MASS TRANSFER WITH EQUILIBRIUM CHEMICAL REACTION,

SULFUR DIOXIDE ABSORPTION IN AQUEOUS SOLUTIONS

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by

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Gas/liquid mass transfer with simultaneous equilibrium chemical reactions was modeled by both film and surface renewal theories. For systems with complicated multiple reactions, approximate solutions of surface renewal theory were obtained by replacing diffusivity ratios by their square roots in the solutions of film theory. This approximation method was tested with single reactions over a wide range of varibles and found to be accurate within 10% for most cases.

The absorption rates of SO_2 from a gas mixture of SO_2 and N_2 into aqueous solutions were measured at $25^{\circ}C$ in a continuous stirred vessel with an unbroken gas-liquid interface. The results were found to be accurately modeled by the theory of surface renewal with equilibrium reactions.

The theory of gas/liquid mass transfer with simultaneous equilibrium reactions was further applied to the absorption of SO_2 from waste gases into lime or limestone slurries:

1. to describe the SO_2 absorption mechanism in scrubbers
2. to model the novel processes such as forced oxidation and buffer additives
3. to evaluate the effectiveness of organic-acid buffer additives and to estimate the amount of additives needed for SO_2 scrubber.

It was found that the absorption of SO_2 by aqueous solutions can be modeled by approximate surface renewal theory with equilibrium reactions. Adipic, sulfopropionic, sulfosuccinic and β-hydroxy-propionic acids were evaluated as the most promising buffer additives for lime/limestone slurry scrubbing of SO_2 from flue gas. 10 - 20 mM adipic acid should be adequate to provide most of the benefit from buffer additives on mass transfer enhancement for a typical lime/limestone slurry scrubber for stack gas desulfurization.

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Chapter 1

INTRODUCTION

More than three quarters of SO_2 emissions in the U.S. result from fossil fuel combustion in utility and industrial boilers, ususlly coal-fired (Kellogg, 1974). On the other hand, the enegy crisis and oil shortage make the high-sulfur fuel an attractive fuel even if some expenses must be tolerated, to solve the SO_2 pollution problem. A number of processes have been developed to alleviate the SO_2 emissions from combustion sources (Nelson, 1974). Among them, the technology with the greatest number of applications is throwaway scrubbing with lime or limestone slurries.

THROWAWAY SCRUBBING PROCESS

A simplified flowsheet of lime/limestone slurry SO_2 scrubbing process is shown in Figure 1-1. The absorption of sulfur dioxide is carried out in the scrubber where intimate contact between the upward flowing flue gas and downward flowing slurry is maintained. The crystallizer plays an important role in the recycle system by providing sufficient time for the scrubber effluent so that the absorbed SO_2 can react with dissolved lime or limestone to crystallize as calcium sulfite or calcium sulfate (gypsum). These precipitates are then purged from the system as solid waste through a liquid/solid separation device. Most current practical approaches to waste disposal contain the concentrated solution or solids in a

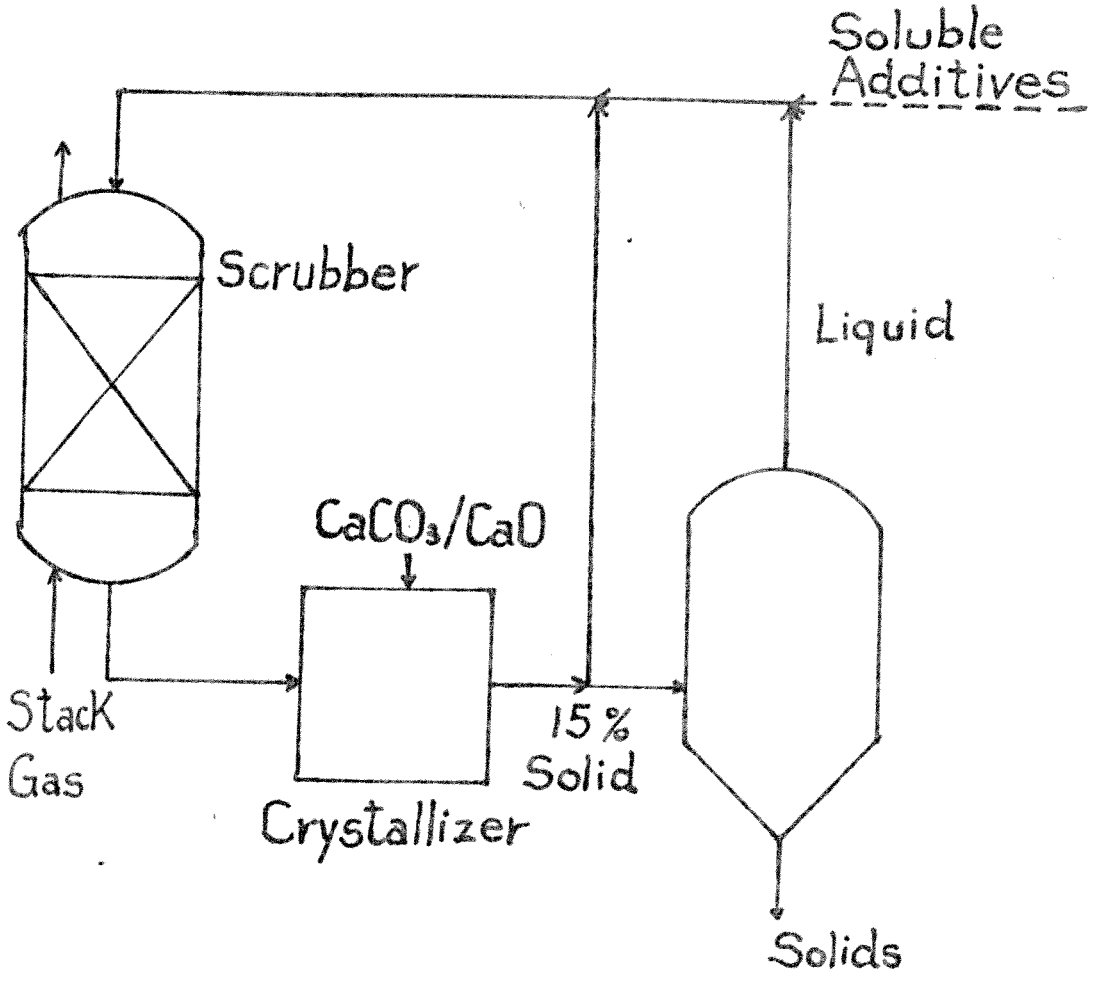

Figure 1-1. Slurry scrubbing

disposal pond or landfill area. Lime or limestone is required to neutralize the acidic SO_2 in the liquid phase and to make up the calcium species lost as solid waste. Some typical conditions of flue gas and scrubbing solution are shown in Table 1-1. (Rochelle, 1978)

A feasible throwaway scrubbing process must perform two important functions: (1) it must effectively remove SO_2 from the flue gas (2) it must produce easy-to-handle and environmentally acceptable waste disposal. It has been observed that gypsum crystallizes in much larger, more easily dewatered crystals than $CaSO_3$. Therefore, forced oxidation of waste $CaSO_3$ solids has been suggested and tested as a means of producing easily dewatered waste solids which are more suitable for landfill disposal.

Chiyoda Engineering in Japan initiated the development of a process to integrate the forced oxidation into the holding tank to provide sufficient residence time for oxidation. Previous work assumed that SO_2 removal in the scrubber occured only by physical absorption. However, Borgwardt (1977) has demonstrated that SO_2 absorption capacity is improved by oxidation of absorbed SO_2 in the scrubber. This mass transfer enhancement phenomena will be discussed in chapter 6 with the aid of the SO_2 absorption model developed by present work.

The limiting factor in throwaway processes with slurry scrubbing is the liquid-phase mass transfer resistance. Liquid-phase mass transfer in simple slurry system is probably accomplished

Table 1-1. Typical conditions of flue gas and scrubbing solutions.

Flue Gas Characteristics

Temperature	150°C
Pressure	Atmosphere
Composition	(mole %)
N_2	74.55
CO_2	12.55
H_2O	7.76
O_2	4.86
SO_2	0.22
NO	0.06
HCl	0.006
SO_3	0.005

Scrubbing Solution Characteristics

Temperature	55°C
Composition (dissolved solids)	(g-mole/liter)
Ca	0.057
Mg	0.01
Cl	0.1
SO_3	0.014
SO_2	0.004

(continue)

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Table 1-1. Typical conditions of flue gas and scrubbing solution.

(continue)

(Alkaline species)	(millimoles/liter)
$SO_3^=$	0.11
$CaSO_3^o$	1.47
$MgSO_3^=$	0.08
HCO_3^-	0.57
$CaHCO_3^+$	0.18
$MgHCO_3^+$	0.02

largely through the buffering couples HCO_3^-/CO_2 and $SO_3^=/HSO_3^-$. At the gas/liquid interphase, HCO_3^- and $SO_3^=$ alkalinities react with dissolved SO_2:

$$SO_3^= + SO_2 + H_2O \rightleftharpoons 2HSO_3^-$$

$$HCO_3^- + SO_2 \rightleftharpoons CO_2 + HSO_3^-$$

The alkaline species HCO_3^- and $SO_3^=$ are regenerated at the liquid/solid interphase by dissolution of $CaCO_3$ and $CaSO_3$.

