R & D NOTES

Absorption of Sulfur Dioxide into Water

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The absorption of sulfur dioxide into water is a process of considerable importance in the chemical industry. A number of experimental studies have been reported in the literature for the rate of sulfur dioxide absorption into water. However, few of these studies attempted to analyze the absorption rate data in the light of the chemical absorption theory, taking into account the hydrolysis reaction of sulfur dioxide. It is the purpose of this note to clarify the absorption mechanism of the sulfur dioxide-water system on the basis of the chemical absorption theory.

CHEMICAL ABSORPTION MECHANISM

When sulfur dioxide is absorbed into water, the following hydrolysis reaction takes place in the liquid phase:

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^- \qquad (1)$$
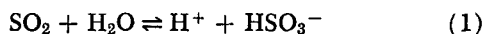
The value of the equilibrium constant K of this reaction is

$$K = \frac{[H^+][HSO_3^-]}{[SO_2]} = 1.7 \times 10^{-2} \text{ g-mole/l}$$

at 25°C and at infinite dilution (Campbell and Maass, 1930; Morgan and Maass, 1931). Reaction (1) is very rapid, and the forward reaction rate constant is 3.4×10^6 (s)$^{-1}$ at 20°C (Eigen et al., 1961). Thus, the absorption of sulfur dioxide into water may be regarded as a process of absorption accompanied by an instantaneous reversible reaction of the form $A \rightleftharpoons E + F$.

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

$$D_A \frac{\partial^2 A}{\partial x^2} + D_E \frac{\partial^2 E}{\partial x^2} = 0 \qquad (2)$$

$$D_A \frac{\partial^2 A}{\partial x^2} + D_F \frac{\partial^2 F}{\partial x^2} = 0 \qquad (3)$$

The initial and boundary conditions for these equations are

$$t = 0, \ x > 0; \quad A = A_0, \ E = E_0, \ F = F_0 \qquad (4)$$

$$t > 0, \ x = 0; \quad A = A_i \qquad (5)$$

$$t \geqq 0, \ x \to \infty; \quad A = A_0, \ E = E_0, \ F = F_0 \qquad (6)$$

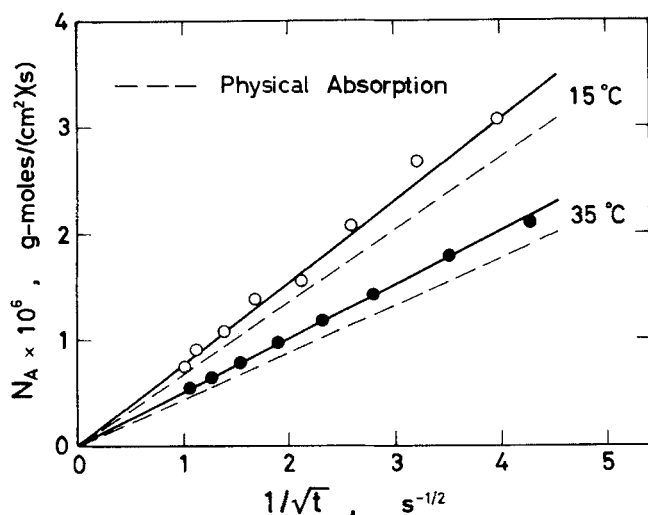Fig. 1. Absorption rates of sulfur dioxide into water at 15° and 35°C.

Fig. 2. Absorption rates of sulfur dioxide into water at 25° and 45°C.

TABLE 1. PHYSICAL PROPERTIES FOR THE SULFUR
DIOXIDE-WATER SYSTEM AT 15°, 25°, 35°, AND 45°C

Temp., °C	A_i, g-mole/1	$D_A \times 10^5$, cm²/s	$K \times 10^2$, g-mole/1
15	1.64	1.34	2.19
25	1.16	1.76	1.70
35	0.831	2.25	1.31
45	0.595	2.81	0.991

$$D_E/D_A = D_F/D_A = 1.32$$

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

$$K = EF/A \qquad (7)$$

The above differential equations cannot be solved analytically. However, the approximate analytical solution can be obtained by replacing the diffusivity ratios in the exact analytical solution based on the film model by the square roots. The final expression for the absorption rate of the solute gas A is given by

$$N_A = \beta(2\sqrt{D_A/\pi t})(A_i - A_0) \qquad (8)$$

with

$$\beta = 1 + \frac{\sqrt{D_E/D_A}}{2(A_i - A_0)}$$

$$\left[\sqrt{(E_0 + \sqrt{D_F/D_E}\,F_0)^2 + 4K\sqrt{D_F/D_E}(A_i - A_0)} \right.$$

$$\left. - (E_0 + \sqrt{D_F/D_E}\,F_0) \right] \qquad (9)$$

If the two reaction products E and F have equal diffusivities and equal bulk concentrations, that is, when $D_E = D_F$ and $E_0 = F_0$, Equation (9) reduces to

$$\beta = 1 + \sqrt{\frac{D_E}{D_A}} \frac{\sqrt{K}}{\sqrt{A_i} + \sqrt{A_0}} \qquad (10)$$

