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Kinetics of Absorption of Carbon Dioxide into Aqueous Sodium Sulfite Solutions

The rates of absorption of pure carbon dioxide into aqueous sodium sulfite solutions containing or not containing sodium sulfate were measured at 15, 25, 35 and 45°C and at atmospheric pressure using a liquid-jet column, a wetted-wall column, and a quiescent-liquid absorber. The experimental results were analyzed by the chemical absorption theory based on the penetration model. The second-order forward rate constants for the reaction between carbon dioxide and sulfite ion in aqueous solutions were calculated and correlated as a function of temperature and ionic strength of the solution. The chemical equilibrium constants for the reaction were also determined from the measurements of the total solubility of carbon dioxide in aqueous sodium sulfite solutions.

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SCOPE

The simultaneous absorption of sulfur dioxide and carbon dioxide into aqueous solutions of sodium sulfite is industrially practiced as the Wellman-Load process for the removal of sulfur dioxide from flue gases. For the rational design of absorption equipment in such a process, the knowledge of the mechanism of chemical absorption for the sulfur dioxide-sodium sulfite system and the carbon dioxide-sodium sulfite system is required. In a previous paper (Hikita et al., 1977), the absorption of sulfur dioxide into aqueous sodium sulfite solutions was studied and found to be accompanied by an instantaneous irreversible reaction between the dissolved sulfur dioxide and sulfite ion in the solution.

The purpose of the study decreased in this paper is to clarify the mechanism and kinetics of chemical absorption of carbon dioxide into aqueous sodium sulfite solutions.

CONCLUSIONS AND SIGNIFICANCE

Experiments have been carried out on the absorption of pure carbon dioxide into aqueous sodium sulfite solutions containing and not containing sodium sulfate at atmospheric pressure and at 15, 25, 35 and 45°C, using a liquid-jet column, a wetted-wall column, and a quiescent-liquid absorber. The measured absorption rates were analyzed by the chemical absorption theory based on the penetration model. The values of the second-order forward rate constant for the reaction between carbon dioxide and sodium sulfite in aqueous solutions were determined from the measured absorption rates by fitting the experimental data to the theoretical equation. The calculated value of the rate constant ranged from 8.44×10^{-3} to 2.10×10^{-1} $m^3/mol \cdot s$ and was found to increase with increasing temperature and ionic strength of the solution.

The chemical equilibrium constant for the reaction between carbon dioxide and sodium sulfite was also determined by measuring the total solubility of carbon dioxide in aqueous sodium sulfite solutions at 15, 25 and 45°C by the method of Markham and Kobe (1941). The equilibrium constant varied from 2.82 to 4.80 and was found to increase with temperature and decrease slightly with an increase in the sodium ion concentration above about 200 mol/m^3.

From the observed values of the rate constant and the equilibrium constant between carbon dioxide and sodium sulfite, it can be concluded that the absorption of carbon dioxide into aqueous sodium sulfite solutions is a process of absorption accompanied by a reversible reaction with a finite reaction rate of the type $A + B \rightleftharpoons E + F$. These results, together with our previous results for the sulfur dioxide-sodium sulfite system (Hikita et al., 1977), may be used to interpret the mechanism of simultaneous absorption of sulfur dioxide and carbon dioxide into aqueous sodium sulfite solutions.

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CHEMICAL ABSORPTION MECHANISM

When carbon dioxide is absorbed into aqueous sodium sulfite solutions, the following reaction may take place in the liquid phase:

$$CO_2 + SO_3^{2-} + H_2O \rightleftharpoons HSO_3^- + HCO_3^- \tag{1}$$

The value of the equilibrium constant K of this reaction is

$$K = \frac{[HSO_3^-][HCO_3^-]}{[CO_2][SO_3^{2-}]} = 7.15$$

at 25°C and at infinite dilution. This value was estimated from the first dissociation constant of carbonic acid (Harned and Owen, 1958) and the second dissociation constant of sulfurous acid (Tartar and Garretson, 1941). Both the forward and reverse reactions of Eq. 1 may be considered second order, i.e., first order with respect to each species. Thus, the absorption of carbon dioxide into aqueous sodium sulfite solutions may be regarded as a process of absorption accompanied by a reversible reaction represented by $A + B \rightleftharpoons E + F$, both the forward and reverse reactions being second order.

For this case, the differential equations describing the diffusion of all species is the liquid phase, based on the penetration model, can be written as:

$$D_A(\partial^2 A/\partial x^2) - \partial A/\partial t = k_2 AB - k_2' EF \tag{2}$$

$$D_B(\partial^2 B/\partial x^2) - \partial B/\partial t = k_2 AB - k_2' EF \tag{3}$$

$$D_E(\partial^2 E/\partial x^2) - \partial E/\partial t = k_2' EF - k_2 AB \tag{4}$$

$$D_F(\partial^2 F/\partial x^2) - \partial F/\partial t = k_2' EF - k_2 AB \tag{5}$$

The initial and boundary conditions for these equations are:

$$t = 0, \quad x > 0; \quad A = A_0, \quad B = B_0, \quad E = E_0, \quad F = F_0 \tag{6}$$

$$t > 0, \quad x = 0; \quad A = A_i, \quad \partial B/\partial x = \partial E/\partial x = \partial F/\partial x = 0 \tag{7}$$

$$t \geq 0, \quad x \to \infty; \quad A = A_0, \quad B = B_0, \quad E = E_0, \quad F = F_0 \tag{8}$$