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{++} + 2HCO_3^-$$

$$CaCO_3 + 2HSO_3^- \rightleftharpoons Ca^{++} + 2SO_3^= + CO_2 + H_2O$$

$$CaSO_3 \rightleftharpoons Ca^{++} + SO_3^=$$

$$CaSO_3 + CO_2 + H_2O \rightleftharpoons Ca^{++} + HSO_3^- + HCO_3^-$$

The rate of SO_2 mass transfer through the liquid boundary layer adjacent to the gas interface will therefore be a strong function of the dissolved alkalinity of the bulk liquid, provided that the reactions are sufficiently rapid. Additives enhance the effect of dissolved alkalinity by increasing the concentrations of HCO_3^- and $SO_3^=$ or by introducing significant concentrations of other buffering couples, such as acetate/acetic acid and other organic acids. Thus, an equivalent level of SO_2 removal can be achieved with better limestone utilization, fewer scrubber stages, less pressure drop, less liquid rate, and/or a simpler scrubber. Alternatively, a given scrubber system can be used to obtain better levels of SO_2 removal. Rochelle and King (1977) have discussed the general criteria of

desirable buffer additives. The mass transfer model developed in the present work will be helpful in the understanding of SO_2 absorption mechanism and in the selection of appropriate buffer additives.

SCOPE OF INVESTIGATION

There are two major objectives of this work:

(1) to model the SO_2 absorption mechanism by mass transfer with equilibrium reactions.

(2) to evaluate buffer additives to improve SO_2 scrubbing performance by lime or limestone slurries.

The equilibrium reaction effects on mass transfer rate were discussed for several general reaction types. Both film and surface renewal theories were used to make material balance for the diffusion process in liquid phase. An approximation method which can estimate the surface renewal theory solutions by replacing diffusivity ratios by their square roots in the solution of film theory was tested over a wide range of variables. This approximation method was further applied to complicated multiple reaction systems so that surface renewal theory mass transfer rate can be easily obtained.

A series of experiments were run to measure the SO_2 absorption rate from a gas mixture of SO_2 and N_2 into aqueous solutions. A continuous stirred vessel with a flat gas-liquid interface was employed as the absorber with a simple geometry. The SO_2 concentration in gas phase was controlled in the same range as in SO_2 scrubber. Pure water, HCl and NaCl solutions were used as the absorbing liquid for the first set of experiments. Only the SO_2 hydrolysis reaction

was considered in the gas absorption mechanism. The presence of various ions can transform the SO_2 hydrolysis into different reaction types. This set of experiments provided data to verify the mass transfer model with single equilibrium reaction for simple SO_2 absorption process.

The second set of experiments was to absorb SO_2 by NaOH solutions. For this system; SO_2 hydrolysis, water ionization and secondary ionization of HSO_3^- should be considered at the same time. Therefore, the experimental data can be used to verify mass transfer with simultaneous multiple equilibrium reaction model.

Acetic acid and adipic acid solutions were utilized to absorb SO_2 for the third set of experiments. The theory of gas/liquid mass transfer with multiple equilibrium reactions was used to model those two buffer additives. This theoretical model was further employed to evaluate the effectiveness of nine other organic-acid buffer additives. The parameters studied included temperature, diffusivities, P_{SO_2}, pH, pKa, concentrations of total sulfite and buffer additives. After taking into account the gas-liquid mass transfer resistance of a typical SO_2 scrubber, the mass transfer model was used to assess the effect of forced oxidation on the SO_2 absorption rate and to estimate the amount of organic acid required to derive most of the mass transfer benefit from buffer additives.

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Chapter 2

SURFACE RENEWAL THEORY FOR SIMULTANEOUS MASS TRANSFER AND EQUILIBRIUM CHEMICAL REACTION

ABSTRACT

The solution of surface renewal theory for the effect of instantaneous reversible reaction on the rate of mass transfer has been computed numerically. The material balance equations were transformed into ordinary differential equations by combination of variables. An explicit, finite difference method was employed to solve the differential equations. At every point along the diffusion path, all the species were assumed to be in equilibrium. The analytical solutions derived from film theory are also presented and compared with those from surface renewal theory.

An approximation method by the use of film theory solutions which can estimate the surface renewal theory solutions was tested over a wide range of variables. It was found that the approximation method can estimate the surface renewal theory solutions within 10% for most cases.

SCOPE

This chapter presents numerical solutions of surface renewal theory for several general cases of instantaneous reversible chemical reactions with diffusivity ratios different from one. Danckwerts

(1968) has provided a model for diffusivity ratios of one. However, some important reactions such as SO_2 absorption in aqueous solutions have diffusivity ratios as large as 7 (Chang and Rochelle, 1979). Olander (1960) has solved the film theory of absorption for several types of instantaneous reversible reactions. However, surface renewal theory is more representative of practical gas-liquid contactors. Secor and Beutler (1967) extended their numerical solutions of finite rate reversible reaction. However, their method is too cumbersome to provide general results for instantaneous reversible reactions.

An approximation method is presented to permit application of surface renewal theory to more complicated reactions. The solution derived from film theory is modified by substituting for any diffusivity ratio its square root.

CONCLUSIONS

1) Mass transfer with instantaneous reversible reactions as complicated as $A + B \rightleftarrows C + D$ can be modeled by surface renewal theory solved by numerical integration using Kutta's - Simpson's rule.
2) Film theory and surface renewal theory give identical enhancement factors with diffusivity ratios of one. However, deviations between the theories can be as much as 100% with a diffusivity ratio of 10.
3) Surface renewal theory can be approximated within 10% within the range of diffusivity ratios of 0.3 to 10.0 by using the film theory solution with diffusivity ratios replaced by their square roots.

This method does not require numerical integration and should be especially useful for complicated reaction systems where surface renewal theory models could be difficult to solve.

4) At large values of the equilibrium constants, the solutions for bimolecular equilibrium reactions asymptotically approach the solutions for instantaneous, irreversible reactions presented by Brian et al (1961).

INTRODUCTION

The problem to be considered is the effect of chemical reaction on the diffusion rate of solute A into a medium in which A undergoes an instantaneous, reversible reaction. The effects of reactions 2-1 through 2-4 will be modeled by surface renewal theory:

$$A \rightleftarrows 2B \qquad (2\text{-}1)$$

$$A \rightleftarrows B + C \qquad (2\text{-}2)$$

$$A + B \rightleftarrows C \qquad (2\text{-}3)$$

$$A + B \rightleftarrows C + D \qquad (2\text{-}4)$$

The basic assumptions can be summarized as follows:

1) Only A can penetrate through the surface of the medium. Species B, C, and D are nonvolatile.
2) The concentration of A at the surface of the medium is a constant.
3) The concentrations of all the species are initially uniform through the medium.
4) Transport of all species is by molecular diffusion alone.
5) Only a single reaction is significant.

6) The chemical reaction is instantaneous and reversible. The chemical equilibrium restriction is valid at every point of the diffusion path.

7) The diffusion coefficient of each species is constant.

8) Heat effects are negligible.

In the treatment that follows, the total component material balance will be used to obtain the differential equations describing the diffusion process. Each differential equation represents the material balance of a certain component in all forms, reactant or product. Unlike the finite reaction rate cases, the diffusion rate of any component other than A is not zero at the medium surface. Even though there is no mass transfer of B, C or D across the interface, part of A which penetrates through the medium surface will transform into those species by the instantaneous, reversible reaction. The stoichiometric relationship will be used to give appropriate boundary conditions for B, C, and D.

Case 1, Reaction $A \rightleftarrows 2B$

According to surface renewal theory, the total component material balance gives

$$\frac{\partial C_A}{\partial t} + \frac{1}{2}\frac{\partial C_B}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + \frac{D_B}{2}\frac{\partial^2 C_B}{\partial x^2} \qquad (2\text{-}5)$$

where A and B are subject to the equilibrium condition

$$C_A K_1 = C_B^2 \qquad (2\text{-}6)$$

The initial and boundary conditions are:

at $t = 0$, $C_A = C_{Ao}$

at $t > 0$ and $x = 0$, $C_A = C_{Ai}$

at $t \geq 0$ and $x \to \infty$, $C_A = C_{Ao}$

The boundary concentrations of species B can be obtained from Equation 2-6. Either C_A or C_B in Equation 2-5 can be eliminated by substituting the equilibrium relation into it. The partial differential equation can be transformed into an ordinary differential equation by combination of variables with

$$w = \frac{x}{\sqrt{D_A t}} \tag{2-7}$$

The dimensionless form of Equation 2-5 can be expressed as:

$$\frac{d^2B^*}{dw^2}(d_1+d_2-d_3B^*) + \frac{w}{2}\frac{dB^*}{dw}(\frac{1}{2} + d_2-d_3B^*) - d_3(\frac{dB^*}{dw})^2 = 0 \tag{2-8}$$

where $d_1 = \frac{D_B}{2D_A}$, $d_2 = \frac{2C_{Bi}}{K_1}$, $d_3 = \frac{2(C_{Bi} - C_{Bo})}{K_1}$

and $B^* = \frac{C_{Bi} - C_B}{C_{Bi} - C_{Bo}}$

Equation 2-8 is a nonlinear differential equation, therefore, no analytical solution can be obtained. However, it can be solved by numerical procedures. A forward integration method suggested by Kutta and Simpson (Levy, 1950) was chosen because it is relatively simple and very accurate. According to this method, the second order ordinary differential equation can be separated into two first order ordinary differential equations by assuming another variable equal to

the gradient of B^*. Integration was performed step by step across the entire domain of w. Adjustments and corrections were made for each increment. The error can be as small as the fifth power of the width of increment (Levy, 1950).

