Goldberg, I., J. S. Rock, A. Ben-Bassat, and R. I. Mateles, "Bacterial Yields on Methanol, Methylamine, Formaldehyde, and Formate," *Biotechnol. Bioeng.*, **18**, 1657 (1976).

Hegedus, L. L., S. H. Oh, and K. Baron, "Multiple Steady States in an Isothermal Integral Reactor," *AIChE J.*, **23**, 632 (1977).

Hirt, W., E. Papoutsakis, E. Krug, H. C. Lim, and G. T. Tsao, "Formaldehyde Incorporation by a New Methylotroph (L3)," *Appl. Environ. Microbiol.*, **36**, 56 (1978).

Horak, J., F. Jiracek, and L. Krausova, "Experimental Study of the Behavior of an Isothermal Continuous Stirred Tank Reactor in the Course of Autocatalytic Reaction," *Chem. Eng. Sci.*, **26**, 1 (1971).

Imanaka, T., T. Kaieda, K. Suto, and H. Taguchi, "Optimization of α-Galactosidase Production in Mold," *J. Ferment. Technol.*, **50**, 633 (1972).

Imanaka, T., T. Kaieda, and H. Taguchi, "Unsteady State Analysis of a Kinetic Model for Cell Growth and α-Galactosidase Production in Mold," *ibid.*, **51**, 423 (1973).

Krug, E., and W. Hirt, "Interference of Nitrate in the Determination of Formaldehyde by the Chromotropic Acid Method," *Anal. Chem.*, **49**, 1865 (1977).

Othmer, H. G., "The Qualitative Dynamics of a Class of Biochemical Control Circuits," *J. Math. Biol.*, **3**, 53 (1976).

Papoutsakis, E., H. C. Lim, and G. T. Tsao, "SCP Production on C_1 Compounds," *AIChE J.*, **24**, 406 (1978a).

Papoutsakis, E., H. C. Lim, and G. T. Tsao, "The Role of Formaldehyde on the Utilization of C_1 Compounds via the RMP Cycle," *Biotechnol. Bioeng.*, **20**, 421 (1978b).

Pawlowsky, V., J. A. Howell, and C. T. Chi, "Mixed Culture Bioxidation of Phenol. III. Existence of Multiple Steady States in Continuous Culture with Wall Growth," *Biotechnol. Bioeng.*, **15**, 905 (1973).

Pirt, S. J., *Principles of Microbe and Cell Cultivation*, J. Wiley and Sons, New York (1975).

Reuss, M., J. Gnieser, H. G. Reng, and F. Wagner, "Extended Culture of Candida Boidini on Methanol," *Eur. J. Appl. Microbiol.*, **1**, 295 (1975).

Rokem (Rock), J. S., I. Goldberg, and R. I. Mateles, "Maintenance Requirements for Bacteria Growing on C_1-Compounds," *Biotechnol. Bioeng.*, **20**, 1557 (1978).

Root, R. B., and R. A. Schmitz, "An Experimental Study of Unstable States in a Loop Reactor," *AIChE J.*, **15**, 670 (1969).

Schmitz, R. A., "Multiplicity, Stability and Sensitivity of States in Chemical Reacting Systems—A Review," *Advances in Chemistry Series*, **148**, 156 (1975).

Yano, T., and S. Koga, "Dynamic Behavior of the Chemostat Subject to Substrate Inhibition," *Biotechnol. Bioeng.*, **11**, 139 (1969).

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SO_2 Absorption Into Aqueous Solutions

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The absorption rate of SO_2 from a gas mixture of SO_2 and N_2 into pure water, HCl, and NaCl solutions has been measured at 25°C in a continuous stirred vessel with an unbroken gas-liquid interface. The rates of liquid-phase mass transfer are accurately modeled by the theory of surface renewal with the instantaneous, reversible hydrolysis of dissolved SO_2. The theory and results are applicable to SO_2 absorption from waste gases.

SCOPE

The absorption of sulfur dioxide into water is a process of simultaneous mass transfer with instantaneous reversible reaction. Danckwerts' (1968) modified physical absorption model was most often used in previous studies. But this model does not consider the sulfur dioxide hydrolysis reaction properly and may result in some error due to the different sulfur dioxide and bisulfite diffusivities. Because no exact analytical solution can be obtained from the rigorous surface renewal model, only the film model (Vivian, 1973) and an approximate penetration model (Hikita, 1978) have been previously used to interpret absorption data. However, the rigorous surface renewal model has been solved numerically by Chang and Rochelle (1980). Their results will be employed to analyze the experimental data of this work.

Most previous experimental studies used pure sulfur dioxide as the gas phase (Groothuis and Kramers, 1955; Lynn et al., 1955; Toor and Chiang, 1959; Hikita et al., 1978). In these cases, the sulfur dioxide hydrolysis reaction is highly depressed and can only enhance the physical absorption rate about 10%. On the other hand, the concentration of sulfur dioxide in stack gas is normally 1000 to 4000 ppm. This work has conducted experiments at SO_2 partial pressures of 0.0002 to 0.98 bar. These results show a greater effect of the hydrolysis reaction and are of greater practical significance.

CONCLUSIONS AND SIGNIFICANCE

The removal of sulfur dioxide from gas mixtures by chemical absorption with aqueous solutions or slurries is an important process for control of air pollution. This process is frequently dominated by liquid-phase mass transfer resistance (Rochelle and King, 1977). Little work has been done on modelling by fundamental theories the enhancement of SO_2 absorption by chemical reactions.

Experiments have been carried out on the absorption of sulfur dioxide, both pure SO_2 and SO_2/N_2 mixtures, into pure water, HCl solutions, and NaCl solutions in a continuous stirred tank. These results have been modeled by the mass transfer theory of surface renewal with instantaneous reversible chemical reaction.

The present work was undertaken to confirm that SO_2 absorption into aqueous solutions can be represented by a rigorous surface renewal model with equilibrium hydrolysis of sulfur dioxide at all points in a baffled agitated vessel with a flat gas-liquid interface.

