(24). If, however, one considers the presence of copper-ascorbate complexes [Equation (A11)], then the expression must be modified. The concentrations of unbound copper and total copper are related by

$$[\mathrm{Cu}]^{2+} = \frac{[\mathrm{Cu}](K_a + [\mathrm{H}^+])}{K_a + [\mathrm{H}^+] + K_a K^M [T_A]} \quad \text{(A19)}$$

Equation (A18) thus can be put into the form of Equation (37):

$$R_{\mathrm{ASC}} = -k_3 K_a K^M \left(\frac{k_1}{k_4} K^{\mathrm{O}_2} K^{DH} \right)^{1/2} \frac{[\mathrm{Cu}][T_A][\mathrm{O}_2]^{1/2}}{K_a + [\mathrm{H}^+] + K_a K^M [T_A]} \quad \text{(A20)}$$

Other mechanisms leading to the same rate expression can also be proposed. One that involves a copper (I)-copper (III) transition rather than copper (II) dimers is as follows:

$$\mathrm{AH_2} \overset{K_a}{\rightleftarrows} \mathrm{AH^-} + \mathrm{H^+}$$

$$\mathrm{AH^-} + \mathrm{Cu^{2+}} \overset{K^M}{\rightleftarrows} [\mathrm{Cu(II)AH}]^+$$

$$[\mathrm{Cu(II)AH}]^+ + \mathrm{Cu^{2+}} \xrightarrow{k_i} 2\mathrm{Cu^+} + \mathrm{A} + \mathrm{H^+}$$

$$\mathrm{Cu^+} + \mathrm{O_2} \xrightarrow{k_1} [\mathrm{Cu(III)O_2}]^+$$

$$[\mathrm{Cu(III)O_2}]^+ + \mathrm{AH^-} \xrightarrow{k_2} \mathrm{HO_2^-} + [\mathrm{Cu(II)A}]^+$$

$$[\mathrm{Cu(II)A}]^+ \xrightarrow{k_3} \mathrm{Cu^+} + \mathrm{A}$$

$$\mathrm{Cu^+} + [\mathrm{Cu(III)O_2}]^+ \xrightarrow{k_t} 2\mathrm{Cu^{2+}} + \mathrm{O_2^{2-}}$$

From this mechanism, expressions (A9) and (A19), and the assumption of equal rates of initiation and termination, a rate expression of the form of Equation (37) results:

$$R_{ASC} = -K_a \left(K^M k_1 k_2 \frac{k_i}{k_t} \right)^{1/2} \frac{[\mathrm{Cu}][T_A][\mathrm{O}_2]^{1/2}}{K_a + [\mathrm{H}^+] + K_a K^M [T_a]} \quad \text{(A21)}$$

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Absorption of Sulfur Dioxide into Aqueous Sodium Hydroxide and Sodium Sulfite Solutions

The rates of absorption of pure sulfur dioxide into aqueous sodium bisulfite, sodium hydroxide, and sodium sulfite solutions with and without a surface active agent were measured at 25°C using a liquid jet column. For the sulfur dioxide-sodium hydroxide system, the rate of absorption into the solution without surface active agent was higher than that into the solution with surface active agent, indicating the existence of the interfacial turbulence. The absorption rates obtained for the present system under the conditions of no interfacial turbulence were in good agreement with the theoretical predictions based on the penetration theory.

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SCOPE

The removal of sulfur dioxide from gas mixtures by contacting the gases with an aqueous alkali hydroxide solution is an important industrial absorption process for control of air pollution. However, there have been very few studies of the mechanism of chemical absorption for the SO_2-OH^- ions system. Goettler (1967) discussed the chemical absorption mechanism for the sulfur dioxide-sodium hydroxide system in his thesis which reported the results of a theoretical and experimental investigation of simultaneous absorption of sulfur dioxide and carbon dioxide into aqueous sodium hydroxide solutions flowing over a single sphere. A model based on the assumption that the reaction between the dissolved sulfur dioxide and OH^- ions is a two-step instantaneous reaction and two reaction planes are formed within the liquid phase was proposed, and a film theory solution for the reaction factor was presented. However, the direct experimental confirmation of this model was not attempted. Onda et al. (1971) absorbed sulfur dioxide into agar-agar gel containing sodium hydroxide or sodium sulfite at very long exposure times of the liquid in the range 900 to 9 000 s. They studied mainly the behavior of the reaction-plane movement by observing the position of the color change plane in the gel solution containing a indicator. The experimental results for the sulfur dioxide-sodium hydroxide system were found to agree with the penetration theory predictions based on the two reaction plane model proposed by Hikita et al. (1972).

The purposes of the study described in this paper are to obtain reliable data on the absorption rate of sulfur dioxide into aqueous sodium bisulfite, sodium hydroxide, and sodium sulfite solutions at the short exposure times encountered in industrial absorbers, to check for the existence of interfacial turbulence in these absorption systems, to propose reasonable methods of predicting the physical properties of the present systems, and to test the applicability of the two reaction plane model presented by Hikita et al. (1972) to the sulfur dioxide-sodium hydroxide system.

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CONCLUSIONS AND SIGNIFICANCE

Experiments have been carried out on the absorption of pure sulfur dioxide into aqueous sodium bisulfite, sodium hydroxide, and sodium sulfite solutions with and without a surface active agent using a liquid jet column.

