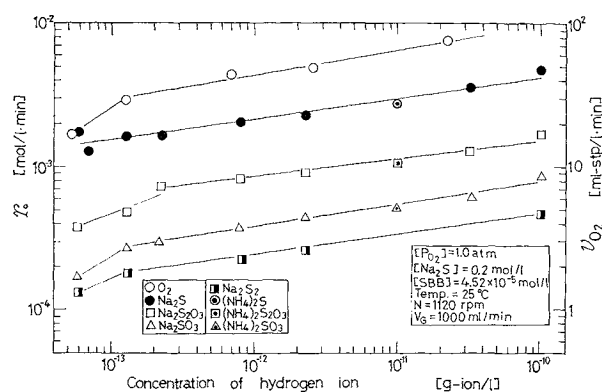**Fig. 5   Temperature dependency of rate constants**

Fig. 6   Effect of hydrogen ion concentration on
$r_{0(Na_2S)}, r_{0(Na_2S_2)}, r_{0(Na_2SO_3)}, r_{0(Na_2S_2O_3)},$ and v_{O_2}

one-eighth that of the first term, and also the value of the second term and that of the third term were compensated by each other.   Consequently, the absorption rate of oxygen became nearly equal to the disappearance rate of sodium sulfide.   It was therefore regarded that 1 mole of sodium sulfide apparently reacted with 1 mole of oxygen.

Nomenclature

k	= rate constant	
	$[l^{1/2}/mol^{1/2}\cdot atm\cdot min],[l^{1/2}/mol^{1/2}\cdot min]$	
N	= rate of stirring	[1/min]
$[Na_2S]$	= concentration of sodium sulfide	[mol/l]
$[Na_2S_2]$	= concentration of sodium disulfide	[mol/l]
$[Na_2SO_3]$	= concentration of sodium sulfite	[mol/l]
$[P_{O_2}]$	= partial pressure of oxygen	[atm]
R	= ideal gas law constant	[atm·l/mol·K]
r	= reaction rate	[mol/l·min]
r_0	= initial rate	[mol/l·min]
[SBB]	= concentration of Sulfur Black B	[mol/l]
T	= temperature	[K]
t	= reaction time	[min]
V_G	= rate of gas flow	[ml/min]
V_{O_2}	= absorption volume of oxygen	[ml-stp/l]
v_{O_2}	= absorption rate of oxygen	[ml-stp/l·min]

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A MODIFIED QUASI-CHEMICAL THEORY BASED ON LOCAL COMPOSITION

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Introduction

Many local composition equations have been proposed since Wilson first advanced this concept. Some are directly or indirectly derived from regular solution theory. Andiappan and McLean[1] and Nagata and Nagashima[7] proposed equations applied directly from the first approximation equation of regular solution theory[3] and discussed the usability of their equations. These equations seem to reduce the equations of regular solution theory to equations having two adjustable parameters rather than to those applying the local composition.

In this investigation a new equation is proposed, in which the regular solution equation is combined with a local composition. By using this equation, some binary and ternary vapor-liquid equilibrium data were correlated and predicted.

1. Derivation and Discussion

According to the first approximation equation of regular solution theory, the excess molar Gibbs free energy is given as the following, provided that the Gibbs free energy may be substituted by the Helmholtz free energy:

$$\frac{g^E}{RT}=\frac{z}{2}\left\{x_1\ln\frac{\beta'+x_1-x_2}{x_1(\beta'+1)}+x_2\ln\frac{\beta'+x_2-x_1}{x_2(\beta'+1)}\right\} \quad (1)$$

$$\beta'=\sqrt{1+4x_1x_2(\eta'^2-1)} \quad (2)$$

$$\eta'=\exp(w'/zRT) \quad (3)$$

where w' denotes the interchange energy.

Andiappan[1] applied this equation directly and distinguished between β' of the first term of Eq. (1) and β' of the second term. According to Eqs. (2) and (3),

this is equivalent to distinguishing between interchange energy w'_{12} and w'_{21}. Andiappan's equation, therefore, has two adjustable parameters.

On the other hand, Nagata[7] proposed a quadratic equation of composition for g^E/RT for a binary system. It is composed of the sum of two terms having β_{12} or β_{21} in each term in place of β' in Eq. (1). Nagata pointed out that Andiappan's equation cannot be applied to multicomponent systems. In fact, Andiappan's original paper and a subsequent paper[2] did not show the calculated results. The multicomponent equation in Nagata's paper is successfully derived but tedious.

In this paper, taking account of the concept of local composition to the number of pairs, a relationship to the free energy is derived. The number of pairs and related quantities are shown in **Table 1**. For convenience let g_{11}, the pair energy per pair, be $g_{11}=(-2\chi_1/z)$ and $g_{22}=-2\chi_2/z$, $g_{12}=(-\chi_1-\chi_2+w'_{12})/z$, $g_{21}=(-\chi_1-\chi_2+w'_{21})/z$, $x_{21}=\xi_{21}/N_1$ and $x_{12}=\xi_{12}/N_2$. Then the configurational energy of mixing is given by

$$E_c=z/2\{N_1x_{21}(g_{21}-g_{11})+N_2x_{12}(g_{12}-g_{22})\} \quad (4)$$

where x_{21} and x_{12} denote the local compositions and are given by

Table 1 Numbers and certain related quantities of pairs

Kind of pair	Number of pair	Energy per pair	Energy of all such pairs
$1\rightarrow1$	$(N_1-\xi_{21})z/2$	$-2\chi_1/z$	$-(N_1-\xi_{21})\chi_1$
$1\rightarrow2$	$\xi_{21}z/2$	$(-\chi_1-\chi_2+w'_{21})/z$	$\xi_{21}(-\chi_1-\chi_2+w'_{21})/2$
$2\rightarrow1$	$\xi_{12}z/2$	$(-\chi_1-\chi_2+w'_{12})/z$	$\xi_{12}(-\chi_1-\chi_2+w'_{12})/2$
$2\rightarrow2$	$(N_2-\xi_{12})z/2$	$-2\chi_2/z$	$-(N_2-\xi_{12})\chi_2$
all	$(N_1+N_2)z/2$	—	$-N_1\chi_1+\xi_{21}(\chi_1-\chi_2+w'_{21})/2$ $-N_2\chi_2+\xi_{12}(-\chi_1+\chi_2+w'_{12})/2$