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For the sulfur dioxide-water system, the gas absorption mechanism can be modeled by mass transfer with an instantaneous reversible reaction of the type A ⇄ 2B. The hydrogen and bisulfite ions possess equal diffusivities to comply with the electrical neutrality requirement.

For the sulfur dioxide-hydrogen chloride system, the equilibrium chemical reaction type becomes A ⇄ B. The mass transfer enhancement factor is independent of gas phase sulfur dioxide partial pressure.

For the sulfur dioxide-sodium chloride system, the absorption can be described by surface renewal theory accompanied by an equilibrium reaction of type A ⇄ B + C. The presence of the relatively high concentration of sodium chloride dissipates any gradient of electric potential and allows hydrogen ion to diffuse much faster. Sodium chloride also increases the value of the effective equilibrium constant through its effect on activity coefficients. These factors are reflected in the increase of the SO_2 absorption rate with the addition of sodium chloride.

CHEMICAL ABSORPTION MECHANISM

The following hydrolysis reaction takes place in the liquid phase when sulfur dioxide is absorbed into pure water:

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^- \tag{1}$$

The forward reaction rate constant at 20°C was estimated to be $3.4 \times 10^6\ (s)^{-1}$ (Eigen et al., 1961) and this reaction can be considered to be instantaneous. The value of the equilibrium constant of reaction (Eq. 1) is:

$$K_a = \frac{a_{H^+} a_{HSO_3^-}}{a_{SO_2}} = 1.3 \times 10^{-2}\ M \tag{2}$$

at 25°C and infinite dilution (Johnstone and Leppla, 1934). The moderately low value of K_a and high reaction rate characterize the equilibrium feature of this hydrolysis reaction. Therefore, the absorption of sulfur dioxide into water can be regarded as a process of gas absorption accompanied by an instantaneous reversible reaction.

In a previous paper, Chang and Rochelle (1980) considered the problem of mass transfer with various single equilibrium reactions. They presented the theoretical analysis based on surface renewal theory and compared the result with that of film theory given by Olander (1963). It was shown that the predictions of the two models are equivalent when the diffusivities of all the diffusing species are equal. The two models differ when the diffusivity ratios deviate from unity. However, results of the surface renewal theory can be estimated by an approximation method which modifies the exact solution of the film theory by replacing the diffusivity ratios with their square roots.

When sulfur dioxide is absorbed into pure water, there are no other ionic species except the two reaction products present in liquid phase. Therefore electrical neutrality requires that the concentration and effective diffusivity of H^+ are always equal to those of HSO_3^-. As a result, the hydrolysis reaction of SO_2 in pure water can be represented as a reversible reaction of the type A ⇄ 2B. The results of surface renewal theory can be obtained by numerical solution of the second-order nonlinear differential material balance equation. The mass transfer enhancement factor can be approximated by (Chang and Rochelle, 1980):

$$\phi_a = 1 + \sqrt{\frac{D_B}{D_A}} \cdot \frac{\sqrt{K_c}}{\sqrt{C_{Ai}} + \sqrt{C_{Ao}}} \tag{3}$$

where D_A and D_B represent the diffusivities of species A and B; K_c, the effective equilibrium constant of reaction (Eq. 1); and C_{Ai} and C_{Ao}, the concentrations of species A at gas-liquid interface and liquid bulk, respectively. The rate of SO_2 absorption, N_A, can be expressed as:

$$N_A = \phi k_L^\circ a(C_{Ai} - C_{Ao}) \tag{4}$$

When SO_2 is absorbed into a HCl solution in which the H^+ ion concentration is much higher than that of HSO_3^- ion, the H^+ ion concentration is almost a constant through the system and the sulfur dioxide hydrolysis effect on H^+ ion distribution is negligible. The absorption of SO_2 into HCl solution becomes a gas absorption process accompanied by an equilibrium reaction of the form A ⇄ B, where B represents the bisulfite ion only. The exact surface renewal theory solution for the mass transfer enhancement factor was given by (Olander, 1960):

$$\phi_s = \sqrt{\left(1 + \frac{D_B}{D_A} K_c'\right)\left(1 + K_c'\right)} \tag{5}$$

and the film theory solution was given:

$$\phi_f = 1 + \frac{D_B}{D_A} K_c' \tag{6}$$

where $K_c' = \dfrac{K_c}{[H^+]}$

If sodium chloride solution is used to absorb sulfur dioxide, electrical neutrality no longer constrains the concentration distribution and diffusivity of H^+ and HSO_3^-. Therefore the reaction which affects the absorption rate of SO_2 into NaCl solution is a reversible reaction of the type A ⇄ B + C. The numerical solution of the surface renewal model can be approximated by (Chang and Rochelle, 1980):

$$\phi_a = 1 + \sqrt{\frac{D_C}{D_A}} \frac{C_{Ci} - C_{Co}}{C_{Ai} - C_{Ao}} \tag{7}$$

in which

$$C_{Ci} = \frac{C_{Co} - \sqrt{\frac{D_B}{D_C}} C_{Bo} + \sqrt{\left(C_{Co} - \sqrt{\frac{D_B}{D_C}} C_{Bo}\right)^2 + 4\sqrt{\frac{D_B}{D_C}} C_{Ai} K_c}}{2}$$

EXPERIMENTAL

Apparatus and procedure

Figure 1 shows a schematic diagram of the experimental apparatus. The agitated vessel, shown in Figure 2(a), was made of lucite with 14 cm i.d. Four equally spaced vertical baffles, each one twelfth of the vessel diameter in width, were attached to the internal wall of the vessel. Another baffle, shown in Figure 2(a), was put on the inner side of the lid under the gas inlet hole. A liquid trap was used to keep a constant liquid level. The liquid holdup in the reactor is usually maintained at 1.4 liter.