For the sulfur dioxide-sodium hydroxide system, the rate of absorption into the solution without surface active agent is higher than that into the solution with surface active agent, and the difference between both rates of absorption becomes larger as the sodium hydroxide concentration and the exposure time of the liquid increase. This higher rate of absorption observed in the case of the solution without surface active agent may be attributed to interfacial turbulence, presumably produced by surface tension gradients during the chemical absorption process. For the sulfur dioxide-sodium bisulfite and sulfur dioxide-sodium-sulfite systems, on the other hand, both rates of absorption into the solutions with and without surface active agent are the same for each system, indicating the absence of the appreciable interfacial turbulence.

The absorption rates obtained for the present system under the conditions of no interfacial turbulence have been compared with the theoretical predictions based on the penetration theory. The absorption of sulfur dioxide into aqueous sodium bisulfite solutions is essentially physical, and the absorption rate can be represented by the well-known Higbie equation. The absorption of sulfur dioxide into aqueous sodium hydroxide solutions is accompanied by a two-step instantaneous reaction between the dissolved sulfur dioxide and OH^- ions in the solution, and the absorption rate data agree well with the theoretical predictions based on the two reaction plane model proposed by Hikita et al. (1972). The absorption of sulfur dioxide into aqueous sodium sulfite solutions is accompanied by an instantaneous irreversible reaction between sulfur dioxide and SO_3^{2-} ions in the solution, and the absorption rate results are in good agreement with the theoretical equation derived by Danckwerts (1950).

CHEMICAL ABSORPTION MECHANISM

When sulfur dioxide is absorbed into aqueous alkaline solutions, the following two reactions should be considered:

$$SO_2 + OH^- \rightleftharpoons HSO_3^- \qquad (1)$$

$$HSO_3^- + OH^- \rightleftharpoons SO_3^{2-} + H_2O \qquad (2)$$

The values of the equilibrium constants for reactions (1) and (2) are designated as K_1 and K_2 and they are given, respectively, as

$$K_1 = \frac{[HSO_3^-]}{[SO_2][OH^-]} = 1.7 \times 10^{12} \text{ l/g-mole}$$

$$K_2 = \frac{[SO_3^{2-}]}{[HSO_3^-][OH^-]} = 6.2 \times 10^{6} \text{ l/g-mole}$$

at 25°C and at infinite dilution. These values were estimated from the dissociation constants of sulfurous acid (Dean, 1973). Reaction (1) is very fast, with a rate constant exceeding 10^9 l/(g-mole) (s) (Saal, 1928). Reaction (2) has a very much higher rate constant than reaction (1), since it is a proton transfer reaction. Thus, both reactions (1) and (2) may be regarded as instantaneous reactions.

In strong hydroxide solutions, reaction (1) is followed by reaction (2). Thus, the overall reaction is

$$SO_2 + 2OH^- \rightarrow SO_3^{2-} + H_2O \qquad (3)$$

In aqueous sulfite solutions, OH^- ions are formed according to the instantaneous reversible reaction

$$SO_3^{2-} + H_2O \rightleftharpoons OH^- + HSO_3^- \qquad (4)$$

which is the reverse reaction of (2). Thus, the overall reaction in this case is

$$SO_2 + SO_3^{2-} + H_2O \rightarrow 2HSO_3^- \qquad (5)$$

Therefore, the reactions which affect the rate of absorption of sulfur dioxide into aqueous alkaline solutions are reaction (2) and the forward part of reaction (1).

In a previous paper, Hikita et al. (1972) considered the problem of gas absorption accompanied by an instantaneous two-step reaction

$$A + B \rightleftharpoons C \qquad (6)$$

followed by

$$C + B \rightleftharpoons E \qquad (7)$$

where the equilibrium constants of reaction steps (6) and (7) are also designated as K_1 and K_2 and are very large. They presented a theoretical analysis based on the penetration theory and found that the mechanism of chemical absorption in this case depends on the equilibrium constant ratio K_1/K_2. In the limiting case of $K_1/K_2 \rightarrow \infty$, it was shown that two reaction planes are formed within the liquid, and the reaction $A + E \rightleftharpoons 2C$ [the sum of reactions (6) and (7) in the reverse direction] and reaction (7) takes place irreversibly at the first reaction plane (which is located closer to the gas-liquid interface) and at the second reaction plane, respectively.

The average rate of absorption N_A of the solute gas A for this case can be represented by

$$N_A = \beta(2A_i\sqrt{D_A/\pi t}) \qquad (8)$$

The reaction factor for the present problem can be obtained from the following equations (Hikita et al., 1976):

$$\beta = 1/\text{erf}(\sigma_1) \qquad (9)$$

$$2\text{erfc}\left(\frac{\sigma_2}{\sqrt{r_B}}\right)\exp\left\{\left(\frac{1}{r_C} - 1\right)\sigma_1^2 + \left(\frac{1}{r_B} - \frac{1}{r_C}\right)\sigma_2^2\right\} = \sqrt{r_B}q_B\,\text{erf}(\sigma_1) \qquad (10)$$