The remaining difficulty occurs in the treatment of the semi-infinite geometry where a finite number of points must be distributed over an infinite range of w. Also an abrupt change of B^* was expected in the first few steps of increment of w. An approach was used to transform the variable w by means of the equation

$$w = \frac{v}{1 - v} \tag{2-9}$$

This equation maps the infinite range of w into a finite range from 0 to 1, that is, at $w = 0$, $v = 0$ and at $w \to \infty$, $v = 1$. Thus, equation 2-8 can be transformed into

$$\frac{dB'}{dv} = B'\left[\frac{2}{1-v} - \frac{v(1+d_2-d_3B^*)}{2(1-v)^3(d_1+d_2-d_3B^*)}\right] + B'^2\left(\frac{d_2}{d_1+d_2-d_3B^*}\right) \tag{2-10}$$

$$B' = \frac{dB^*}{dv} \tag{2-11}$$

The boundary conditions for these equations are

$$v = 0, \quad B^* = 0$$

$$v = 1, \quad B^* = 1$$

Because this is a boundary value problem, an initial value of B' must be assumed to start the integration. Then, the final value of B^* at $v = 1$ obtained from the numerical integration is compared with the boundary value 1 at $v = 1$. If the difference is greater than the desired

tolerance, a correction is made and a new initial value of B' is set to start the integration again until the final solution reaches the desired limit of accuracy. Figure 2-1 shows the numerical integration results for several different initial values of B'. The width of each increment was set at 0.01. The correct initial value of B' should lie in between 0.295 and 0.300. The preceding techniques have been incorporated into a Fortran IV program with computer iteration.

The mass transfer enhancement factor is calculated from the results of the numerical integration. According to the stoichiometry of reaction 1, the absorption rate can be written as:

$$N = -(D_A \frac{\partial C_A}{\partial x} + \frac{D_B}{2} \frac{\partial C_B}{\partial x}) \Big| \; x = 0 \qquad (2\text{-}12)$$

Substituting the equilibrium relation

$$N = \sqrt{\frac{D_A}{t}} \, (C_{Bi} - C_{Bo})(d_1 + d_2)B' \Big| \; _{v=0} \qquad (2\text{-}13)$$

According to surface renewal theory

$$N_{ave} = \int_0^\infty Nse^{-st}dt = 2\sqrt{D_A \pi s} \, (C_{Bi}-C_{Bo})(d_1+d_2)B' \; | \; _{v=0} \qquad (2\text{-}14)$$

the total mass transfer rate of A across the interface without chemical reaction can be written

$$N_{phy} = \sqrt{D_A s} \; (C_{Ai} - C_{Ao}) \qquad (2\text{-}15)$$

The mass transfer enhancement factor can be obtained as the ratio of Equation 2-14 to 2-15 with substitution of Equation 2-6:

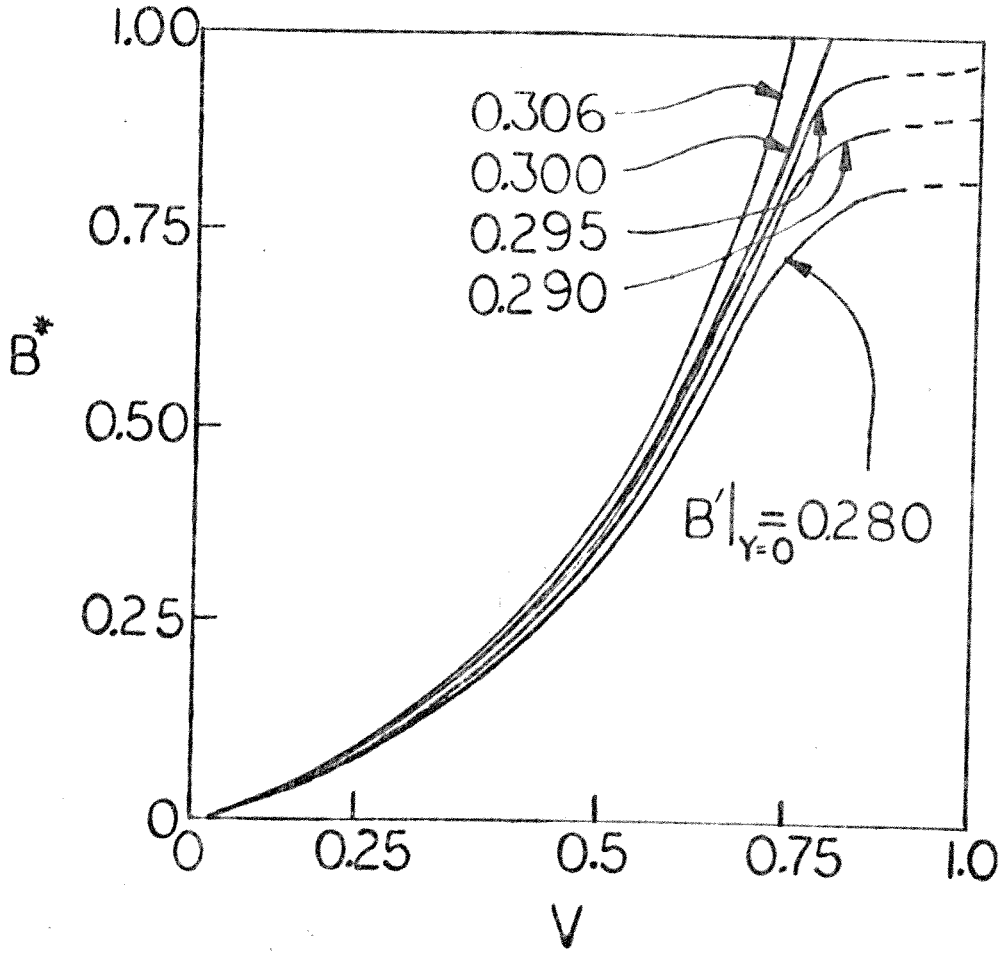

Figure 2-1. Some iterative results for case 1, $A \rightleftharpoons 2B$.

$$\phi_{s1} = \left. \frac{2\sqrt{\pi}\ (1+D_B\sqrt{K_1/C_{Ai}}/4D_A)B'}{1+\sqrt{C_{Ao}/C_{Ai}}} \right|_{v=0} \qquad (2\text{-}16)$$

where B' at v = 0 is the iterative constant obtained directly from the numerical solution of Equations 2-10 and 2-11.

Figure 2-2 shows a plot of ϕ_{s1} versus K_1/C_{Ai} with the parameter D_B/D_A. As the value of K_1/C_{Ai} becomes less than 0.1, the effect of chemical reaction on the mass transfer rate is almost negligible. However, at greater values of K_1/C_{Ai}, the mass transfer rate increases very fast. This can be explained by the extent of dissociation of A for various values of K_1/C_{Ai}. In real gas absorption cases, high K_1/C_{A1} corresponds to either very high value of K_1 or very dilute A in gas phase.

The mass transfer enhancement factor for reaction 2-1 derived from the film model was given by Olander (1960):

$$\phi_{f1} = 1 + \frac{D_B}{D_A}\frac{\sqrt{K_1/4}}{\sqrt{C_{Ai}}+\sqrt{C_{Ao}}} \qquad (2\text{-}17)$$

Values of ϕ_{f1} are compared with ϕ_{s1} in Figure 2-2. When the diffusivity ratio equals one, ϕ_{f1} is equivalent to ϕ_{s1}. The difference between ϕ_{f1} and ϕ_{s1} increases when D_B/D_A deviates further from 1. ϕ_{f1} is greater than ϕ_{s1} for D_A/D_B greater than 1, and less than ϕ_{s1} for D_B/D_A less than 1. It was found that the film theory solution of ϕ could be as much as 100% higher than that of surface renewal theory when D_B/D_A gets close to 10.