The gas phase stirrer, shown in Figure 2(b), was a propeller with three flat blades and was placed in the center of the gas phase. The liquid stirrer, shown in Figure 2(c), was a propeller with three blades smaller

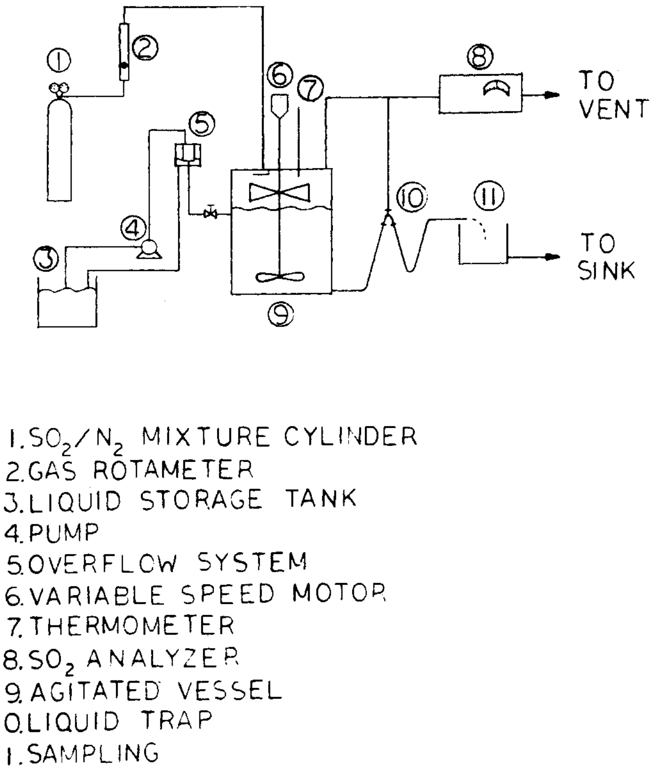

Figure 1. Experimental apparatus.

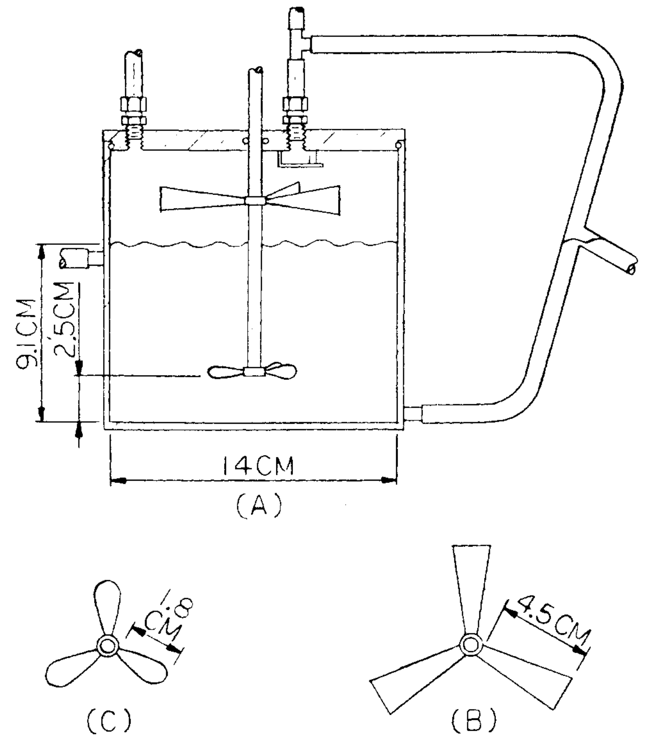

Figure 2. Agitated vessel and stirrers. (a) Agitated vessel (b) Gas stirrer (c) Liquid stirrer.

than those of the gas stirrer and was placed about one inch above the bottom of the vessel. The two stirrers were fastened to the same shaft. A variable speed motor with 1/40 hp was used to drive the agitator. The stirrer speed could be adjusted from 0 ~ 350 rpm and was measured by a strobe light. For most runs, the stirrer speed was kept at 300 rpm.

The gas phase was pure SO_2 or a mixture of sulfur dioxide and nitrogen. It was assumed that the gas phase was saturated with water vapor at the temperature of the experiment. The partial pressure of SO_2 in the gas phase was varied from 0.0002 to 0.98 bar. The absorbing liquids used were pure water and aqueous solutions of HCl, NaOH, or NaCl of concentration varying from 0.01 to 1 g-mol/L.

All the experiments were carried out in flow operation with respect to both gas and liquid. Pure SO_2 or premixed SO_2/N_2 were taken from pressurized cylinder, passed into the vessel through a gas rotameter and then vented into the exhaust line. The volumetric flow rate of gas was maintained constant in the range of 200 to 2000 cm^3/min with a needle valve. The liquid flow rate was maintained constant in the range of 60 to 450 cm^3/min by an overflow device.

As soon as the liquid in the vessel reached desired level, agitation in both phases was started. The SO_2 gas stream was then introduced into the vessel and the absorption gradually reached steady state. Liquid samples were taken from the sample port at the outlet of the liquid trap at regular intervals of the liquid residence time in the vessel. The system was assumed to be at steady state when the concentration of total sulfite in the sample attained a final constant value. The sulfur dioxide absorption rate was calculated from the liquid phase material balance.

The total dissolved sulfur dioxide in the solution was determined by iodometric titration using starch as an indicator. In order to avoid air oxidation of the dissolved sulfur dioxide in the sample, the liquid sample was flowed directly into the iodine solution. Several samples were taken with hydrogen peroxide solution to oxidize the dissolved sulfur dioxide totally into sulfate. An ion chromatograph was used to analyze the sulfate concentration. The results showed that the oxidation of absorbed SO_2 in the vessel was negligible. The SO_2 concentration of the exit gas stream was determined by a pulsed fluorescent SO_2 analyzer (Thermoelectron Model 40).

Prediction of physical properties

Sulfur dioxide in aqueous solution is present as hydrated SO_2 molecules and HSO_3^- ions at pH less than 5. Rabe and Harris (1963) measured the physical solubility of sulfur dioxide in pure water with wide range of temperature and concentration. They presented their results in the form of Henry's law constant for nonionized SO_2:

$$H = \exp(2851.1/T - 9.3795) \tag{8}$$

TABLE 1. PARAMETERS FOR THE ESTIMATION OF ACTIVITY COEFFICIENTS AT 25°C

	C_{3j}	C_{4j}
H^+	6.0	0.4
HSO_3^-	4.5	0.0

This empirical equation also fits the data given by Johnstone and Leppla (1934). Hence the concentration of the nonionized sulfur dioxide in pure water can be obtained from:

$$C_{Aiw} = P_{SO_2} \cdot H \tag{9}$$

where P_{SO_2} is the partial pressure of SO_2 in gas phase.