$$\text{erfc}\left(\frac{\sigma_2}{\sqrt{r_{E3}}}\right)\exp\left\{\left(\frac{1}{r_{E2}} - 1\right)\sigma_1^2 + \left(\frac{1}{r_{E3}} - \frac{1}{r_{E2}}\right)\sigma_2^2\right\}$$
$$- 2\text{erfc}\left(\frac{\sigma_2}{\sqrt{r_{E3}}}\right)\exp\left\{\left(\frac{1}{r_C} - 1\right)\sigma_1^2 + \left(\frac{1}{r_{E3}} - \frac{1}{r_C}\right)\sigma_2^2\right\} + \sqrt{\frac{r_{E3}}{r_{E2}}}\,\text{erf}\left(\frac{\sigma_2}{\sqrt{r_{E2}}}\right)$$
$$- \text{erfc}\left(\frac{\sigma_1}{\sqrt{r_{E2}}}\right)\exp\left\{\left(\frac{1}{r_{E2}} - 1\right)\sigma_1^2\right\}$$

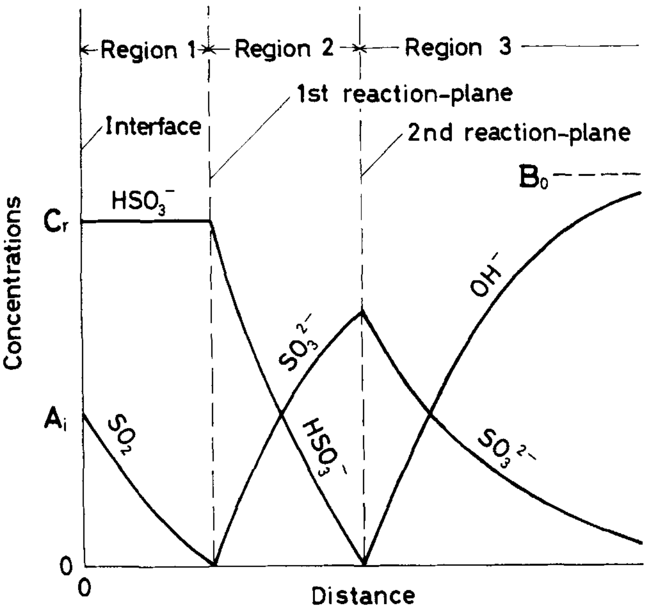

Fig. 1. Schematic diagram of concentration profiles for the absorption of sulfur dioxide into aqueous sodium hydroxide solution.

$$= \sqrt{r_{E3} q_E}\,\mathrm{erf}(\sigma_1) \qquad (11)$$

Here, σ_1 and σ_2 are the constants representing the dimensionless positions of the first and second reaction planes, and q_B, q_E, r_B, r_C, r_{E2}, and r_{E3} are the dimensionless parameters defined by

$$q_B = B_O/A_i \qquad q_E = E_O/A_i \qquad (12)$$

$$r_B = D_B/D_A \qquad r_C = D_C/D_A \qquad (13a)$$

$$r_{E2} = D_{E2}/D_A \qquad r_{E3} = D_{E3}/D_A \qquad (13b)$$

where the subscripts 2 and 3 for D_E denote the values in region 2 (the region between the first and second reaction planes) and region 3 (the region from the second reaction plane to infinite depth of the liquid phase), respectively. This absorption mechanism is called the two reaction plane model (Hikita et al., 1972).

When the species B is not present in the liquid phase, region 3 does not exist, and only the reaction $A + E \rightleftarrows 2C$ proceeds irreversibly at a single reaction plane. In this case, Equations (10) and (11) reduce to

$$\mathrm{erfc}\left(\frac{\sigma_1}{\sqrt{r_{E2}}}\right)\exp\left\{\left(\frac{1}{r_{E2}} - 1\right)\sigma_1^2\right\} = \sqrt{r_{E2} q_E}\,\mathrm{erf}(\sigma_1) \qquad (14)$$

from which the constant σ_1 can be determined. Therefore, the reaction factor in this case is the same as that for the infinitely rapid irreversible reaction represented by $A + E \rightarrow 2C$.

As stated above, the values of the equilibrium constants of reactions (1) and (2), K_1 and K_2, are 1.7×10^{12} and 6.2×10^6 l/g-mole, respectively. Hence, the equilibrium constant ratio k_1/K_2 is 2.7×10^5. Therefore, the chemical absorption theory described above may be applicable to the present system. According to this theory, the concentration profiles of each species for the SO_2-OH^- and SO_2-SO_3^{2-} systems will be similar to those shown in Figures 1 and 2. In the case of the SO_2-OH^- system, the irreversible reactions (5) and (2) may take place at the first and second reaction planes, respectively. On the other hand, in the case of the SO_2-SO_3^{2-} system, only the irreversible reaction (5) may occur at the single reaction plane.