The effect of the bulk concentration, C_{Ao}, on mass transfer enhancement factor is shown in Figure 2-3. It is interesting to note

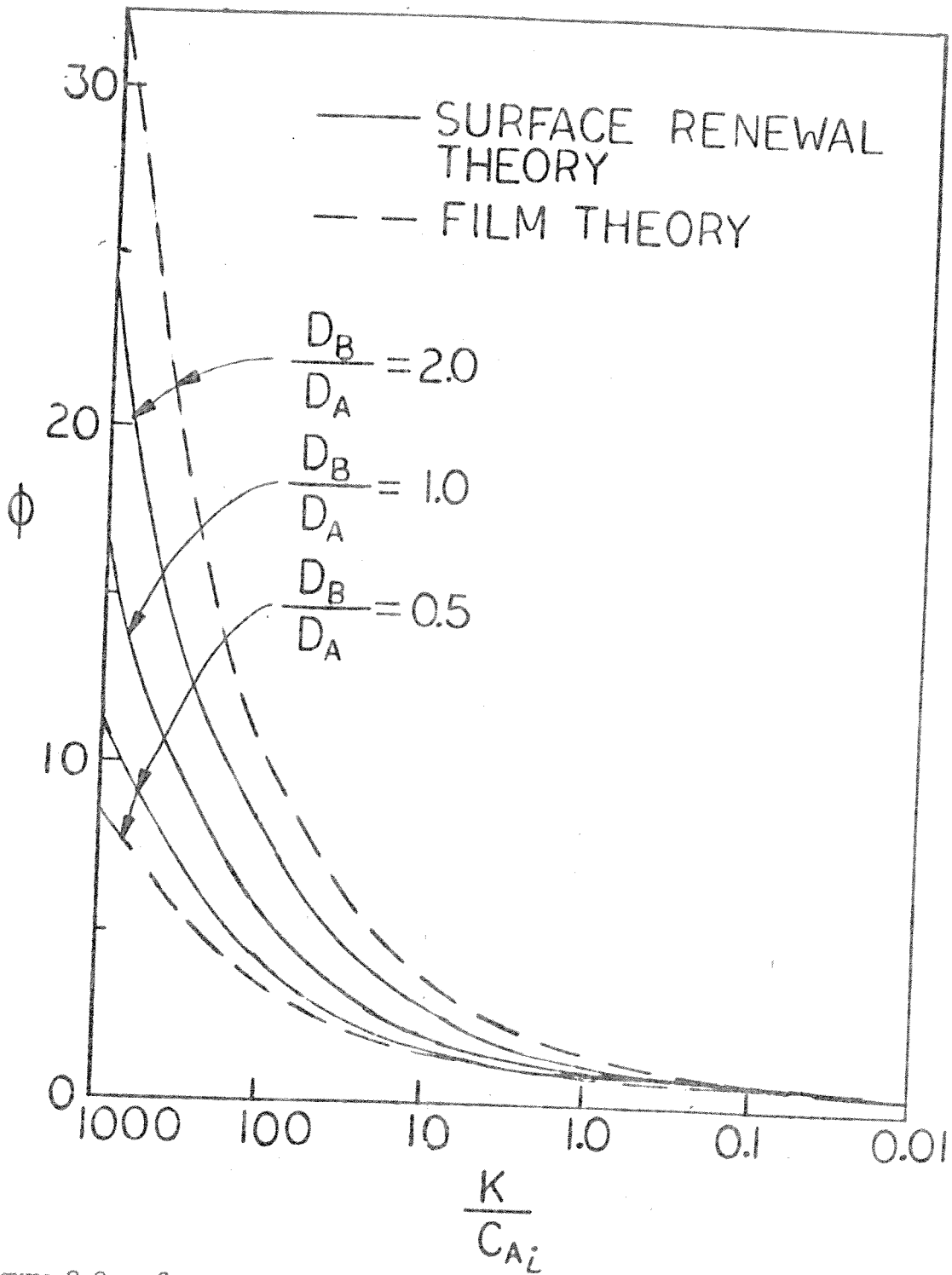

Figure 2-2. Comparison of mass transfer enhancement factors predicted by film theory and surface renewal theory for $A \rightleftharpoons 2B$ ($C_{Ao} = 0$).

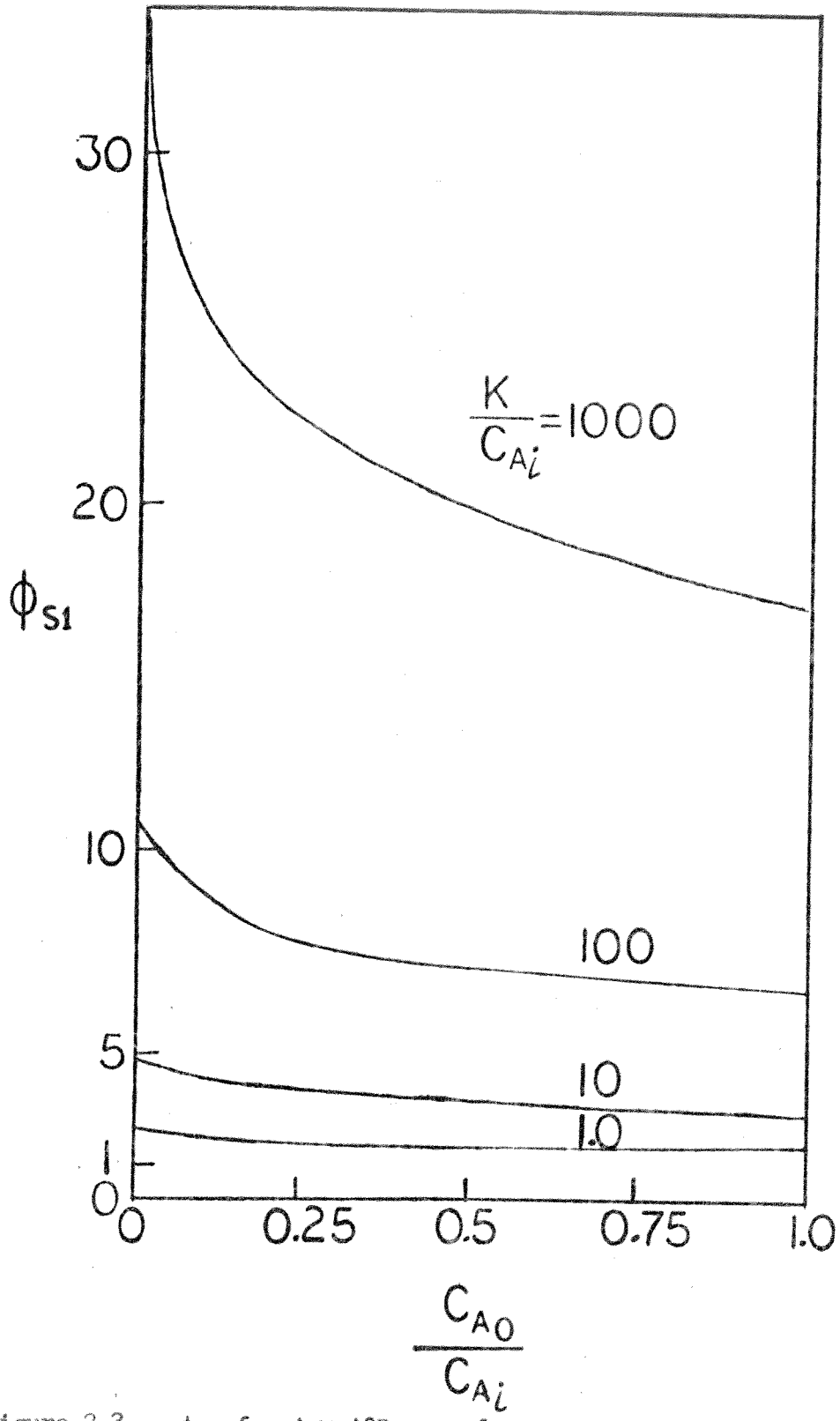

Figure 2-3. ϕ_{S1} for $A \rightleftharpoons 2B$ as a function of C_{Ao}/C_{Ai} $(D_B/D_A = 1.0)$.

that the value of ϕ will not be 1.0 even though the mass transfer rate become zero when C_{Ao} equals to C_{Ai}.

Another simplified model which considers the equilibrium relation only at boundaries, the bulk and the surface of medium, was proposed by Danckwerts (1968):

$$N = (\Delta C_{At}) \sqrt{D/\pi t} \tag{2-18}$$

where the diffusivities of both species, A and B, are taken to be equal to D. ΔC_{At} represents the amount of A which must be added to a unit volume of reacting medium in order to raise the concentration of unreacted A from its initial value C_{Ao} to the final equilibrium value, C_{Ai}, and simultaneously to raise the concentration of A in the reacted form by the amount required by the equilibrium condition. According to surface renewal theory and equilibrium relation, Equation 2-18 can be expressed as:

$$N_{ave} = \sqrt{Ds}\ (C_{Ai} + \sqrt{C_{Ai}K_1} - C_{Ao} - \sqrt{C_{Ao}K_1}) \tag{2-19}$$

The mass transfer enhancement factor is

$$\phi_{Di} = 1 + \frac{\sqrt{K_1/4}}{\sqrt{C_{Ai}} + \sqrt{C_{Ao}}} \tag{2-20}$$

Comparing Equation 2-20 with 2-17, it is seen that Danckwerts' model can be considered as a special case of the film model with equal diffusivities. As such it is also equivalent to a rigorous surface renewal model with equal diffusivities.