The physical solubility of sulfur dioxide in aqueous HCl and NaCl solutions were estimated from (Van Krevelen and Hoftijzer, 1948):

$$\log(C_{Ai}/C_{Aiw}) = -K_s I \tag{10}$$

where C_{Ai} is the physical solubility of sulfur dioxide in aqueous solution and K_s is the salting-out parameter expressed as the sum of the contributions due to the positive and negative ions present and the dissolved gas. I represents the ionic strength of the solution. The values of K_s for HCl and NaCl solutions at 25°C are −0.084 and 0.01, respectively.

The equilibrium constant of reaction (Eq. 1) was calculated from the correlation (Rabe and Harris, 1963):

$$K_a = \exp(1972.5/T - 10.9670) \tag{11}$$

in which K_a has thermodynamic units. Therefore, appropriate activity coefficients must be incorporated with the concentration of each component to estimate its activity a_j,

$$a_j = \gamma_j \cdot C_j \tag{12}$$

Individual ion activity coefficients at 25°C were calculated by a modified Debye-Huckel limiting law (Lowell et al., 1970):

$$\log \gamma_j = 0.512 n_j^2 \left[\frac{-I^{1/2}}{1 + 0.312 C_{3j} I^{1/2}} + C_{4j} I \right] \tag{13}$$

where n_j is the charge on the jth ion, and C_{3j} and C_{4j} are characteristic parameters for each ion species. Table 1 lists all the values of those constants and parameters on a molar concentration basis. The activity coefficient of the hydrated sulfur dioxide in solution was estimated by (Harned and Owen, 1958):

$$\log \gamma = 0.076\, I \tag{14}$$

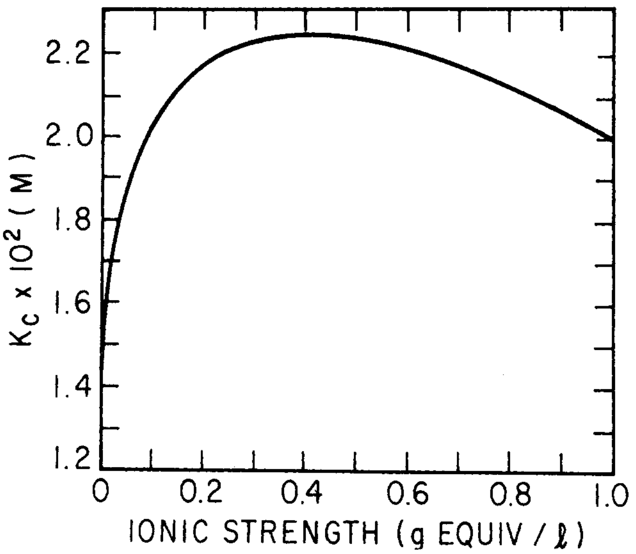

Figure 3. Effect of ionic strength on equilibrium constant of reaction (1) at 25°C.

Figure 3 shows the values of effective equilibrium constant K_c in concentration units, calculated from Eqs. 11 to 14 vs. ionic strength.

The liquid phase diffusivity D_{Aw} of sulfur dioxide in pure water was taken as 2.00×10^{-5} cm²/s at 30°C (Peaceman, 1951). The value of D_{Aw} at 25°C was predicted by correcting for the temperature and viscosity of water according to the Stokes-Einstein relation.

The true diffusivities of H^+ and HSO_3^- are related to their equivalent ion conductivities:

$$D\pm = \frac{RT\gamma^\circ_\pm}{(Fa)^2} \tag{15}$$

where Fa is the Faraday number and $\gamma\pm$ is the equivalent ion conductivity. The ionic conductivities of H^+ and HSO_3^- at 25°C and infinite dilution are 350 and 50 cm²/mol · ohm, respectively (Landolt-Bornstein, 1960). Therefore, H^+ tends to move seven times faster than HSO_3^-.

In pure water, electrical neutrality requires that H^+ and HSO_3^- move at the same rate, therefore an electrical potential gradient develops which slows down H^+ and speeds up HSO_3^-. The effective diffusivity of both H^+ and HSO_3^- is given by (Newman, 1967):

$$D_{eff} = \frac{RT(1/n^+ + 1/n^-)}{(Fa)^2(1/\lambda^\circ_+ + 1/\lambda^\circ_-)} \tag{16}$$

The value of D_{eff} for H^+ and HSO_3^- in pure water at 25°C is $2.33 \cdot 10^{-5}$ cm²/s.

In NaCl and HCl solutions the potential gradient is dispersed by a concentration gradient of Na^+ and Cl^-. Furthermore, according to the analysis of Vinograd and McBain (1941), the interference of electrical potential gradient on diffusion of electrolytes can be avoided if sufficient relative excess of any salt is distributed in uniform concentration throughout the system. It was found according to the equation of Vinograd and McBain (1941) that the effective diffusivity of H^+ deviates from its true value by less than 2% if the concentration of NaCl is fifty times higher than that of bisulfite. In HCl solutions, the difference between the effective and true diffusivity of HSO_3^- is less than 1% when the concentration ratio of HCl to HSO_3^- is 10. All of the experiments with NaCl and HCl meet those conditions. Therefore the effective diffusivities of H^+ and HSO_3^- were assumed to be equal to their true diffusivities, $9.37 \cdot 10^{-5}$ and $1.33 \cdot 10^{-5}$ cm²/sec at 25°C, respectively.

Only the ratios of diffusivities were used for the estimation of mass transfer enhancement factors. It was assumed that these diffusivity ratios were independent of temperature and viscosity.

RESULTS AND DISCUSSIONS

Gas and liquid phase mass transfer coefficients

The gas phase mass transfer coefficient was measured by absorbing sulfur dioxide from SO_2/N_2 mixture into NaOH solutions (0.7 to 1 M). In this system, the dissolved sulfur dioxide reacts instantaneously and irreversibly with a large excess of reactant at the gas-liquid interface. Therefore, the liquid phase mass transfer resistance is considered to be negligible. The values of $k_g a$ were calculated from the measured absorption rate, assuming that the gas phase is complete mixed.