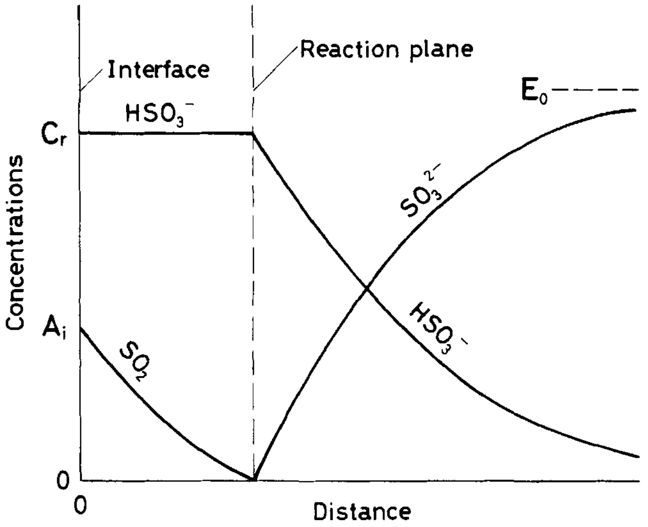

Fig. 2. Schematic diagram of concentration profiles for the absorption of sulfur dioxide into aqueous sodium sulfite solution.

Table 1. Compositions of Solutions Used

	Concentration of reactant, g-moles/l	
Solution	With surface active agent	Without surface active agent
Aq. $NaHSO_3$	2.0	2.0
Aq. NaOH	0.125	0.125
	0.25	0.25
	0.5	0.5
	1.0	1.0
	—	1.3
	—	1.6
	2.0	2.0
Aq. $NaSO_3$	—	0.069
	—	0.259
	0.960	0.960

EXPERIMENTAL

Apparatus and Procedure

Absorption experiments were carried out with a liquid jet column which was similar to that used by Hikita et al. (1968, 1973, 1976) in previous work. The laminar liquid jet was formed by a bell shaped glass nozzle with an exit diameter of 1.00 mm. The liquid flow rate was kept constant at about 4.3 cm^3/s, and the exposure time of the liquid to the gas was varied from 0.0008 to 0.017 s by changing the jet length from 0.5 to 8 cm. Absorption rate was determined volumetrically by means of a soap-film meter. All the experiments were conducted at atmospheric pressure and at 25°C.

The gas phase was pure sulfur dioxide saturated with water vapor, and the absorbents used were aqueous solutions of sodium bisulfite, sodium hydroxide, and sodium sulfite with and without 0.05 vol % of a surface active agent, Emulgen 147 (Kao-Atlas Co.). The compositions of the solutions are shown in Table 1.

Results

Sulfur dioxide-sodium bisulfite system. Experimental results obtained on the physical absorption of sulfur dioxide into 2.0 g-moles/l aqueous sodium bisulfite solution with and without surface active agent at 25°C are shown in Figure 3, where the average absorption rate N_A^* of sulfur dioxide is plotted against the exposure time t on logarithmic coordinates. The straight line in this figure represents the theoretical line for physical absorption, calculated from the well-known Higbie equation

$$N_A^* = 2A_i\sqrt{D_A/\pi t} \qquad (15)$$

where the physical solubility A_i and the liquid-phase diffusivity D_A of sulfur dioxide into 2.0 g-moles/l aqueous sodium bisul-

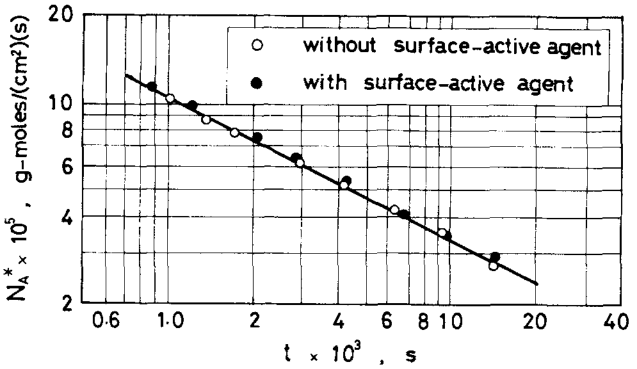

Fig. 3. Absorption rate of sulfur dioxide into 2.0 g-moles/l aqueous sodium bisulfite solution at 25°C.

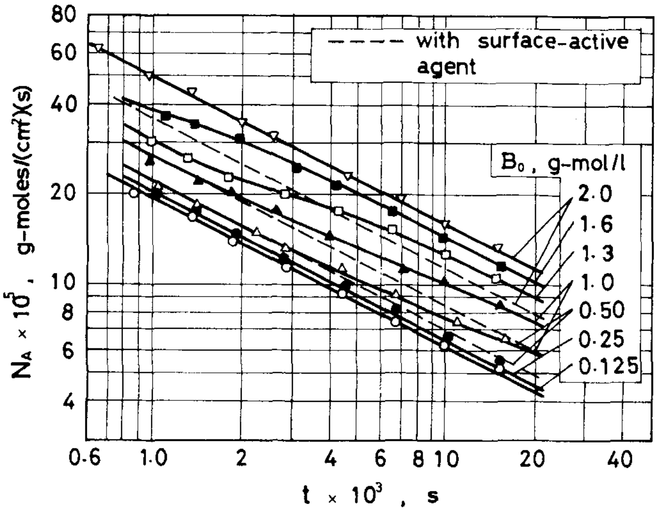

Fig. 5. Absorption rate of sulfur dioxide into aqueous sodium hydroxide solutions without surface active agent at 25°C.

fite solution are taken as 0.822 g-moles/l and 1.33×10^{-5} cm^2/s, respectively, which were estimated from the methods described below. It can be seen that the measured rates of absorption into the solutions with and without surface active agent are the same and agree very well with the theoretical line. This indicates that the penetration theory may be applicable to the analysis of the results of chemical absorption experiments and that interfacial turbulence may be absent in this system.