Further, the chemical equilibrium of reaction $A + B \rightleftharpoons E + F$ is established in the bulk of the liquid, so that the following condition should be fulfilled:

$$K = k_2/k_2' = E_0 F_0 / A_0 B_0 \tag{9}$$

The above differential equations are nonlinear and cannot be solved analytically. However, an approximate analytical solution can be obtained by assuming the concentrations of the species B, E and F in the liquid near the gas-liquid interface to be constant equal to their interfacial concentrations, being independent of the exposure time of the liquid to the gas. Similar assumption has been successfully used by Hikita and Asai (1963, 1964) to solve the problem of absorption accompanied by an irreversible reaction on the basis of the penetration model. For the case when $A_0 = E_0 = F_0 = 0$, the final expression for the absorption rate of the solute gas A is given by:

$$N_A = \beta(2\sqrt{D_A/\pi t})A_i \tag{10}$$

with

$$\beta = \left\{1 - \frac{(\beta'_\infty - \beta_\infty)(\beta - 1)^2}{(\beta_\infty - 1)^2(\beta'_\infty - \beta)}\right\}\left\{\left(\gamma\eta + \frac{\pi}{8\gamma\eta}\right)\mathrm{erf}\left(\frac{2}{\sqrt{\pi}}\gamma\eta\right) + \frac{1}{2}\exp\left(-\frac{4}{\pi}\gamma^2\eta^2\right)\right\} \tag{11}$$

where γ and η are the dimensionless parameters defined by

$$\gamma = (\sqrt{\pi}/2)\sqrt{k_2 B_0 t} \tag{12}$$

and

$$\eta = \sqrt{\frac{\beta'_\infty - \beta}{\beta'_\infty - 1} + \frac{(\beta - 1)(\beta'_\infty - \beta)}{(\beta_\infty - 1)^2(\beta'_\infty - 1)}} \tag{13}$$

In Eqs. 11 and 13, β_∞ represents the reaction factor for the case when reaction $A + B \rightleftharpoons E + F$ is assumed to take place instantaneously, and it is approximately given by the following equation:

$$\beta_\infty = 1 + \frac{1}{2}\left\{\sqrt{K^2\frac{D_E D_F}{D_A D_B} + 4K\frac{\sqrt{D_E D_F}}{D_A}\left(\frac{B_0}{A_i}\right)} - K\sqrt{\frac{D_E D_F}{D_A D_B}}\right\} \tag{14}$$

which is obtained by replacing the terms D_E/D_A and D_F/D_B in the exact analytical solution solved on the basis of the film model for the case when $A_0 = E_0 = F_0 = 0$ (Secor and Beutler, 1967) by $\sqrt{D_E/D_A}$ and $\sqrt{D_F/D_B}$, respectively. Further, β'_∞ represents the reaction factor for the case when reaction $A + B \rightleftharpoons E + F$ is assumed to be an irreversible instantaneous reaction, and it is approximately given by (Danckwerts, 1950):

$$\beta'_\infty = 1 + \sqrt{\frac{D_B}{D_A}}\left(\frac{B_0}{A_i}\right) \tag{15}$$

which is the limit of Eq. 14 as $K \to \infty$.

The above approximate solution for the reaction factor β, Eqs. 11 to 13, is in good agreement with the numerical solution obtained by Secor and Beutler (1967), the maximum deviation being about 6%.

EXPERIMENTAL

Apparatus and Procedure

A liquid-jet column, a wetted-wall column, and a quiescent-liquid absorber were used as the absorption apparatus. Most of the experiments were carried out by using the wetted-wall column.

The wetted-wall column used in this study was of a modified form and was the same as that used by Hikita et al. (1967, 1976) in previous work. The falling liquid film was formed on the outside of a stainless-steel vertical rod 1.3 cm in diameter with a hemispherical end. The liquid flow rate was kept constant at about 4.0 to 4.5 cm^3/s and the exposure time of the liquid to the gas was varied from 0.03 to 1.1 s by changing the film height from 3.0 to 46.0 cm. Absorption rate was measured by means of a soap-film meter.

The liquid-jet column was similar to that used by Hikita et al. (1968, 1976) in previous work. The laminar liquid jet was formed by a bell-shaped glass nozzle with an exit diameter of 0.13 cm. The exposure time was varied from 0.0013 to 0.021 s by keeping the liquid flow rate constant at about 4.0 cm^3/s and changing the jet length from 0.5 to 8.0 cm. Absorption rate was also determined by a soap-film meter.

The quiescent-liquid absorber was similar to that described in a previous paper (Hikita et al., 1976). In this absorber, the gas was brought into contact with the quiescent absorbent. The exposure time ranged from 30 to 7,200 s. The absorption rate was measured by observing the displacement of a small amount of concentrated aqueous sodium chloride solution in the capillary tube connected to the absorber.

All the experiments were conducted at atmospheric pressure and at 15, 25, 35 and 45°C. The gas phase was always pure carbon dioxide saturated with water vapor at the temperature of the experiment. The absorbents used were aqueous sodium sulfite solutions containing 1.0 mol/m^3 EDTA-2Na as an antioxidant. In some experimental runs, sodium sulfate was added to the absorbent to increase the ionic strength of the solution. In the experiments with the wetted-wall column, 0.05 to 0.2 vol % of a surface active agent, Emal NC (Kao-Atlas Co.), was added to the absorbent to prevent rippling on the falling liquid film. In the experiments with the quiescent-liquid absorber, the absorbent was gelled by adding 1 wt % agar-agar of high purity to eliminate natural convection in the liquid. The compositions of the solutions are shown in Table 1.