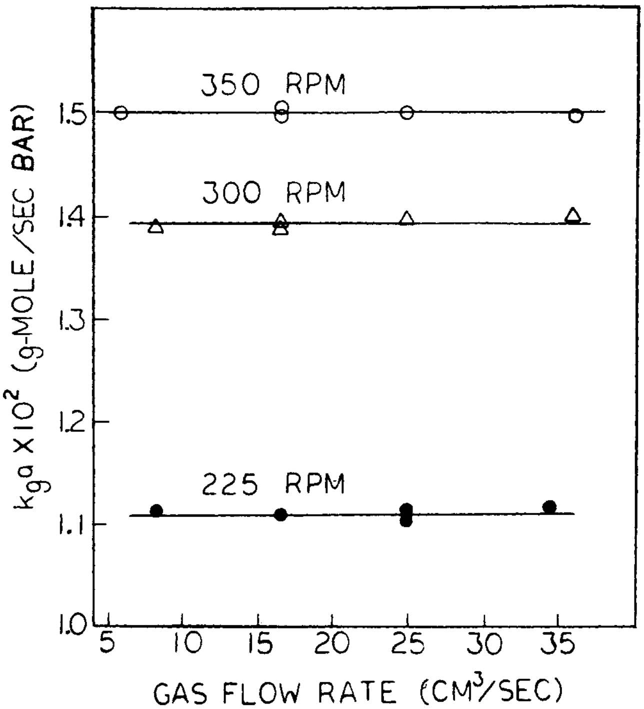

Figure 4. Effect of gas flow rate on gas-phase mass transfer coefficient (absorption of SO_2 into aqueous NaOH solutions).

The effect of gas flow rate on the value of $k_g a$ is shown in Figure 4. It can be seen that the $k_g a$ values are independent of the gas flow rate, providing necessary, but not sufficient, proof that the gas is completely mixed. The temperature effect on $k_g a$ was found to be negligible in the range of the experiments (15 to 30°C).

The liquid phase mass transfer coefficient, $k^\circ_L a$, was determined at constant stirrer speed (300 rpm) by measuring the rate of physical absorption of pure sulfur dioxide into HCl solution (1 M). It was assumed that there was no mass transfer resistance in the pure SO_2 gas phase. According to Eq. (5), the chemical reaction effect on the mass transfer rate is negligible in 1 M HCl

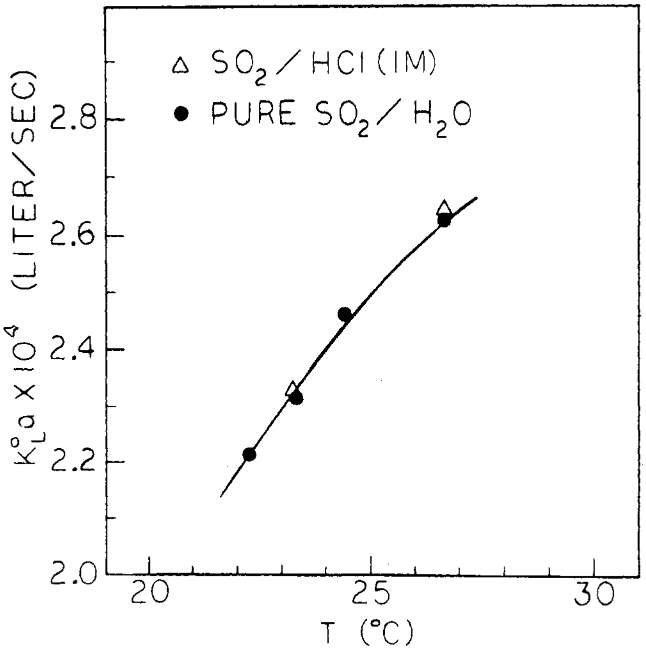

Figure 5. Liquid-phase physical mass transfer coefficient of sulfur dioxide into water at 300 rpm.

Table 2. Experimental Conditions and Absorption Rate Data of Pure SO_2-H_2O

Run	T (°C)	L (cm³/s)	C_{Ai} (M)	C_{Ao} (M)	$\phi k^\circ_L a$ (L/s)	$k^\circ_L a$ (L/s)
1	26.5	4.5	1.09	0.066	2.90×10^{-4}	2.63×10^{-4}
2	24.5	7.3	1.17	0.042	2.71×10^{-4}	2.47×10^{-4}
3	23.3	5	1.22	0.0595	2.56×10^{-4}	2.33×10^{-4}
4	22.2	5.3	1.27	0.056	2.46×10^{-4}	2.24×10^{-4}

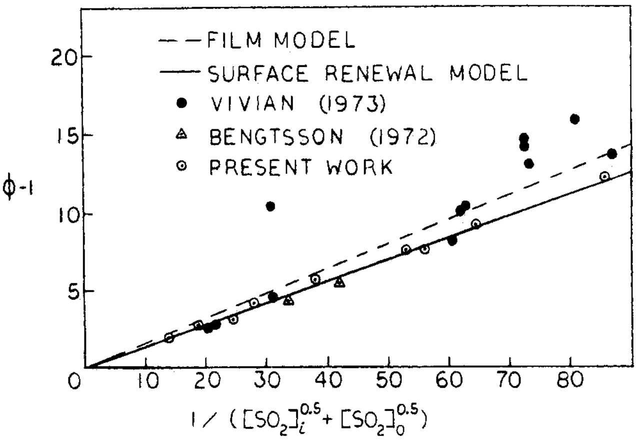

Figure 6. Comparison of theoretical mass transfer enhancement factor with experimental data for SO_2/N_2-H_2O system at 25°C.