The absorption of sulfur dioxide into pure water is a process of

gas absorption accompanied by instantaneous reversible reaction of case 1. The following hydrolysis reaction takes place in liquid phase

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^- \qquad (2\text{-}21)$$

Because the absorbent is pure water and the products are only two ionic species of opposite sign, electrical neutrality not only requires that the concentrations of H^+ and HSO_3^- are always equal but also forces them to diffuse together with the same effective diffusivities. Chang and Rochelle (1979) have discussed this process in detail and compared the predictions of surface renewal model with experimental data.

Case 2, Reaction $A \rightleftarrows B + C$

The total component material balances on each of the species A and B are:

$$\text{Species A:} \quad \frac{\partial C_A}{\partial t} + \frac{\partial C_B}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + D_B \frac{\partial^2 C_B}{\partial x^2} \qquad (2\text{-}22)$$

$$\text{Species B:} \quad \frac{\partial C_B}{\partial t} - \frac{\partial C_C}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - D_C \frac{\partial^2 C_C}{\partial x^2} \qquad (2\text{-}23)$$

The equilibrium relation is

$$C_A K_2 = C_B C_C \qquad (2\text{-}24)$$

The initial and boundary conditions for this case are

at $t = 0$, $C_A = C_{Ao}$, $C_B = C_{Bo}$

at $t > 0$ and $x = 0$, $C_A = C_{Ai}$

at $t \geq 0$ and $x \to \infty$, $C_A = C_{Ao}$, $C_B = C_{Bo}$

The boundary concentration of species C can be obtained from the equilibrium relation of Equation 2-24. The final boundary condition which reflects the inability of B or C to diffuse across the interface is

$$\text{at } t > 0 \text{ and } x = 0,\ D_B \frac{\partial C_B}{\partial x} - D_C \frac{\partial C_C}{\partial x} = 0$$

Equations 2-22 and 2-23 can be transformed into dimensionless forms by the same mathematical procedures as in case 1:

$$\frac{dB'}{dv} = B' \left[\frac{2}{1-v} + \frac{v}{2d_4(1-v)^3} \left(\frac{D_c}{D_A} + \frac{D_C(C_{Ci}-\Delta C_C C^*)}{D_A K_2} + \frac{D_B(C_{Bi}-\Delta C_B B^*)}{D_A K_2}\right)\right] - C' \frac{\Delta C_C v}{2\Delta C_B d_4 (1-v)^3} \left(\frac{D_C}{D_B} - 1\right)\left(\frac{C_{Bi}-\Delta C_B B^*}{K_2}\right) + \frac{2D_C \Delta C_C}{D_A d_4 K_2} B'C' \qquad (2\text{-}25)$$

$$\frac{dC'}{dv} = B' \left(\frac{\Delta C_B v}{2\Delta C_C d_4 (1-v)^3}\right)\left(1 - \frac{D_B}{D_A}\right)\left(\frac{C_{Ci}-\Delta C_C C^*}{K_2}\right) - C' \left[\frac{2}{1-v} + \frac{v}{2d_4(1-v)^3}\left(\frac{D_B}{D_A} + \frac{D_B}{D_A}\frac{(C_{Bi}-\Delta C_B B^*)}{K_2} + \frac{D_C}{D_A}\frac{(C_{Ci}-\Delta C_C C^*)}{K_2}\right)\right] + \frac{2D_B \Delta C_B}{D_A d_4 K_2} B'C' \qquad (2\text{-}26)$$

$$\frac{dC^*}{dv} = C' \qquad (2\text{-}27)$$

where

$$C^* = \frac{C_{Ci}-C_C}{C_{Ci}-C_{Co}}, \quad \Delta C_B = C_{Bi}-C_{Bo}, \quad \Delta C_C = C_{Ci} - C_{Co}$$

$$d_4 = \frac{D_B D_C}{D_A^2} + \frac{D_B C_B}{D_A K_2} + \frac{D_C C_C}{D_A K_2}$$

The boundary conditions become

at $v = 0$, $B^* = 0$, $C^* = 0$

at $v = 1$, $B^* = 1$, $C^* = 1$

The numerical method, Kutta's-Simpson's rule, was used to solve the simultaneous nonlinear differential Equations 2-25, 2-26, 2-27, and 2-11. Due to the nature of the boundary value problem, two initial conditions need to be guessed to start the numerical procedure. They are either C_{Bi}, B' or C_{Ci}, C'. Iterative adjustments were made to continue the calculation until the final computed values of B' and C' matched the known boundary conditions.

The mass transfer rate of species A across the interface can be expressed as:

$$N = -\left(D_A \frac{\partial C_A}{\partial x} + D_C \frac{\partial C_C}{\partial x}\right)\Big|_{x = 0} \qquad (2\text{-}28)$$

In accordance with surface renewal theory, the steady state absorption rate can be obtained from Equations 2-24 and 2-28 as

$$N_{ave} = \sqrt{D_A \pi s}\ \Delta C_C b_1 C'\Big|_{v = 0} \qquad (2\text{-}29)$$

where

$$b_1 = \frac{C_{Bi}}{K_2} + \frac{D_C C_{Ci}}{D_B K_2} + \frac{D_C}{D_A}$$

The mass transfer enhancement factor is

$$\phi_{s2} = \frac{\sqrt{\pi} b_1 \Delta C_C C'}{(C_{Ai} - C_{Ao})} \Big|_{v=0} \qquad (2\text{-}30)$$

where $C'|_{v=0}$ and C_{Ci} are constants obtained from the numerical solution of Equations 2-25, 2-26, 2-27, and 2-11. Some values of ϕ_{s2} are shown in Figure 2-4 by solid curves with parameters C_{Ai}/K_2 and D_B/D_A.

On the other hand, the material balance according to film theory gives two homogeneous ordinary differential equations

$$D_A \frac{d^2 C_A}{dx^2} + D_B \frac{d^2 C_B}{dx^2} = 0 \qquad (2\text{-}31)$$

$$D_B \frac{d^2 C_B}{dx^2} - D_C \frac{d^2 C_C}{dx^2} = 0 \qquad (2\text{-}32)$$

The boundary conditions are

$$\text{at } x = 0, \quad C_A = C_{Ai}, \quad D_B \frac{dC_B}{dx} - D_C \frac{dC_C}{dx} = 0$$

$$\text{at } x = \delta, \quad C_A = C_{Ao}, \quad C_B = C_{Bo}$$

The general solutions to Equations 2-31 and 2-32 are

$$D_A C_A + D_B C_B = b_4 x + b_5 \qquad (2\text{-}33)$$

$$D_B C_B - D_C C_C = b_6 x + b_7 \qquad (2\text{-}34)$$

Substituting boundary conditions into Equations 2-33 and 2-34, b_6 must be equal to zero and the other three constants can be expressed by the combinations of diffusivities and boundary conditions. Therefore, the