Prior to the chemical absorption experiments, the chemical equilibrium constant for reaction 1 was determined by measuring the total solubility of carbon dioxide in aqueous sodium sulfite solutions by the method of Markham and Kobe (1941). The experimental procedure was as follows. A known quantity of gas-free solution (usually about 400 to 600 cm^3) was introduced into the absorption cell having a volume of about 1,000 cm^3. Pure carbon dioxide was supplied to the absorption cell and the solution in the cell was agitated by a magnetic stirrer until equilibrium was established. The amount of gas dissolved, i.e., the total solubility of carbon dioxide, was found from the change in the volume of the gas in the buret connected to the absorption cell. The vapor pressure of sulfur dioxide over

TABLE 1. COMPOSITIONS OF SOLUTIONS USED

Solution	Temp. t_L, °C	$[Na_2SO_3]$ B_0, mol/m³	$[Na_2SO_4]$ J_0, mol/m³	$[Na^+]$ mol/m³	I mol/m³
1	15	66.5	0	133	200
2	15	235	0	470	706
3	15	526	0	1050	1580
4	25	66.1	0	132	198
5	25	238	0	476	715
6	25	528	0	1060	1580
7	25	516	274	1580	2370
8	25	522	557	2160	3240
9	25	523	835	2720	4070
10	25	524	1140	3320	4980
11	35	66.9	0	134	201
12	35	238	0	476	715
13	35	526	0	1050	1580
14	35	506	564	2140	3210
15	35	507	840	2700	4040
16	35	525	1130	3300	4950
17	35	526	274	1600	2400
18	45	66.9	0	134	201
19	45	238	0	476	714
20	45	526	0	1050	1580

the aqueous sodium sulfite solution, estimated from the equilibrium constants of the relevant reactions, was always negligible.

Results

Some examples of the experimental results are shown in Figures 1 to 5, where the average absorption rate N_A of carbon dioxide is plotted against the exposure of time t of the liquid to the gas on logarithmic coordinates.

Figures 1, 2 and 3 present the experimental data obtained at 25°C with the liquid-jet column, wetted-wall column and quiescent-liquid absorber, respectively, and represent the effects of the exposure time and the sodium sulfite concentration on the absorption rate. It can be seen from Figure 1 that the absorption rate for the short exposure times decreases with increasing sodium sulfite concentration and the data points for each solution fall on a straight line with a slope of $-1/2$. This implies that the absorption of carbon dioxide into aqueous sodium sulfite solutions in the liquid-jet column may take place in the physical absorption regime. The decrease in the absorption rate with increasing sodium sulfite concentration may be attributed to the reduced solubility of carbon dioxide in the solution of higher concentrations due to the salting-out effect and to the greater viscosity of the solution and the corresponding decrease in the liquid-phase diffusivity of carbon dioxide. The results in Figure 3 show that the absorption rate for the long exposure times increases with increasing sodium sulfite concentration and the relation that N_A varies with $t^{-1/2}$ approximately holds. This indicates that the absorption of carbon dioxide into aqueous sodium sulfite solutions in the quiescent-liquid absorber may take place in the near instantaneous reaction regime. Further, it can be seen from Figure 2 that for the intermediate exposure times the effect of the exposure time upon the absorption rate is less than those in the physical absorption regime and the instantaneous reaction regime, and it decreases as the sodium sulfite concentration and the exposure time increase. This indicates that the absorption of carbon dioxide into aqueous sodium sulfite solutions in the wetted-wall column may take place in the near pseudo first-order reaction regime.

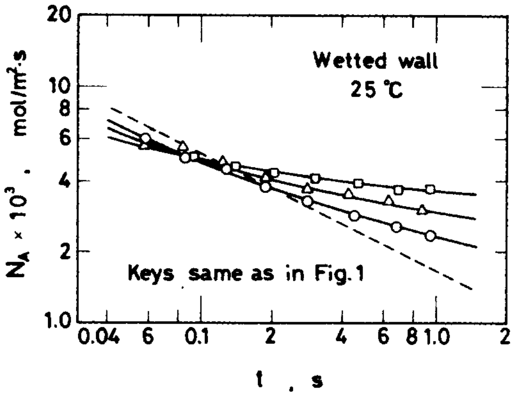

Figure 2. Absorption rate of carbon dioxide into aqueous sodium sulfite solutions in a wetted-wall column at 25°C.

Figures 4 and 5 present the experimental results obtained with the wetted-wall column and show the effects of the temperature and the addition of sodium sulfate to the solution, respectively. As shown in these figures, the dependence of the absorption rate on the exposure time in both cases is similar to that in Figure 2, indicating that the absorption occurs in the near pseudo first-order reaction regime.

ANALYSIS AND DISCUSSION

Prediction of Physical Properties

In order to analyze the experimental results using the theoretical equations described above, it is necessary to know the values of the physical properties of the present system, such as A_i, D_A, D_B, D_E, D_F, etc. These physical properties were evaluated under the condition of an irreversible pseudo first-order reaction, i.e., approximately for the composition of the feed solution.