EXPERIMENTAL

Absorption experiments were carried out using a wetted wall column. The wetted wall column was a modified form
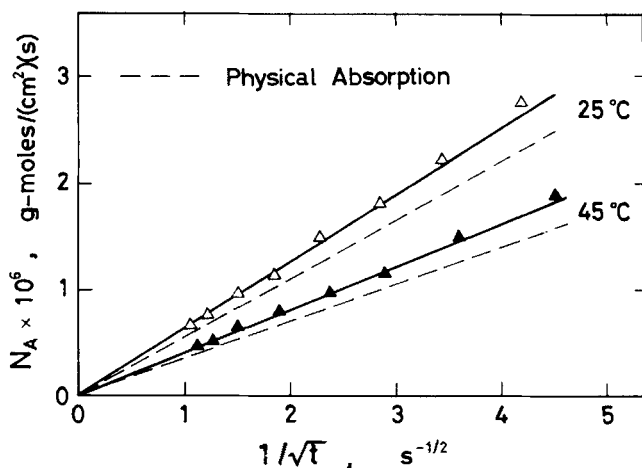
in which the end effect due to the presence of the stagnant film could be eliminated and was the same as that used by Hikita et al. (1967, 1976) in previous work. To prevent rippling on the falling liquid film, 0.05 vol % of a surface active agent, Emal NC (Kao-Atlas Co.), was added to the absorbent. The exposure time of the liquid to the gas was varied from 0.049 to 0.97 s by changing the liquid flow rate and the film height. Absorption rate was determined volumetrically by means of a soap-film meter. All the experiments were conducted at atmospheric pressure and at 15°, 25°, 35°, and 45°C. The gas phase was pure sulfur dioxide saturated with water vapor at the temperature of the experiment. The absorbent used was water.

Prior to the sulfur dioxide absorption runs, preliminary runs on the physical absorption of pure carbon dioxide into water were carried out in the same apparatus in order to check the hydrodynamics of the falling liquid film. The measured absorption rates were in good agreement with the theoretical line representing the Higbie equation, lending strong support to the applicability of the penetration model to the analysis of the results of the sulfur dioxide adsorption runs.

RESULTS AND DISCUSSION

Prediction of Physical Properties

The physical solubility A_i of sulfur dioxide in water was estimated from the empirical formula for the Henry's law constant (Rabe and Harris, 1963).

The liquid-phase diffusivity D_A of sulfur dioxide in water 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 for the temperature and viscosity of water according to the well-known Stokes-Einstein relation.

In the present system, the reaction products are only two ionic species of opposite sign, and there are no other ionic species present in solution. Therefore, the condition of electrical neutrality requires that each of the two ionic species, H^+ and HSO_3^- ions, has the same diffusivity. The ratio of the effective diffusivity D_E of H^+ ions or D_F (= D_E) of HSO_3^- ions to the liquid-phase diffusivity of sulfur dioxide, that is D_E/D_A or D_F/D_A, was assumed to be equal to that at infinite dilution. The value of D_E or D_F at infinite dilution was estimated from the Nernst equation (Robinson and Stokes, 1959) using the values of the ionic conductance for these species reported in the literature (Landolt-Börnstein, 1960).

The equilibrium constant K of reaction (1) was calculated from the equation

$$\log K = 6.7369 - (770.5/T) - 0.01986T \quad (11)$$

which correlates the data of Campbell and Maass (1930), Morgan and Maass (1931), and Wang and Himmelblau (1964) very well.

The predicted values of the physical properties for the sulfur dioxide-water system are listed in Table 1.

Comparison of Experimental Results with Theory

The experimental results are shown in Figures 1 and 2 as the plots of the absorption rate N_A of sulfur dioxide against the reciprocal square root of the exposure time $1/\sqrt{t}$. The solid lines in these figures represent the theoretical lines for absorption with an instantaneous reversible reaction, calculated from Equations (8) and (10) with $A_0 = 0$ using the physical properties predicted by the above-mentioned methods, while the dashed lines show the theoretical lines for physical absorption, calculated from the Higbie equation, that is, Equation (8) with $A_0 = 0$ and $\beta = 1$. As can be seen in these figures, the measured values of the absorption rate are in good agreement with the theoretical lines.

NOTATION

A = concentration of sulfur dioxide in solution, g-mole/l

A_i = interfacial concentration or physical solubility of sulfur dioxide in solution, g-mole/l

A_0 = concentration of sulfur dioxide in bulk of solution, g-mole/l

D_A = liquid-phase diffusivity of sulfur dioxide in solution, cm²/s

D_E, D_F = effective diffusivities of H^+ and HSO_3^- ions in solution, cm²/s

E, F = concentrations of H^+ and HSO_3^- ions in solution, g-mole/l

E_0, F_0 = concentrations of H^+ and HSO_3^- ions in bulk of solution, g-mole/l

K = equilibrium constant of reaction (1), g-mole/l

N_A = average rate of absorption of sulfur dioxide, g-mole/(cm²)(s)

T = absolute temperature of solution, °K

t = exposure time of liquid to gas, s

x = distance from interface into liquid, cm

β = reaction factor

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Kinetic Behavior of Weak Base Anion Exchangers

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In this work, twelve different weak base anion exchangers were studied as to their decrease of breakthrough capacity with increasing specific loading. From the curves, the rate coefficients were calculated and correlated with the values characterizing the ion exchanger. It was found that the sorption rate of acid increases with decreasing average molality of functional groups in the ion exchanger.

SCOPE

The present tendency in the demineralization of water by means of ion exchange resins is to operate at a high specific loading of the resin. For this purpose, only ion exchangers with good mechanical-osmotic stability and with the best kinetic properties can be used. The strong electrolyte resins exhibit an ion exchange rate sufficiently high so that their breakthrough capacity decreases relatively slowly with increasing specific loading. On the other hand, the slower kinetics of weak electrolyte resins results in a considerable drop of breakthrough capacity at