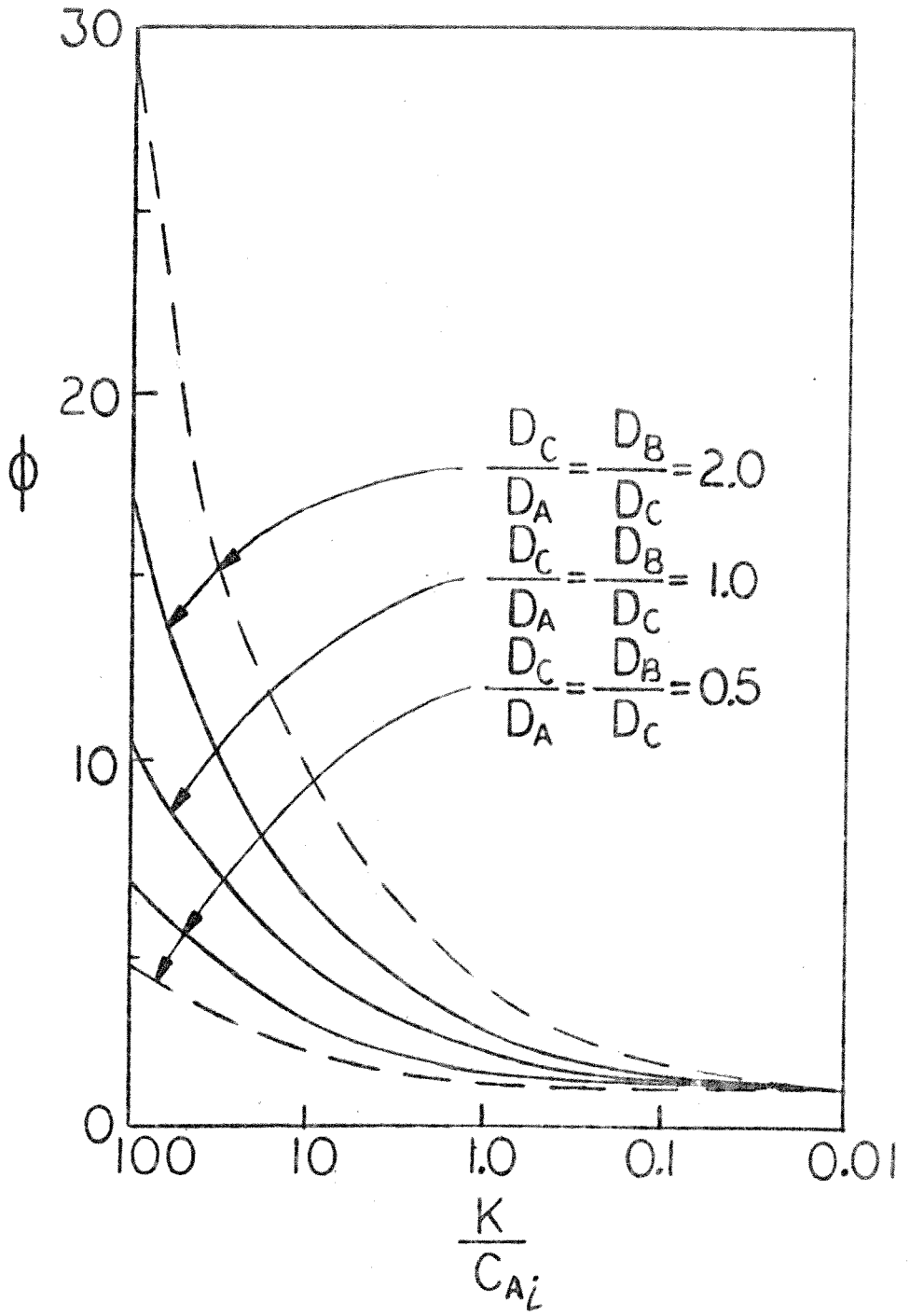

Figure 2-4. Comparison of mass transfer enhancement factors predicted by film theory and surface renewal theory for $A \rightleftharpoons B + C$ ($C_{Ao} = C_{Bo} = C_{Co} = 0$).

mass transfer enhancement factor can be obtained as

$$\phi_{f2} = 1 + \frac{D_C(C_{Ci}-C_{Co})}{D_A(C_{Ai}-C_{Ao})} \qquad (2\text{-}35)$$

where

$$C_{Ci} = \frac{C_{Co} - \frac{D_B}{D_C} C_{Bo} - \sqrt{(C_{Co} - \frac{D_B}{D_C} C_{Bo})^2 + \frac{4D_B C_{Ai} K_2}{D_C}}}{2}$$

The film theory mass transfer enhancement factor, ϕ_{f2}, is also shown in Figure 2-4 by dashed curves. It can be seen that reversal of the relative values of ϕ_{f2} and ϕ_{s2} occurs when the diffusivity ratio (D_B/D_A) changes from greater than 1 to less than 1.

Actually, case 1 can be considered as a special condition of case 2 where C_{Bo} is equal to C_{Co} and D_B is equal to D_C.

When sulfur dioxide is absorbed by an aqueous solution of strong electrolyte such as NaCl, electrical neutrality no longer restricts the diffusion behavior of the ionic products. The two product ions of the hydrolysis reaction, H^+ and HSO_3^-, can migrate with different diffusivities. Therefore, the absorption process becomes mass transfer accompanied by an instantaneous, reversible reaction of case 2. (Chang and Rochelle, 1979)

Case 3, Reaction $A + B \rightleftharpoons C$

The differences between this case and case 2 are the boundary conditions and equilibrium relation. The total component material balance gives

$$\text{Species A,} \quad \frac{\partial C_A}{\partial t} - \frac{\partial C_B}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - D_B \frac{\partial^2 C_B}{\partial x^2} \qquad (2\text{-}36)$$

$$\text{Species B,} \quad \frac{\partial C_B}{\partial t} + \frac{\partial C_C}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} + D_C \frac{\partial^2 C_C}{\partial x^2} \tag{2-37}$$

where A, B, and C are subject to the equilibrium relation

$$C_A C_B K_3 = C_C \tag{2-38}$$

The initial and boundary conditions are

$$\text{at } t = 0, \qquad C_A = C_{Ao}, \quad C_B = C_{Bo}$$

$$\text{at } t > 0 \text{ and } x = 0, \quad C_A = C_{Ai}, \quad D_B \frac{\partial C_B}{\partial x} + D_C \frac{\partial C_C}{\partial x} = 0$$

$$\text{at } t > 0 \text{ and } x \to \infty, \quad C_A = C_{Ao}, \quad C_B = C_{Bo}$$

The same numerical procedures used for case 2 can be applied to this system. The mass transfer rate can be expressed as

$$N_{ave} = \sqrt{D_A \pi s}\; b_2\; \Delta C_A A' \big|_{v=0} \tag{2-39}$$

where

$$b_2 = 1 + \frac{D_B D_C C_{Bi} K_3}{(D_B + D_C C_{Ai} K_3) D_A}$$

and

$$\frac{dA^*}{dv} = A', \quad A^* = \frac{C_{Ai} - C_A}{C_{Ai} - C_{Ao}}$$

The mass transfer enhancement factor can be written

$$\phi_{s3} = \sqrt{\pi}\; b_2 A' \big|_{v=0} \tag{2-40}$$

where $A' \big|_{v=0}$ is a constant obtained from the numerical solution of Equations 2-36, 2-37, 2-38, and 2-11. Some values of ϕ_{s3} are shown in Figure 2-5. along with the film theory mass transfer enhancement

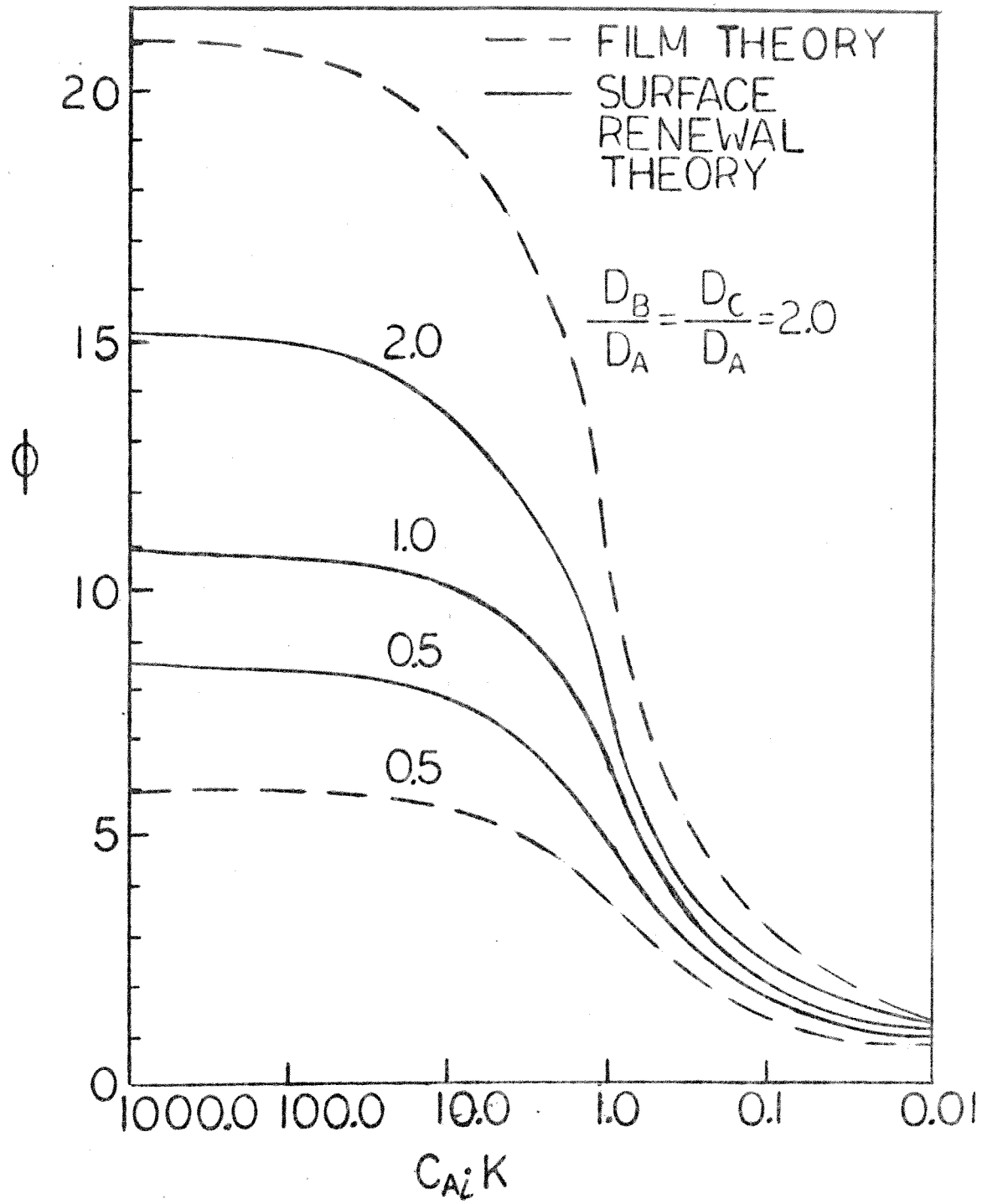

Figure 2-5. Comparison of mass transfer enhancement factors predicted by film theory and surface renewal theory for $A + B \rightleftharpoons C$ ($C_{Ao} = C_{Co} = 0$, $C_{Bo}/C_{Ai} = 10$).

factors given by Olander (1960).