The physical solubility A_i of carbon dioxide in aqueous sodium sulfite solutions containing sodium sulfate was estimated from the following equation proposed for the solubility in mixed electrolyte solutions (Danckwerts and Gillham, 1966):

$$\log(A_i/A_{iw}) = -(k_{sB}I_B + k_{sJ}I_J) \qquad (16)$$

where A_{iw} is the physical solubility of carbon dioxide in water and k_{sB} and k_{sJ} are the slating-out parameters for sodium sulfite and sodium sulfate with ionic strengths I_B and I_J, respectively. The salting-out parameter k_s is expressed as the sum of the contributions

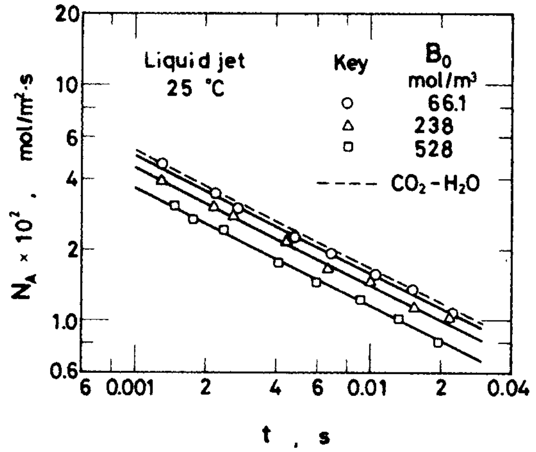

Figure 1. Absorption rate of carbon dioxide into aqueous sodium sulfite solutions in a liquid-jet column at 25°C.

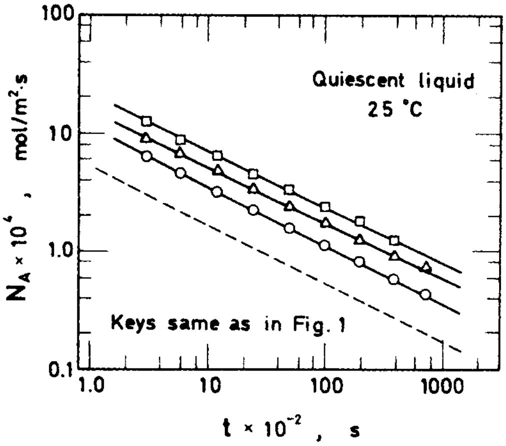

Figure 3. Absorption rate of carbon dioxide into aqueous sodium sulfite solutions in a quiescent-liquid absorber at 25°C.

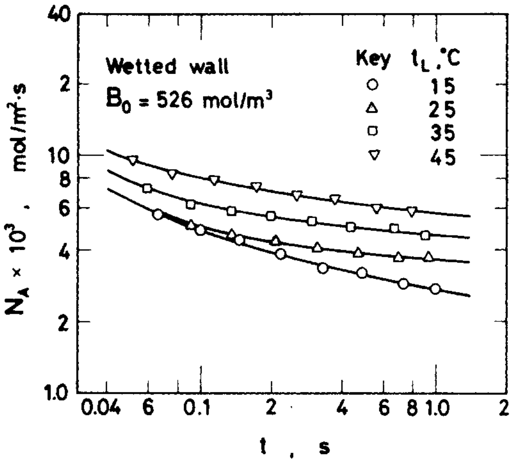

Figure 4. Absorption rate of carbon dioxide into 526 mol/m³ aqueous sodium sulfite solution in a wetted-wall column at 15, 25, 35 and 45°C.

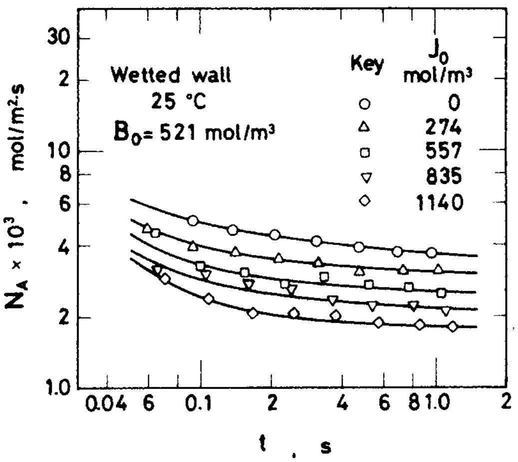

Figure 5. Absorption rate of carbon dioxide into 521 mol/m³ aqueous sodium sulfite solutions containing sodium sulfate in a wetted-wall column at 25°C.

of the positive and negative ions and the dissolved gas (van Krevelen and Hoftijzer, 1948):

$$k_s = i_+ + i_- + i_g \tag{17}$$

The values of i for Na^+ and SO_4^{2-} ions and of i_g for carbon dioxide at various temperatures were obtained from the data of van Krevelen and Hoftijzer (1948). The value of i_- for SO_3^{2-} ion was estimated as 1.0 m³/mol by analyzing the data on the absorption rate of carbon dioxide into aqueous sodium sulfite solutions measured under the condition of physical absorption regime (Appendix A). The values of A_{iw} at various temperatures were obtained from the book of Linke and Seidell (1958).