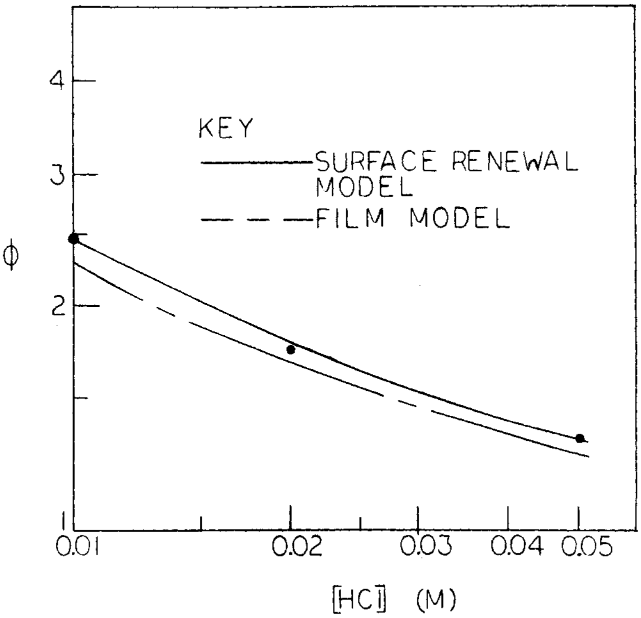

Figure 7. Comparison of theoretical mass transfer enhancement factor with experimental data for SO_2/N_2-HCl system at 23.5°C.

solution and only physical absorption of SO_2 occurred in liquid phase. Experimental results for the liquid-side mass transfer coefficient are shown in Figure 5 as a plot of $k^\circ_L a$ vs. temperature. Liquid flow rate did not affect $k^\circ_L a$. It was found that $k_g a$ is about forty times greater than $Hk^\circ_L a$. Therefore, in most experiments the mass transfer rates were controlled by liquid-phase resistance. In all cases the effect of gas-phase resistance was included in calculations of ϕ.

SO_2 – H_2O System. Experimental results obtained with pure SO_2 and pure H_2O at different temperatures are listed in Table 2. The gas phase mass transfer resistance was assumed to be negligible in pure SO_2 runs. Because of the high sulfur dioxide concentration at the interface, the mass transfer enhancement factors calculated from Eq. 3 were all about 1.1. The liquid phase physical mass transfer coefficient was estimated from these data at various temperatures by taking into account the 10% mass transfer enhancement caused by SO_2 hydrolysis. The black dots in Figure 5 represent the $k^\circ_L a$ computed from pure SO_2-H_2O data. They are in good agreement with those obtained from pure physical SO_2 absorption in 1 M HCl.

Figure 6 represents the experimental data obtained for the dilute SO_2-H_2O system at 25°C. The experimental values of the mass transfer enhancement factors are shown in Figure 6 by circles along with those values obtained by other investigators. Vivian (1973) conducted a series of experiments with dilute SO_2/N_2 mixture and pure water in a short wetted wall column. Instead of measuring the gas and liquid phase physical mass transfer coefficients, some correlations were used to calculate these values. His data are shown in Figure 6 by black dots. The two triangles in the same figure represent the data obtained by Bengtsson et al. (1972) from a laminar jet.

The solid line represents the theoretical line for absorption with an instantaneous reversible reaction of type A $\rightleftarrows$ 2B predicted by surface renewal theory. The film theory predictions are represented by the dotted line. Because the effective diffusivity ratio of bisulfite ion to dissolved sulfur dioxide is not far from unity, the predictions by film theory are quite close to those by surface renewal theory.

SO_2 – HCl System. Experimental results on the absorption of SO_2 into HCl solutions are shown in Figure 7, where the experimental mass transfer enhancement factors, ϕ, are plotted against the HCl concentrations. The solid curve in this figure represents the theoretical mass transfer enhancement factor predicted by surface renewal model on the assumption that the reversible reaction of type A $\rightleftarrows$ B takes place instantaneously along the diffusion path, while the broken curve shows the corresponding film theory predictions.

Eq. 5 indicates that the mass transfer enhancement factor in this case should be a function of diffusivity ratio and equilibrium constant only. The value of ϕ remains a constant irrespective of the sulfur dioxide partial pressure variation in gas phase. This is quite different from the gas absorption cases with other equilibrium chemical reaction types. Experimental data in Figure 8 show that the change of gas phase SO_2 concentration does not affect the value of ϕ, as long as the temperature and the HCl concentration remain the same.

SO_2 – NaCl System. Figure 9 presents the experimental data obtained for the SO_2–NaCl system at 24°C and 1250 ppm SO_2 gas phase concentration. The absorption rate increases with the rise of the NaCl concentration and reaches a maximum at about 0.4 M NaCl concentration, then decreases very slowly as NaCl concentration increases further. Two factors, diffusivity and equilibrium constant, contribute to this absorption rate change. The ionic strength increases with the addition of NaCl which affects the effective equilibrium constant K_c as shown in Figure 3. The similarity between the shape of the curves in Figures 3

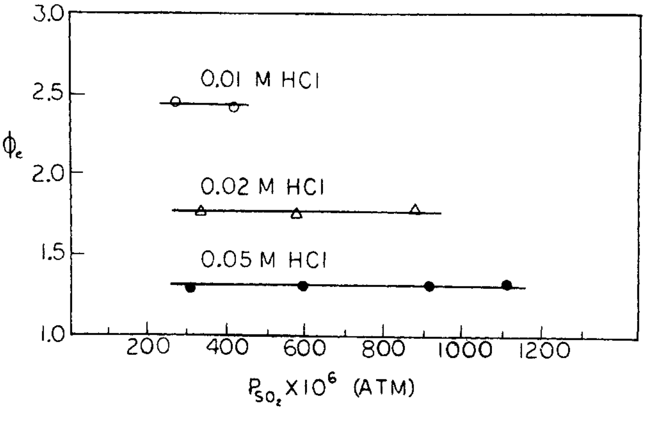

Figure 8. Effect of SO_2 partial pressure on liquid phase mass transfer enhancement factor at 23.5°C.