If K_3 becomes large, the system approaches that of instantaneous irreversible, second-order reaction which has been discussed in detail in the literature. As K_3 approaches infinity, the group $1/C_{Ai}K_3$ in Figure 2-5 approaches zero and both film theory and surface renewal theory mass transfer enhancement factors reach asymptotic values. Olander (1960) showed that the asymptotic value of ϕ_{f3} was equivalent to Hatta's (1928) equation for reaction type of this case. It was found from present work that the asymptotic values of ϕ_{s3} corresponded to the solutions given by Danckwerts (1970) and Sherwood and Pigford (1952) for this reaction type under instantaneous and irreversible conditions.

Case 4, Reaction $A + B \rightleftharpoons C + D$

There are four components in this system, therefore, four equations are needed to solve for the mass transfer rate of species A. The equilibrium relation provides one equation, the other three can be obtained from material balances. The total component material balance gives:

$$\text{Species A,}\quad \frac{\partial C_A}{\partial t} - \frac{\partial C_B}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - D_B \frac{\partial^2 C_B}{\partial x^2} \tag{2-41}$$

$$\text{Species B,}\quad \frac{\partial C_B}{\partial t} + \frac{\partial C_C}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} + D_C \frac{\partial^2 C_C}{\partial x^2} \tag{2-42}$$

$$\text{Species D,}\quad \frac{\partial C_B}{\partial t} + \frac{\partial C_D}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} + D_D \frac{\partial^2 C_D}{\partial x^2} \tag{2-43}$$

where A, B, C, and D are subject to the equilibrium relation:

$$K_4 C_A C_B = C_C C_D \tag{2-44}$$

The initial and boundary conditions are

at $t = 0$, $\quad C_A = C_{Ao}$, $C_B = C_{Bo}$, $C_C = C_{Co}$

at $t > 0$ and $x \to \infty$, $C_A = C_{Ao}$, $C_B = C_{Bo}$, $C_C = C_{Co}$

at $t > 0$ and $x=0$, $\quad C_A = C_{Ai}$, $D_B \dfrac{\partial C_B}{\partial x} + D_C \dfrac{\partial C_C}{\partial x} = 0$

$$D_B \frac{\partial C_B}{\partial x} + D_D \frac{\partial C_D}{\partial x} = 0$$

The numerical procedure, Kutta's-Simpson's rule, can also be used to solve for the mass transfer rate of A of this case. But three initial conditions, for example, C_{Bi}, C_{Ci}, and B', must be set to start the integration. Three variables B^*, C^*, and D^* should reach the boundary condition of 1 at the same time when appropriate initial conditions were given for the numerical integration. The mass transfer rate of A across the interface can be written as

$$N = -\left(D_A \frac{\partial C_A}{\partial x} - D_B \frac{\partial C_B}{\partial x}\right)\Big|_{x = 0} \tag{2-45}$$

The mass transfer enhancement factor according to surface renewal theory is:

$$\phi_{s4} = \frac{\sqrt{\pi}\, b_3 B'}{\Delta C_A}\Big|_{v = 0} \tag{2-46}$$

where

$$b_3 = \frac{D_B C_{Ci}}{D_D K_4 C_{Bi}} + \frac{D_B C_{Di}}{D_C K_4 C_{Bi}} + \frac{C_{Ai}}{C_{Bi}} + \frac{D_B}{D_A}$$

Values of ϕ_{s4} obtained from numerical solution of Equations 2-11, 2-27, 2-41, 2-42, 2-43, and 2-44 are shown in Figure 2-6. The corresponding values of film theory mass transfer enhancement factor are also presented as dashed curves. Those values were calculated from the equations equivalent to those given by Olander (1960) and Danckwerts (1970).

$$\phi_{f4} = 1 + \frac{D_C(C_{Ci}-C_{Co})}{D_A(C_{Ai}-C_{Ao})} \tag{2-47}$$

where

$$C_{Ci} = 2D_D C_{Ai} K_4 \left(\frac{C_{Bo}}{D_C} + \frac{C_{Co}}{D_B}\right) \Big/ \left\{ \left[\left(\frac{D_D}{D_C} C_{Do} + \frac{D_D}{D_B} C_{Ai} K_4 - C_{Co}\right)^2 + 4D_D C_{Ai} K_4 \left(\frac{C_{Bo}}{D_C} + \frac{C_{Co}}{D_B}\right)\right]^{1/2} + \left(\frac{D_D}{D_C} C_{Do} + \frac{D_D}{D_B} C_{Ai} K_4 - C_{Co}\right) \right\}$$

If we take the limit of C_{Ci} as K_4 approaches infinity and substitute it into Equation 2-47, the mass transfer enhancement factor becomes

$$\lim_{K_4 \to \infty} \phi_{f4} = 1 + \frac{D_B C_{Bo}}{D_A C_{Ai}} \tag{2-48}$$

which is the Hatta (1928) equation for the reaction type of case 3. Therefore, when the equilibrium constant approaches infinity, case 4 is actually equivalent to case 3 and the physical properties of the reaction products do not affect the mass transfer rate any more. It can be seen from Figures 5 and 6 that even though ϕ_{s3} and ϕ_{s4} are quite different from each other at moderate values of equilibrium constants,

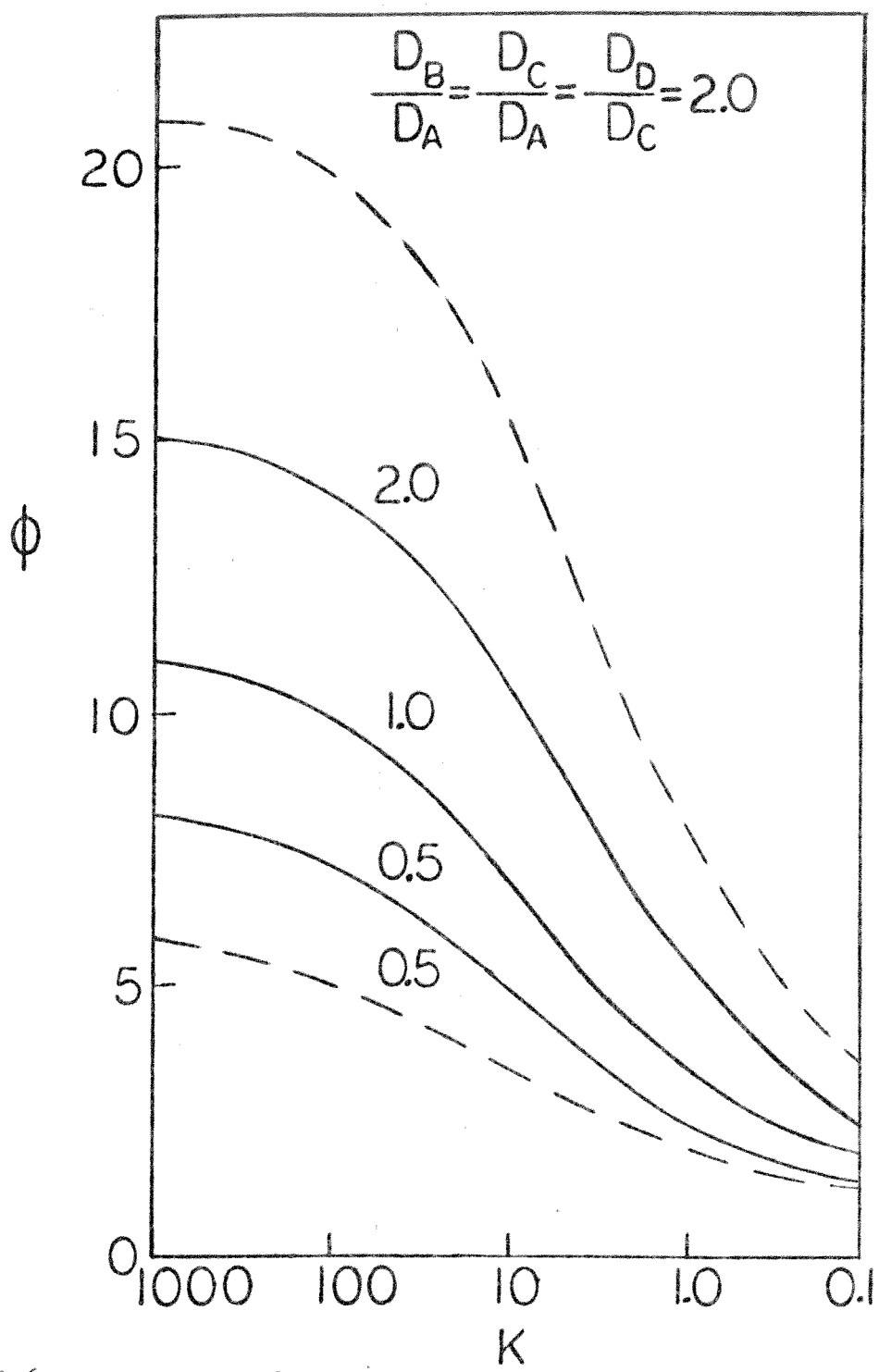

Figure 2-6. Comparison of mass transfer enhancement factors predicted by film theory and surface renewal theory for $A + B \rightleftharpoons C + D$ ($C_{Ao} = C_{Co} = C_{Do} = 0$, $C_{Bo}/C_{Ai} = 10$).

they tend to approach the same asymptotic values as K_3 and K_4 become very large.