The liquid-phase diffusivity D_A of carbon dioxide in aqueous sodium sulfite solutions containing sodium sulfate was estimated from the following equation proposed by Hikita et al. (1979) for the diffusivity in mixed electrolyte solutions:

$$D_A/D_{Aw} = 1 - (\xi_B B + \xi_J J) \tag{18}$$

where D_{Aw} is the liquid-phase diffusivity of carbon dioxide in water, and ξ_B and ξ_J are the constants for sodium sulfite and sodium sulfate solutions whose concentrations are B and J, and were found from the viscosity data to be 278 and 244 m³/mol, respectively, being independent of temperature. The values of D_{Aw} at various temperatures were predicted from the value of 1.97×10^{-9} m²/s obtained at 25°C (Peaceman, 1951), by correcting for temperature and viscosity of water, according to the well-known Stokes-Einstein relation.

The ratios of the effective diffusivities of SO_3^{2-}, HSO_3^-, and HCO_3^- ions to the liquid-phase diffusivity of carbon dioxide, that is, D_B/D_A, D_E/D_A, and D_F/D_A, were assumed to be equal to those at infinite dilution, and to be independent of temperature. The effective diffusivities of SO_3^{2-}, HSO_3^-, and HCO_3^- ions at infinite dilution were estimated by the method of Vinograd and McBain (1941) (Appendix B).

The predicted values of the physical properties are listed in Table 2.

Chemical Equilibrium Constant

The values of the chemical equilibrium constant K for reaction 1 were calculated from the measurements of the total solubility A_T of carbon dioxide using the following equation:

$$K = \frac{(A_T - A_i)^2}{A_i(B_0 - A_T + A_i)} \tag{19}$$

where A_i is the saturated concentration of unreacted carbon dioxide in the solution where the chemical equilibrium of reaction 1 is established and was estimated from the expression similar to Eq. 16 taking into account the salting-out effect due to the presence of sodium bisulfite and sodium bicarbonate formed by reaction 1. In Figure 6, the calculated values of K at 15, 25 and 45°C are plotted against the Na^+ ion concentration $[Na^+]$ of the solution on semilogarithmic coordinates. The K value at 25°C and infinite dilution

TABLE 2. PHYSICAL PROPERTIES FOR THE CARBON DIOXIDE-AQUEOUS SODIUM SULFITE SOLUTION SYSTEM

Solution	A_i mol/m³	$D_A \times 10^9$ m²/s	D_B/D_A	D_E/D_A	D_F/D_A	K	$k_2 \times 10^3$ m³/mol·s
1	43.0	1.46	0.549	0.645	0.577	3.37	8.44
2	38.9	1.39	0.558	0.655	0.586	3.07	8.68
3	32.8	1.27	0.564	0.660	0.591	2.94	9.82
4	31.7	1.93	0.550	0.646	0.578	3.89	24.9
5	28.9	1.84	0.559	0.656	0.587	3.54	26.2
6	24.7	1.68	0.565	0.661	0.591	3.39	30.3
7	20.6	1.57	0.591	0.673	0.603	3.33	33.7
8	17.0	1.44	0.589	0.672	0.601	3.29	36.2
9	14.1	1.32	0.587	0.683	0.611	3.26	43.4
10	11.5	1.18	0.586	0.682	0.610	3.25	47.7
11	24.2	2.47	0.551	0.647	0.579	4.44	64.9
12	22.2	2.35	0.560	0.656	0.587	4.04	72.9
13	19.3	2.15	0.566	0.662	0.592	3.87	82.3
14	13.7	1.85	0.589	0.672	0.601	3.76	101
15	11.5	1.69	0.587	0.682	0.611	3.73	117
16	9.51	1.52	0.586	0.681	0.609	3.71	132
17	16.2	2.00	0.590	0.685	0.613	3.80	90.4
18	18.8	3.08	0.551	0.647	0.579	5.04	166
19	17.4	2.93	0.561	0.657	0.588	4.58	187
20	15.3	2.68	0.566	0.662	0.593	4.39	210

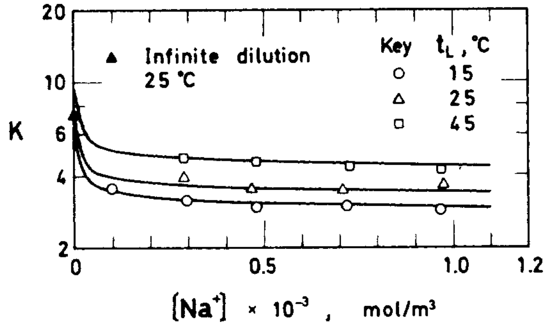

Figure 6. Effect of Na^+ ion concentration on equilibrium constant for reaction between carbon dioxide and sulfite ion.

shown in this figure was estimated from the first dissociation constant of carbonic acid and the second dissociation constant of sulfurous acid, as described above. It can be seen that above 200 mol/m^3 of $[Na^+]$ the equilibrium constant K is affected slightly by the Na^+ ion concentration and decreases with an increase in the value of $[Na^+]$. The solid lines in the figure represent the following empirical equation

$$\log K = 2.642 - 533.2/T - \frac{0.07959[Na^+]^{1/2}}{1 + 0.2149[Na^+]^{1/2}} \qquad (20)$$

where $[Na^+]$ is in mol/m^3, and correlate well the K values in the present work with an average deviation of 3.9%.

The value of K for each solution given in Table 2 was calculated by using Eq. 20.