Sulfur dioxide-sodium hydroxide system. Figures 4 and 5 show the results for the absorption of sulfur dioxide into aqueous sodium hydroxide solutions with and without surface active agent at 25°C, respectively, as log-log plots of the average absorption rate N_A of sulfur dioxide vs. the exposure time t. The dashed lines in Figure 5 represent the results shown in Figure 4, that is, the absorption rates obtained for the solutions with surface active agent. It can be seen from this figure that the absorption rate into the solution without surface active agent, in general, is higher than that into the solution with surface active agent, and that the difference between the both absorption rates becomes larger as the sodium hydroxide concentration and the exposure time increase. This higher absorption rate observed in the case of the solution without surface active agent may be attributed to interfacial turbulence, presumably produced by surface tension gradients during the chemical absorption process, as found by Hikita et al. (1968, 1971) for the hydrogen sulfide-sodium hydroxide, hydrogen sulfide-ammonia, and carbon dioxide-ammonia systems and by Brian et al. (1967) for the carbon dioxide-monoethanolamine system. Therefore, in comparing the experimental results with the theory, the data obtained for the solutions with surface active agent, shown in Figure 4, were employed. It can be seen in Figure 4 that data points for each solution with a given sodium hydroxide concentration fall on a straight line with a slope of $-\frac{1}{2}$. This implies that the absorption of sulfur dioxide into aqueous sodium hydroxide solutions is accompanied by an instantaneous chemical reaction between the dissolved sulfur dioxide and OH^- ions.

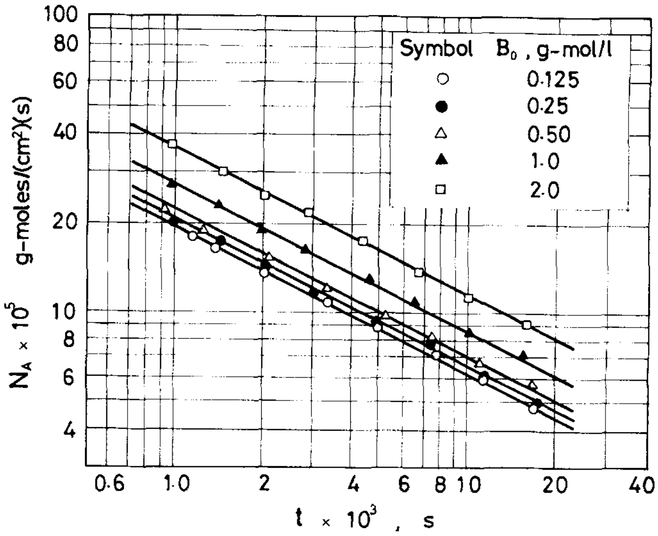

Fig. 4. Absorption rate of sulfur dioxide into aqueous sodium hydroxide solutions with surface active agent at 25°C.

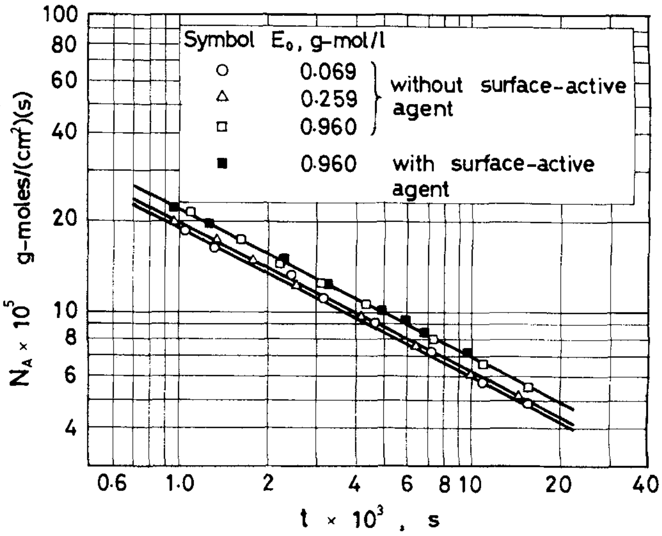

Fig. 6. Absorption rate of sulfur dioxide into aqueous sodium sulfite solutions at 25°C.

Sulfur dioxide-sodium sulfite system. Figure 6 presents the experimental data obtained for the absorption of sulfur dioxide into aqueous sodium sulfite solutions at 25°C as a log-log plot of N_A vs. t. The effect of the addition of surface active agents was studied only for the case of 0.96 g-moles/l sodium sulfite solution, and it was found that the rates of absorption into the solutions with and without surface active agents were the same. This means that interfacial turbulence is absent in this system. Figure 6 shows that the relation that N_A varies with $t^{-1/2}$ holds, indicating that the absorption of sulfur dioxide into aqueous sodium sulfite solutions is accompanied by an instantaneous reaction between the dissolved sulfur dioxide and SO_3^{2-} ions.