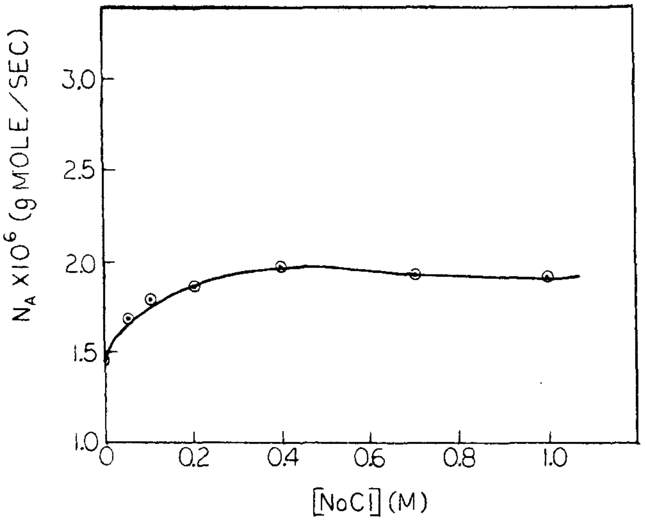

Figure 9. Absorption rate of SO_2 into aqueous NaCl solutions at 24°C with 1250 ppm SO_2 in N_2.

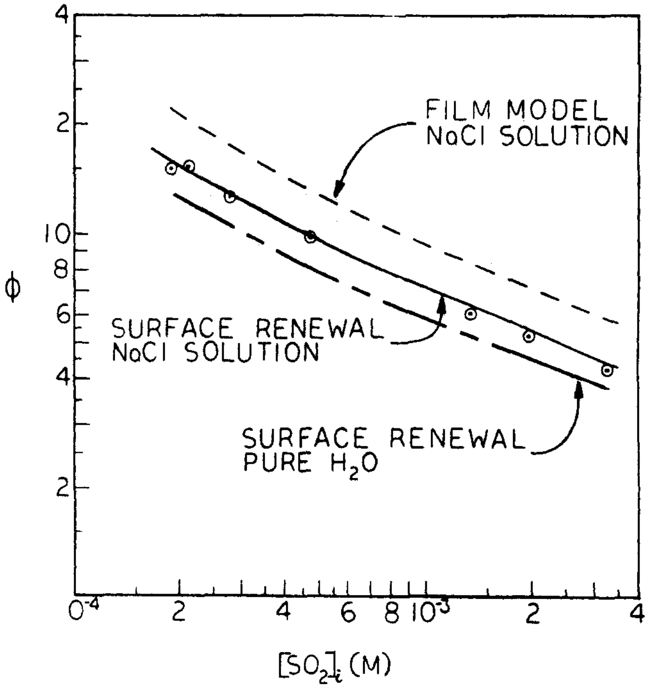

Figure 10. Comparison of theoretical mass transfer enhancement factor with experimental data for SO_2 (1200 ppm)-NaCl (0.4 M) system at 25°C.

and 9 reflects the effect of equilibrium constant on absorption rate caused by ionic strength variation. However, only part of the absorption rate increase can be attributed to the equilibrium constant change. The other factor which causes the absorption rate rise with the increase of NaCl concentration is the diffusivity change.

As mentioned earlier, when sufficient excess of salt is added to the system, the electrical gradient effect on the ionic diffusion is suppressed and the moving ions can migrate freely. Therefore, the fast moving hydrogen ion is gradually liberated from the influence of the other ions as the sodium chloride is added into the aqueous solution. When a sufficient amount of salt is present (0.1 to 0.2 M in this case), the hydrogen ion is not bound by the other ions anymore. The absorption rate of sulfur dioxide is also accelerated along with the release of the hydrogen ion.

The experimental results of sulfur dioxide absorption rate in NaCl solutions are shown in Figure 10 as a plot of enhancement factor ϕ vs interface equilibrium concentration of sulfur dioxide. The solid curve gives the surface renewal theory solution for gas absorption with an instantaneous reversible reaction of the type $A \rightleftarrows B + C$ and can reasonably represent the data. The dashed curve shows the predictions of surface renewal model with reaction of the type $A \rightleftarrows 2B$. The figure shows that the released hydrogen ion increases the SO_2 absorption rate by more than 20%. The broken curve represents the film theory model. The difference between the film model and the surface renewal model is much larger than in pure water or HCl solution. This is because the fast moving hydrogen ion makes the diffusivity ratios in this case deviate from unity much farther than the $SO_2 - H_2O$ and SO_2 − HCl systems.

NOTATION

a = component activity, g-mol/L
C = concentration, g-mol/L
C_{3j}, C_{4j} = parameter in Eq. 13
D = diffusivity of component, cm^2/s
D_{eff} = effective diffusivity defined by Eq. 16, cm^2/s
$D\pm$ = effective diffusivity of ions defined by Eq. 15, cm^2/s
Fa = Faraday = 96488 coulombs/g-equivalent
G = gas flow rate, cm^3/s
H = Henry's law constant, g-mol/bar-L
I = ionic strength, g-mol/L
K_a = thermodynamic equilibrium constant, g-mol/L
K_c = effective equilibrium constant in concentration units, g-mol/L
$K_{c'}$ = equilibrium constant defined by Eq. 6
$k_g a$ = gas-phase mass transfer coefficient, g-mol/s-bar
$k_L^\circ a$ = liquid-phase mass transfer coefficient, L/s
K_s = salting out parameter, L/g-mol
L = liquid flow rate, cm^3/s
M = molarity, g-mol/L
N_A = absorption rate, g-mol/s
$n\pm$, n_j = valence
P_{SO_2} = SO_2 partial pressure, bar
R = gas constant = 8.315 J/°K-g-mol
T = temperature, °K
ϕ_a, ϕ_s, ϕ_f, ϕ_e = mass transfer enhancement factor obtained from approximation method, penetration model, film model and experiment
γ_j = activity coefficient of component, j
$\overset{\circ}{\lambda}\pm$ = equivalent ion conductance, cm^2/g-mol/ohm

Subscripts

A, B, C = components A, B, C
i = concentration at gas-liquid interface
o = concentration in bulk liquid
w = value for pure water
[ ] = concentration, g-mol/L

LITERATURE CITED

Bengtsson, I. B. S., and K. Färnkvist, "Absorption of SO_2 in $CaCO_3$-Slurry in a Laminar Jet Absorber," *Chem. Engr. Sci.*, **27**, 1853 (1972).