Reaction Rate Constant

The values of the forward rate constant k_2 for reaction 1 were determined from the results of the chemical absorption experiments by fitting the data points representing the values of the reaction factor β calculated from the measured absorption rates to the theoretical line representing Eqs. 11 to 15, which were derived for the case of absorption accompanied by the reversible reaction given by $A + B \rightleftharpoons E + F$. In calculating the theoretical lines, the K values were estimated from Eq. 20.

Figures 7 to 9 show the log-log plots of β vs. γ for the experimental data given in Figures 1 to 5. The solid lines in these figures represent the theoretical Eqs. 11 to 15. In computing the value of γ for each experimental run, the value of k_2 determined above was used. It can be seen that the data points are in good agreement with the theoretical lines. The broken lines in these figures represent the following equation:

$$\beta = \left(\gamma + \frac{\pi}{8\gamma}\right) \operatorname{erf}\left(\frac{2\gamma}{\sqrt{\pi}}\right) + \frac{1}{2}\exp\left(-\frac{4\gamma^2}{\pi}\right) \qquad (21)$$

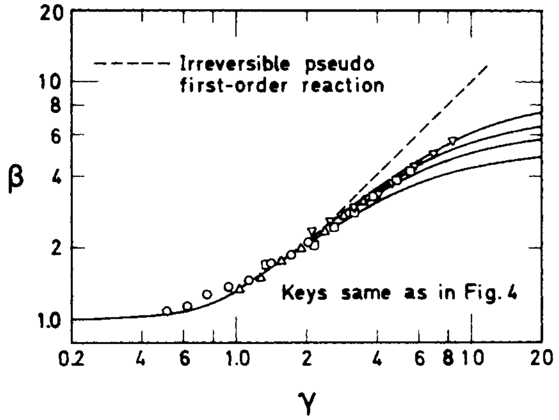

Figure 8. Reaction factor for absorption of carbon dioxide into 526 mol/m^3 aqueous sodium sulfite solution in a wetted-wall column at 15, 25, 35 and 45°C.

which is the theoretical equation for absorption accompanied by an irreversible pseudo first-order reaction and can be obtained by substituting $\beta_\infty \rightarrow \infty$, $\beta'_\infty \rightarrow \infty$ and $\eta = 1$ into Eq. 11.

All the k_2 values obtained by matching the measured values of β with the theoretical lines are given in Table 2 and shown in Figure 10 as a semilogarithmic plot of the k_2 value against the ionic strength I of the solution. Figure 10 indicates that the rate constant increases with increasing ionic strength and temperature. Figure 11 shows an Arrhenius plot of the k_2 values obtained from the experimental data at three constant values of I. The activation energy was found to be 77.4 kJ/mol, being independent of the ionic strength of the solution. All the k_2 values were correlated by the following empirical equation:

$$\log k_2 = 11.96 + 6.0 \times 10^{-5} I - 4050/T \qquad (22)$$

with an average deviation of 1.8%.

NOTATION

A = concentration of carbon dioxide in solution, mol/m^3
A_i = interfacial concentration or physical solubility of carbon dioxide in solution, mol/m^3
A_{iw} = physical solubility of carbon dioxide in water, mol/m^3
A_T = total solubility of carbon dioxide in solution, mol/m^3
A_0 = concentration of unreacted carbon dioxide in bulk of solution, mol/m^3

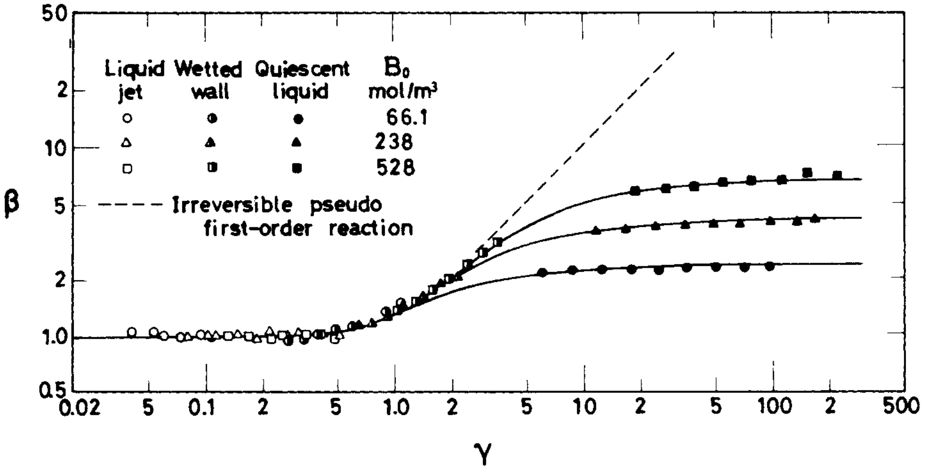

Figure 7. Reaction factor for absorption of carbon dioxide into aqueous sodium sulfite solutions at 25°C.

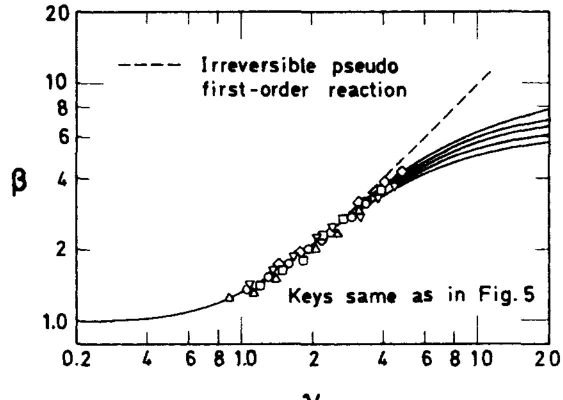

Figure 9. Reaction factor for absorption of carbon dioxide into 521 mol/m³ aqueous sodium sulfite solutions containing sodium sulfate in a wetted-wall column at 25°C.