DISCUSSION OF RESULTS

Prediction of Physical Properties

In order to compare the experimental results with the theoretical equations described above, it is necessary to know the values of the physical properties such as A_i, D_A, D_B, D_C, D_E, etc., of the sulfur dioxide-sodium hydroxide and sulfur dioxide-sodium sulfite systems.

Table 2. Physical Properties for the Sulfur Dioxide-Sodium Hydroxide System at 25°C

B_0, g-moles/l	C_r, g-moles/l	A_i, g-moles/l	$D_A \times 10^5$ cm/s
0.125	0.130	1.13	1.73
0.25	0.277	1.10	1.70
0.5	0.565	1.05	1.63
1.0	1.14	0.952	1.50
2.0	2.30	0.781	1.24

$r_B = 1.94$, $r_C = 0.705$, $r_{E2} = 0.614$, $r_{E3} = 0.932$

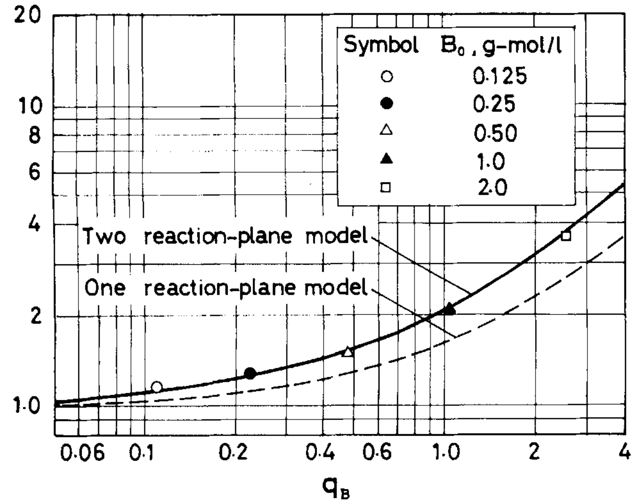

Fig. 7. Reaction factor for the absorption of sulfur dioxide into aqueous sodium hydroxide solutions.

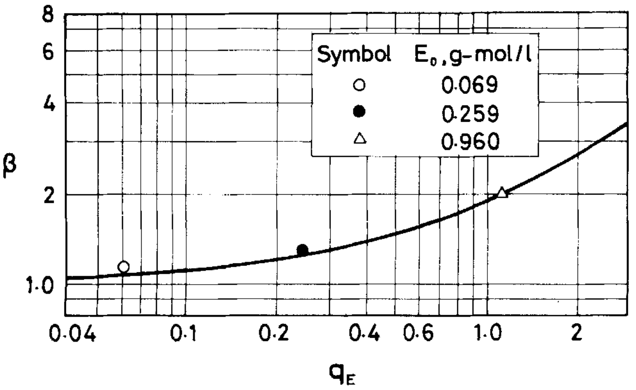

Fig. 8. Reaction factor for the absorption of sulfur dioxide into aqueous sodium sulfite solutions.

Sulfur dioxide-sodium hydroxide system. When the two-step reaction between the dissolved sulfur dioxide and sodium hydroxide in solution proceeds instantaneously, two reaction planes are formed within the liquid, as shown in Figure 1, and an aqueous sodium bisulfite ($= Na^+ + HSO_3^-$) solution of uniform concentration exists in region 1, the region between the gas-liquid interface and the first reaction plane. This uniform concentration C_r of sodium bisulfite is given by the equation (Hikita et al., 1972)

$$C_r = B_0 \sqrt{\frac{r_B}{r_C}} \exp\left\{ \left(\frac{1}{r_C} - \frac{1}{r_B}\right) \sigma_2^2 \right\} \frac{\operatorname{erf}(\sigma_2/\sqrt{r_C}) - \operatorname{erf}(\sigma_1/\sqrt{r_C})}{\operatorname{erfc}(\sigma_2/\sqrt{r_B})} \qquad (16)$$

Table 3. Physical Properties for the Sulfur Dioxide-Sodium Sulfite System at 25°C

E_0 g-moles/l	C_r, g-moles/l	A_i, g-moles/l	$D_A \times 10^5$, cm²/s
0.069	0.136	1.13	1.73
0.259	0.507	1.06	1.65
0.960	1.85	0.844	1.34

$r_C = 0.705$, $r_{E2} = 0.614$

Therefore, the physical solubility and the liquid-phase diffusivity of sulfur dioxide in this solution should be taken as the values of A_i and D_A, respectively.

The physical solubility A_i of sulfur dioxide in aqueous sodium bisulfite solutions was estimated from (van Krevelen and Hoftijzer, 1948)

$$\log(A_i/A_{iw}) = -k_s I \qquad (17)$$

The value of A_{iw} was obtained from the Henry's law constant for the sulfur dioxide-water system (Rabe and Harris, 1963), and was taken as 1.16 g-moles/l at 25°C. The value of k_s at 25°C was taken to be equal to 0.074 l/g-ion (see Appendix).