Chang, C. S., and G. T. Rochelle, "Surface Renewal Theory for Simultaneous Mass Transfer and Equilibrium Chemical Reaction," Presented at AIChE 88th National Meeting, Philadelphia, June 8-12, 1980.

Danckwerts, P. V., "Gas Absorption with Instantaneous Reaction," *Chem. Eng. Sci.*, **23**, 1045 (1968).

Eigen, M., K. Kustin and G. Maas, "Die Geschwindigkeit der Hydratation von SO_2 in Wässriger Lösung," Z. *Phys. Chem.*, Frankfurt, **30**, 130 (1961).

Groothuis, H. and H. Kramers, "Gas Absorption by Single Drops during Formation," *Chem. Eng. Sci.*, **4**, 17 (1955).

Harned, H. S. and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd. ed., Reinhold, NY (1958).

Hikita, H., S. Asai, and H. Nose, "Absorption of Sulfur Dioxide into Water," *AIChE J.*, **24**, 1, 147 (1978).

Johnstone, H. F., and P. W. Leppla, "The Solubility of Sulfur Dioxide at Low Pressures. The Ionization Constant and Heat of Ionization of Sulfurous Acid," *J. Am. Chem. Soc.*, **56**, 2233 (1934).

Landolt-Börnstein Physikalisch-Chemische Tabellen, Bd II-7, P. 25f, Springer-Verlag, Berlin, Germany (1960).

Lowell, P. S., D. M. Ottmers, K. Schwitzgebel, T. I. Strange, and D. W. Deberry, P.B. 193-029, U.S. Environmental Protection Agency (1970).

Lynn, S., J. R. Straatemeier, and H. Kramers, "Absorption Studies in the Light of the Penetration Theory, I. Long Wetted Wall Columns," *Chem. Eng. Sci.*, **4**, 49 (1955).

Newman, J. S., In C. W. Tobias, ed., "Advances in Electrochemistry and Electrochemical Engineering," **5**, Interscience, Wily, NY (1967).

Olander, D. R., "Simultaneous Mass Transfer and Equilibrium Chemical Reaction," *AIChE J.*, **6**, 2, 233 (1960).

Peaceman, D. W., "Liquid-Side Resistance in Gas Absorption with and without Chemical Reaction," Sc.D. thesis, Mass. Inst. Tech., Cambridge, MA (1951).

Rabe, A. E., and J. F. Harris, "Vapor Liquid Equilibrium Data for the Binary System, Sulfur Dioxide and Water," *J. Chem. Eng. Data*, **8**, 333 (1963).

Rochelle, G. T., and C. J. King, "The Effect of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of SO_2 from Waste Gases," *Ind. Eng. Chem. Fundam.*, **16**, 67 (1977).

Toor, H. L., and S. H. Chiang, "Diffusion Controlled Chemical Reactions," *AIChE J.*, **5**, 3, 339 (1959).

van Krevelen, D. W., and P. J. Hoftyzer, "Sur la Solubilite des Gaz dans les Solutions Aqueous," *Chim. Ind. XXI^{me} Congr. Int. Chim. Ind.*, Soc. Chim. Ind., Paris, 168 (1948).

Vinograd, J. R., and J. W. McBain, "Diffusion of Electrolytes and of the Ions in Their Mixtures," *J. Am. Chem. Soc.*, **63**, 2008 (1941).

Vivian, J. W., "Absorption of SO_2 into Lime Slurries: Absorption Rates and Kinetics," EPA-650/2-73-047 (1973).

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R & D NOTES

Developing Mass Transfer Boundary Layer with Power Law Velocity Profiles and Wall Boundary Conditions

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Recent work by the authors on the condensation of sulfuric acid from flue gases [Verhoff and Choi (1979)] focused attention on the problem of boundary layer mass transfer with varying wall concentration. The influence of varying wall concentration was mathematically simplified by assuming a power law dependency. The analysis also permitted the use of a power law velocity profile. It is the goal of this note to present a general derivation of the integral boundary layer analysis for developing mass transfer with a power law wall concentration function and a developed power law velocity profile.

Power law temperature boundary conditions have been used in thermal boundary layer analysis over the last thirty years [Chapman and Rubesin (1949), Levy (1952), Sparrow and Gregg (1958), and Nagendra and Tirunarayanan (1970)]. Similarly, power law velocity profiles have been used for heat and mass transfer boundary layer analysis [e.g. Mixon and Carberry (1960) and Levy (1952)].

Mixon and Carberry (1960) have shown that the power dependency of the Nusselt (Sherwood) Number on the Prandtl (Schmidt) Number depends upon the power law velocity function. Levy (1952) has shown that the power dependency of the Nusselt Number on the Prandtl Number depends upon both the power law velocity and the power law wall temperature boundary condition. However, since Levy's analysis was numerical he could not ascertain the exact dependency.

Theory

Herein, the problem of interest is the formation of the mass transfer boundary layer in a steady flowing stream such as may occur when the temperature of the surface drops below a condensation temperature or as may occur because of a change in surface concentration. The velocity distribution is assumed to be well established such that

$$v_y = 0 \tag{1}$$

$$\frac{\delta v_x}{\delta x} = 0 \text{ and } v_x = v_x(y) \tag{2}$$

Here, v_y represents the velocity in the y direction which is perpendicular to the flat plate and v_x represents the velocity in direction x which is parallel to the plate. This velocity function $v_x(y)$ is presumed known.

A mass balance on an incremental distance in the x direction yields the following equation

$$v_x \frac{\partial C}{\delta x} = D \frac{\delta^2 C}{\delta y^2} \tag{3}$$

The boundary conditions associated with this equation are as follows

$$@\ x = 0 \qquad C = C_\infty \tag{4}$$

$$y = \infty \qquad C = C_\infty \tag{5}$$

$$y = 0 \qquad C = C_o(x) \tag{6}$$

This problem could be solved by any of several techniques such as numerical integration of the differential equations, superposition of constant boundary condition equations, similarly

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