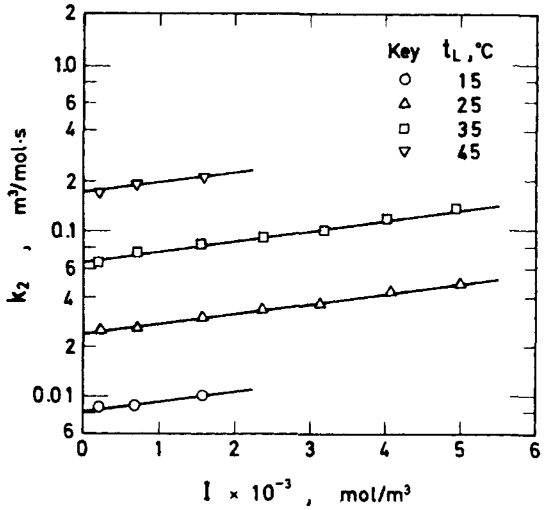

Figure 10. Effect of ionic strength on forward rate constant for reaction between carbon dioxide and sulfite ion.

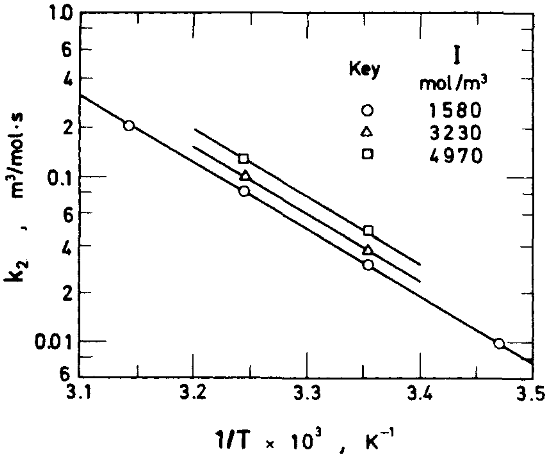

Figure 11. Effect of temperature on forward rate constant for reaction between carbon dioxide and sulfite ion.

B = concentration of SO_3^{2-} ion in solution, mol/m³
B_0 = concentration of SO_3^{2-} ion in bulk of solution, mol/m³
D_A = liquid-phase diffusivity of carbon dioxide in solution, m²/s
D_{Aw} = liquid-phase diffusivity of carbon dioxide in water, m²/s
D_B, D_E, D_F = effective diffusivities of SO_3^{2-}, HSO_3^-, HCO_3^- ions in solution, m²/s
D_B^*, D_E^*, D_F^* = self-diffusivities of SO_3^{2-}, HSO_3^-, HCO_3^- ions in solution, m²/s
E = concentration of HSO_3^- ion in solution, mol/m³
E_0 = concentration of HSO_3^- ion in bulk of solution, mol./m³
F = concentration of HCO_3^- ion in solution, mol/m³
F_0 = concentration of HCO_3^- ion in bulk of solution, mol/m³
Fa = Faraday constant, C/mol
I = ionic strength of solution, mol/m³
i_+, i_-, i_g = contributions of positive ions, negative ions, solute gas to salting-out parameter, m³/mol
J = concentration of SO_4^{2-} ion in solution, mol/m³
K = equilibrium constant of reaction 1
k_s = salting-out parameter, m³/mol
k_2, k_2' = second-order rate constants for forward and reverse parts of reaction 1, m³/mol·s
N_A = average absorption rate of carbon dioxide, mol/m²·s
R = gas constant, J/mol·K
T = temperature of solution, K
t = exposure time of liquid to gas, s
t_L = temperature of solution, °C
x = distance from interface into liquid, m
x_L = liquid film thickness, m

Greek Letters

β = reaction factor
β_∞ = reaction factor for the case when reaction 1 is instantaneous
β_∞' = reaction factor for the case when reaction 1 is instantaneous and irreversible
γ = parameter defined by Eq. 12
η = parameter defined by Eq. 13
$\lambda_B, \lambda_E, \lambda_F$ = ionic conductances of SO_3^{2-}, HSO_3^-, HCO_3^- ions, m²/Ω·mol
ξ = coefficient in Eq. 18, m³/mol

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APPENDIX A: THE PHYSICAL SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS SODIUM SULFITE SOLUTIONS

As described above, the absorption of carbon dioxide into aqueous sodium sulfite solutions in the liquid-jet column may be considered to be a process of physical absorption. In the present work, the physical solubility A_i of carbon dioxide in aqueous sodium sulfite solutions at 25°C was determined from the absorption rates N_A given in Figure 1 using the well-known Higbie equation

$$N_A = 2A_i\sqrt{D_A/\pi t} \tag{A1}$$

and the liquid-phase diffusivity D_A of carbon dioxide in the solutions predicted from Eq. 18. The results obtained are shown in Figure A1, as a semi logarithmic plot of A/A_{iw} against the ionic strength I of the sodium sulfite solution. This figure indicates that the physical solubility of carbon dioxide in aqueous sodium sulfite solutions is well correlated by the following equation:

$$\log(A_i/A_{iw}) = -k_s I \tag{A2}$$

The value of the salting-out parameter k_s was calculated from the slope of the straight line in Figure A1 as 78 m^3/mol. From this value of k_s and the known values of i for carbon dioxide and Na$^+$ ion (van Krevelen and Hoftijzer, 1948), the value of i_- for SO$_3^{2-}$ ion was calculated as 1.0 m^3/mol.