The liquid-phase diffusivity D_A of sulfur dioxide in aqueous sodium bisulfite solutions was estimated from (Ratcliff and Holdcroft, 1963)

$$D_A/D_{Aw} = -\xi C_e \qquad (18)$$

The value of ξ was estimated from viscosity data for aqueous sodium bisulfite solutions and the empirical equation proposed by Ratcliff and Holdcroft (1963) and was taken as 0.129 l/g-mole. The value of D_{Aw} at 25°C was taken to be equal to 1.76×10^{-5} cm²/s; this was predicted from the value of 2.00×10^{-5} cm²/s, estimated at 30°C for molecular sulfur dioxide in water (Peaceman, 1951) by correcting the temperature and viscosity of water according to the well-known Stokes-Einstein relation.

The ratios of the effective diffusivities of OH^-, HSO_3^-, and SO_3^{2-} ions to the liquid-phase diffusivity of sulfur dioxide, that is, r_B, r_C, and r_E, were assumed to be equal to those at infinite dilution or in water. The effective diffusivities D_B, D_C, and D_E of OH^-, HSO_3^-, and SO_3^{2-} ions at infinite dilution were estimated by the method of Vinograd and McBain (1941) using the values of the ionic conductance for these species reported in the literature (Landolt-Börnstein, 1960). The calculated values of the effective diffusivity of SO_3^{2-} ions in regions 2 and 3, D_{E2} and D_{E3}, were considerably different from each other, D_{E3} being 52% greater than D_{E2}.

The predicted values of the physical properties for the sulfur dioxide-sodium hydroxide system are listed in Table 2.

Sulfur dioxide-sodium sulfite system. When the instantaneous irreversible reaction between the dissolved sulfur dioxide and sodium sulfite in solution takes place, the concentration profiles may be shown in Figure 2, and the uniform concentration of sodium bisulfite near the gas-liquid interface can be calculated from the equation (Hikita et al., 1968;Danckwerts, 1970)

$$C_r = 2E_0 \sqrt{\frac{r_{E2}}{r_C}} \exp\left\{ \left(\frac{1}{r_C} - \frac{1}{r_{E2}}\right) \sigma_1^2 \right\} \frac{\operatorname{erfc}(\sigma_1/\sqrt{r_C})}{\operatorname{erfc}(\sigma_1/\sqrt{r_{E2}})} \qquad (19)$$

The physical solubility A_i of sulfur dioxide in aqueous sodium bisulfite solutions was estimated from Equation (17) with $A_{iw} = 1.16$ g-moles/l and $k_s = 0.074$ l/g-ion.

The liquid-phase diffusivity D_A of sulfur dioxide in aqueous sodium bisulfite solutions was obtained from Equation (18), with $D_{Aw} = 1.76 \times 10^{-5}$ cm^2/s and $\xi = 0.129$ l/g-mole.

The diffusivity ratios r_B, r_C, and r_E for the present system were estimated by means of the same procedure as employed for the sulfur dioxide-sodium hydroxide system.

Table 3 shows the predicted values of the physical properties for the sulfur dioxide-sodium sulfite system.

Comparison of Experimental Results with Theory

The experimental results for the sulfur dioxide-sodium hydroxide system are shown in Figure 7 as a log-log plot of the reaction factor β vs. the concentration ratio q_B. The value of β was calculated from the measured absorption rate N_A using the values of A_i and D_A estimated by the above-mentioned methods and the measured exposure time t. The solid line in this figure represents the two reaction plane model, calculated from Equations (9), (10), and (11). The dashed line in Figure 7 shows the model based on the assumption that the overall reaction (3) takes place at a single reaction plane, that is, the one reaction plane model (Hikita et al., 1972), and was calculated from the following equations (Danckwerts, 1950):

$$\beta = 1/\mathrm{erf}(\sigma) \tag{20}$$

$$2\mathrm{erfc}(\sigma/\sqrt{r_B})\exp\left\{\left(\frac{1}{r_B} - 1\right)\sigma^2\right\} = \sqrt{r_B}q_B\,\mathrm{erf}(\sigma) \tag{21}$$

It can be seen that the measured values of β are in good agreement with the theoretical line based on the two reaction plane model.

Figure 8 presents the experimental results for the sulfur dioxide-sodium sulfite system as a log-log plot of β vs. q_E. The solid line in this figure represents Equations (9) and (14), which are the theoretical equations for absorption accompanied by the instantaneous irreversible reaction given by reaction (5). As can be seen in this figure, the agreement between the experimental results and the theoretical line is good.

NOTATION

A_i = interfacial concentration or physical solubility of sulfur dioxide or solute gas A in solution, g-moles/l

A_{iw} = physical solubility of sulfur dioxide or solute gas A in water, g-moles/l

B_O = concentration of OH^- ions in bulk of solution, g-moles/l

C_e = concentration of HSO_3^- ions or electrolyte in solution, g-moles/l

C_r = uniform concentration of HSO_3^- ions near gas-liquid interface, g-moles/l

D_A = liquid-phase diffusivity of sulfur dioxide in solution, cm^2/s

D_{Aw} = liquid-phase diffusivity of sulfur dioxide in water, cm^2/s

D_B, D_C, D_E = effective diffusivities of OH^-, HSO_3^-, SO_3^{2-} ions in solution, cm^2/s

D_{E2}, D_{E3} = effective diffusivities of SO_3^{2-} ions in regions 2 and 3 of solution, cm^2/s