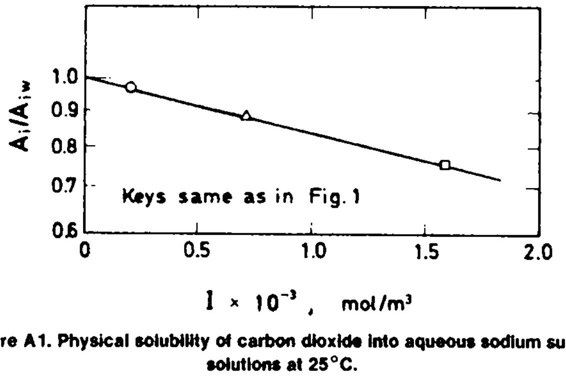

Figure A1. Physical solubility of carbon dioxide into aqueous sodium sulfite solutions at 25°C.

APPENDIX B: THE EFFECTIVE DIFFUSIVITIES OF SULFITE, BISULFITE, AND BICARBONATE IONS AT INFINITE DILUTION

The effective diffusivities of SO$_3^{2-}$, HSO$_3^-$, and HCO$_3^-$ ions, that is, D_B, D_E and D_F, at infinite dilution were calculated by using the equations of Vinograd and McBain (1941). The average values of the concentrations and the concentration gradients of all the ions present were estimated from the concentration profiles shown in Figure B1, which were derived on the basis of the film model for absorption with the instantaneous reversible reaction represented by Eq. 1, assuming that the concentration profile for each ion is linear. The resulting expression giving the ratio of the effective diffusivity to the self diffusivity for SO$_3^{2-}$ ion, i.e., D_B/D_B^* is a biquadratic equation and is represented as

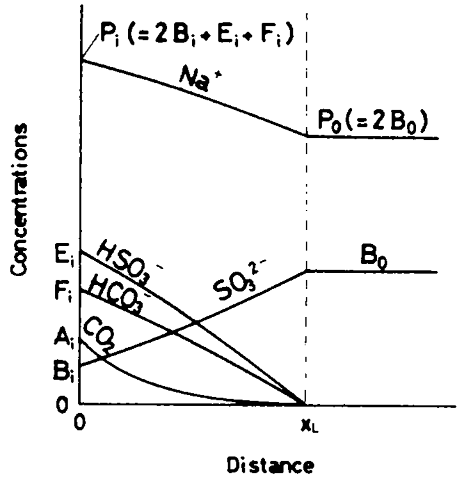

Figure B1. Concentration profiles for absorption of carbon dioxide into aqueous sodium sulfite solution.

$$a(D_B/D_B^*)^4 + b(D_B/D_B^*)^3 + c(D_B/D_B^*)^2 + d(D_B/D_B^*) + e = 0 \tag{B1}$$

The coefficients in this equation are given by

$$\left.\begin{aligned}
a &= (pq-1)^2\{4(pq+1)s - p^2q^2r\}\\
b &= (pq-1)\{48(pq+1)s - 2(4-pq)p^2q^2r\}\\
c &= 72(3-p^2q^2)s + (3p^2q^2 + 22pq - 18)p^2q^2r\\
d &= -6(72s + 5p^3q^3r)\\
e &= 27(12s + p^2q^2r)
\end{aligned}\right\} \tag{B2}$$

with

$$\begin{aligned}
p &= D_E^*/D_F^* + 1\\
q &= D_B^*/D_E^*\\
r &= KD_E^*D_F^*/D_AD_B^*\\
s &= D_B^*B_0/D_AA_i
\end{aligned} \tag{B3}$$

where D_E^* and D_F^* are the self diffusivities of HSO$_3^-$ and HCO$_3^-$ ions, respectively. The ratios of the effective diffusivity to the self diffusivity for HSO$_3^-$ and HCO$_3^-$ ions, D_E/D_E^* and D_F/D_F^*, are given by

$$D_E/D_E^* = D_F/D_F^* = 2pq(D_B/D_B^*)/\{3 + (pq-1)(D_B/D_B^*)\} \tag{B4}$$

The self diffusivities of SO$_3^{2-}$, HSO$_3^-$, and HCO$_3^-$ ions are related to the ionic conductances by

$$\begin{aligned}
D_B^* &= (\lambda_B/4)RT/\mathrm{Fa}^2\\
D_E^* &= \lambda_E RT/\mathrm{Fa}^2\\
D_F^* &= \lambda_F RT/\mathrm{Fa}^2
\end{aligned} \tag{B5}$$

where λ_B, λ_E, and λ_F are the ionic conductances for SO$_3^{2-}$, HSO$_3^-$, and HCO$_3^-$ ions, R is the gas constant and Fa is the Faraday constant. The values of λ_B, λ_E, and λ_F were taken from the literature (Landolt-Börnstein, 1960).

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