E_O = concentration of SO_3^{2-} ions in bulk of solution, g-moles/l

I = ionic strength of aqueous sodium bisulfite solution or electrolyte solution, g-ions/l

i_+, i_-, i_g = contributions of positive ions, negative ions, solute gas to salting-out parameter, l/g-ion

K_1 = equilibrium constant of reaction (1) or reaction (6), l/g-mole

K_2 = equilibrium constant of reaction (2) or reaction (7), l/g-mole

k_s = salting-out parameter, l/g-ion

N_A, N_A^* = average rates of absorption of sulfur dioxide with and without chemical reaction, g-moles/(cm^2) (s)

q_B, q_E = concentration ratios defined as B_o/A_i, E_o/A_i

r_B, r_C, r_{E2}, r_{E3} = diffusivity ratios defined as D_B/D_A, D_C/D_A, D_{E2}/D_A, D_{E3}/D_A

t = exposure time of liquid to gas, s

β = reaction factor defined as N_A/N_A^*

ξ = coefficient in Equation (18)

σ = dimensionless parameter to be determined from Equation (20)

σ_1, σ_2 = dimensionless parameters to be determined from Equations (10) and (11)

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APPENDIX A: THE PHYSICAL SOLUBILITY OF SULFUR DIOXIDE IN AQUEOUS SODIUM BISULFITE SOLUTIONS

The physical solubility of a gas in aqueous electrolyte solutions can be correlated by the following expression (van Krevelen and Hoftijzer, 1948):

$$\log(A_i/A_{iw}) = -k_s I \qquad (17)$$

The coefficient k_s is the salting-out parameter and is expressed as the sum of the contributions due to the positive and negative ions present and the dissolved gas:

$$k_s = i_+ + i_- + i_g \qquad (A1)$$

The values of i for various ions and gases were reported by van Krevelen and Hoftijzer (1948). However, since the value of i_- for HSO_3^- ions is not known, the salting-out parameter for the sulfur dioxide-sodium bisulfite system cannot be predicted. In the present work, therefore, measurements were made of the total solubility of sulfur dioxide in aqueous sodium bisulfite solutions, from which the physical solubility A_i of sulfur dioxide was calculated by correcting for the effect of the hydrolysis reaction by use of the values for the hydrolysis equilibrium constant reported by Campbell and Maass (1930). The correction was less than 2.8% in the range of the sodium bisulfite concentration covered in the present work.

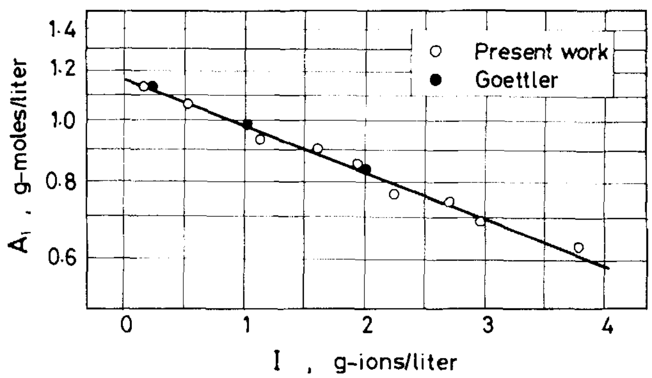

Fig. A-1. Physical solubility of sulfur dioxide into aqueous sodium bisulfite solutions at 25°C.

The results obtained are shown in Figure A1, as a semilogarithmic plot of A_i against the ionic strength I of the solution. This figure indicates that the physical solubility of sulfur dioxide in aqueous sodium bisulfite solutions is well correlated by Equation (17). In Figure A1, the physical solubility data of Goettler (1967) are also shown. The agreement between the present and Goettler's data is very good. The value of k_s was calculated from the slope of the straight line in Figure A1 as 0.074 l/g-ion. From this value of k_s and the known values of i for sulfur dioxide and Na^+ ions (van Krevelen and Hoftijzer, 1948), the value of i_- for HSO_3^- ions was calculated as 0.085 l/g-ion.

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Mechanisms and Idealized Dissolution Modes for High Density ($\rho > 1$), Immiscible Chemicals Spilled in Flowing Aqueous Environments

A plausible spill mechanism is proposed and idealized dissolution modes are developed for the prediction of lifetime and downstream cup-mixing concentration of spilled liquids. Four models are developed which reveal that detailed knowledge of the quantity and distribution of geometric shapes that make up the bottom residing interface between the spillage and the overlaying water are the independent variables of primary importance.

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SCOPE

Predictions of the environmental effects of man-made chemicals is increasingly being recognized as a responsibility of the manufacturer of the chemical. A significant number of hazardous chemicals transported upon water routes are more dense than water and come to rest upon the bottom following accidents. Dissolution commences immediately, and the rate determines the in-stream cup-mixing concentration of the spilled chemical. In the interest of protecting stream biota and downstream water users from excessive exposure, a means of predicting chemical concentrations and exposure times likely to result from an inadvertent spill is needed.

Spill mechanisms have been verified in our laboratory. These observations along with previous developments in chemical engineering science have been focused upon a partial solution of this complex problem. Information available on liquid droplet formation from nozzles and coalescence in liquid-liquid extraction provides a fundamental understanding of the mechanism that will produce a bottom residing interface (Meister and Scheele, 1969,