Case 4 can also be equivalent to case 3 when C (or D) has high concentration and/or low diffusitivity relative to those of other species. Under such circumstances, the concentration of C (or D) is almost constant throughout the system and the chemical reaction effect on its concentration distribution is negligible.

Approximation Method

From prior sections, it is seen that the solution of surface renewal theory for mass transfer with chemical reactions involves numerical integration and tedious trial and error procedures. On the other hand, the exact solution of film theory is easily obtained in algebraic form. It was found that the exact surface renewal theory solutions could be approximated by replacing the diffusivity ratios by their square roots in the exact analytical solution based on film theory.

It can be shown from the previous analysis of Danckwerts' theory (1968) that the effects of chemical reaction on mass transfer rate for both film theory and surface renewal theory are equivalent when the diffusivities of all components are the same. The relative magnitude of the mass transfer enhancement factors switch when the diffusivity ratio goes across 1.0 as shown in Figures 2-2, 2-4, 2-5, and 2-6.

All the equations needed to approximate the surface renewal theory mass transfer enhancement factors for cases 1, 2, 3, and 4 are

listed in Table 2-1. Figures 2-7, 2-8, 2-9, and 2-10 show the deviation between the enhancement factor obtained by exact numerical solution, ϕ_s, and the enhancement factor, ϕ_a, calculated by the use of the equations in Table 2-1. The deviations were found to be most sensitive to variations in the diffusivity ratios. The ϕ_a is actually equal to ϕ_s when all the diffusivity ratios are equal to unity. The differences between the predictions of the approximation method and that of the surface renewal theory become larger as the diffusivity ratios deviate from one. Figure 2-11, 2-12, 2-13, and 2-14 show comparisons of ϕ_s and ϕ_a for more extensive variations of the boundary conditions and other parameters for all four reaction types. For most cases the values of exact solutions of the surface renewal theory can be approximated by this method within 10% when the diffusivity ratios lie between 0.3 and 10.

As previously mentioned, if the equilibrium constants become very large, both the systems of cases 3 and 4 approach the instantaneous, irreversible reaction type problem. From Table 2-1, it can be seen that as the equilibrium constants approach infinity, the mass transfer enhancement factors in both Equations (T-3) and (T-4) reduce to

$$\lim_{K \to \infty} \phi_{a,34} = 1 + \frac{D_B}{D_A} \frac{C_{Bo}}{C_{Ai}} \qquad (2\text{-}49)$$

which corresponds to replacing by its square root the diffusivity ratio of Hatta's equation (1928) of this reaction type. Brian et al. (1961) analyzed the solutions for surface renewal theory with instantaneous irreversible bimolecular reaction and suggested Equation 2-49

Table 2-1. Summary of the equations for the approximation method for cases 1, 2, 3, and 4.

Case 1
$$\phi_{a1} = 1 + \sqrt{\frac{D_B}{D_A}} \frac{\sqrt{K_1/4}}{\sqrt{C_{Ai}} + \sqrt{C_{Ao}}} \qquad \text{(T-1)}$$

Case 2
$$\phi_{a2} = 1 + \sqrt{\frac{D_C}{D_A}} \frac{\left[\left(C_{Co} - \sqrt{\frac{D_B}{D_C}} C_{Bo}\right)^2 + 4\sqrt{\frac{D_B}{D_C}} C_{Ai} K_2\right]^{\frac{1}{2}} - C_{Co} - \sqrt{\frac{D_B}{D_C}} C_{Bo}}{2(C_{Ai} - C_{Ao})} \qquad \text{(T-2)}$$

Case 3
$$\phi_{a3} = 1 + \sqrt{\frac{D_B}{D_A}} \frac{C_{Bo}}{C_{Ai} + \sqrt{\frac{D_B}{D_C}} \frac{1}{K_3}} \qquad \text{(T-3)}$$

Case 4
$$\phi_{a4} = 1 + \sqrt{\frac{D_C}{D_A}} \frac{(C_{Ci} - C_{Co})}{(C_{Ai} - C_{Ao})} \qquad \text{(T-4)}$$

$$C_{Ci} = \frac{1}{2} \left\{ \left[\left(\sqrt{\frac{D_D}{D_C}} C_{Do} + \sqrt{\frac{D_D}{D_B}} C_{Ai} K_4 - C_{Co} \right)^2 + 4 C_{Ai} K_4 \right.\right.$$

$$\left.\left. \left(\sqrt{\frac{D_D}{D_C}} C_{Bo} + \sqrt{\frac{D_D}{D_B}} C_{Co} \right) \right]^{\frac{1}{2}} - \left(\sqrt{\frac{D_D}{D_C}} C_{Do} + \sqrt{\frac{D_D}{D_B}} C_{Ai} K_4 - C_{Co} \right) \right\}$$

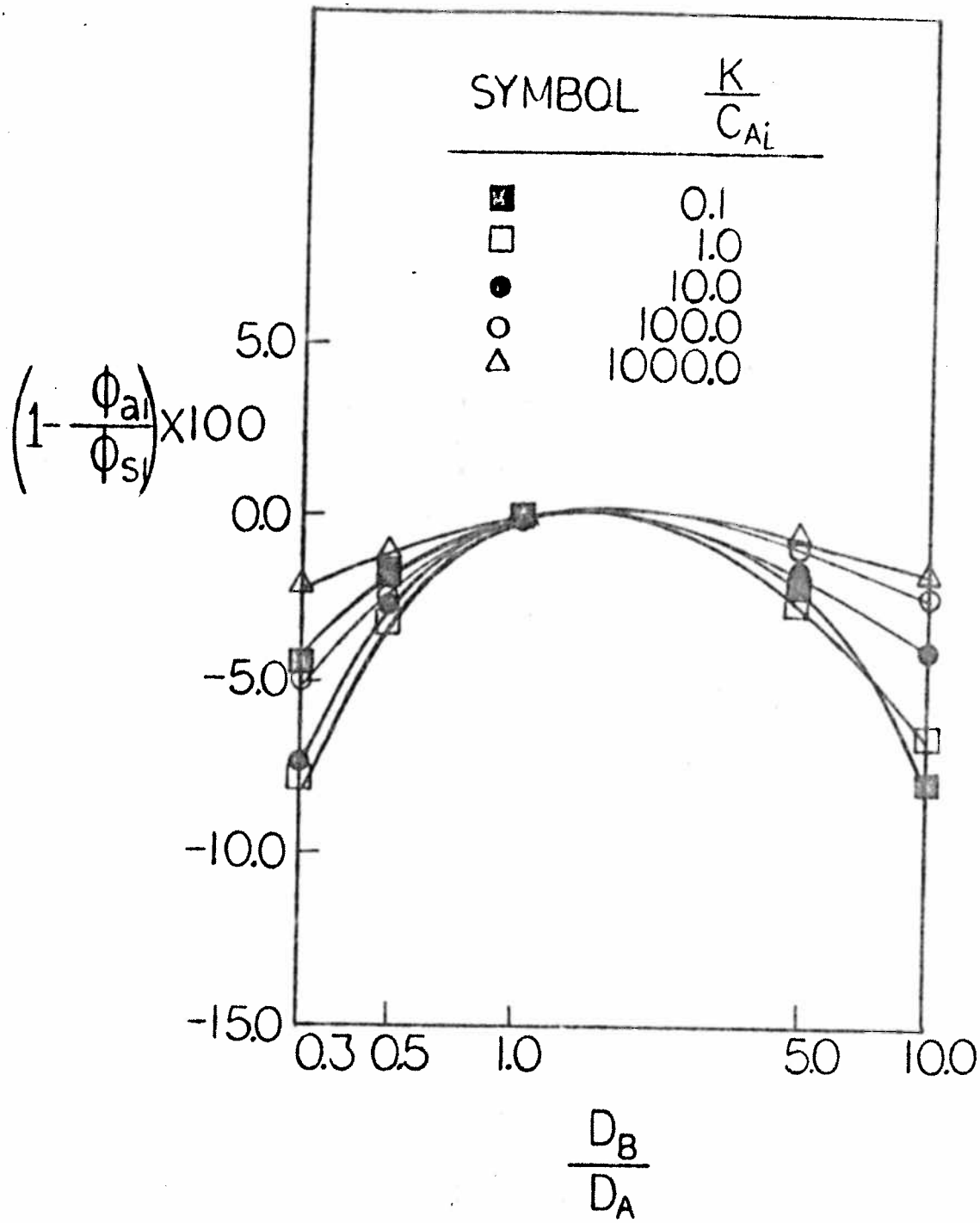

Figure 2-7. Deviation of ϕ_{al} from ϕ_{sl} for $A \rightleftharpoons 2B$ ($C_{Ao} = 0$).

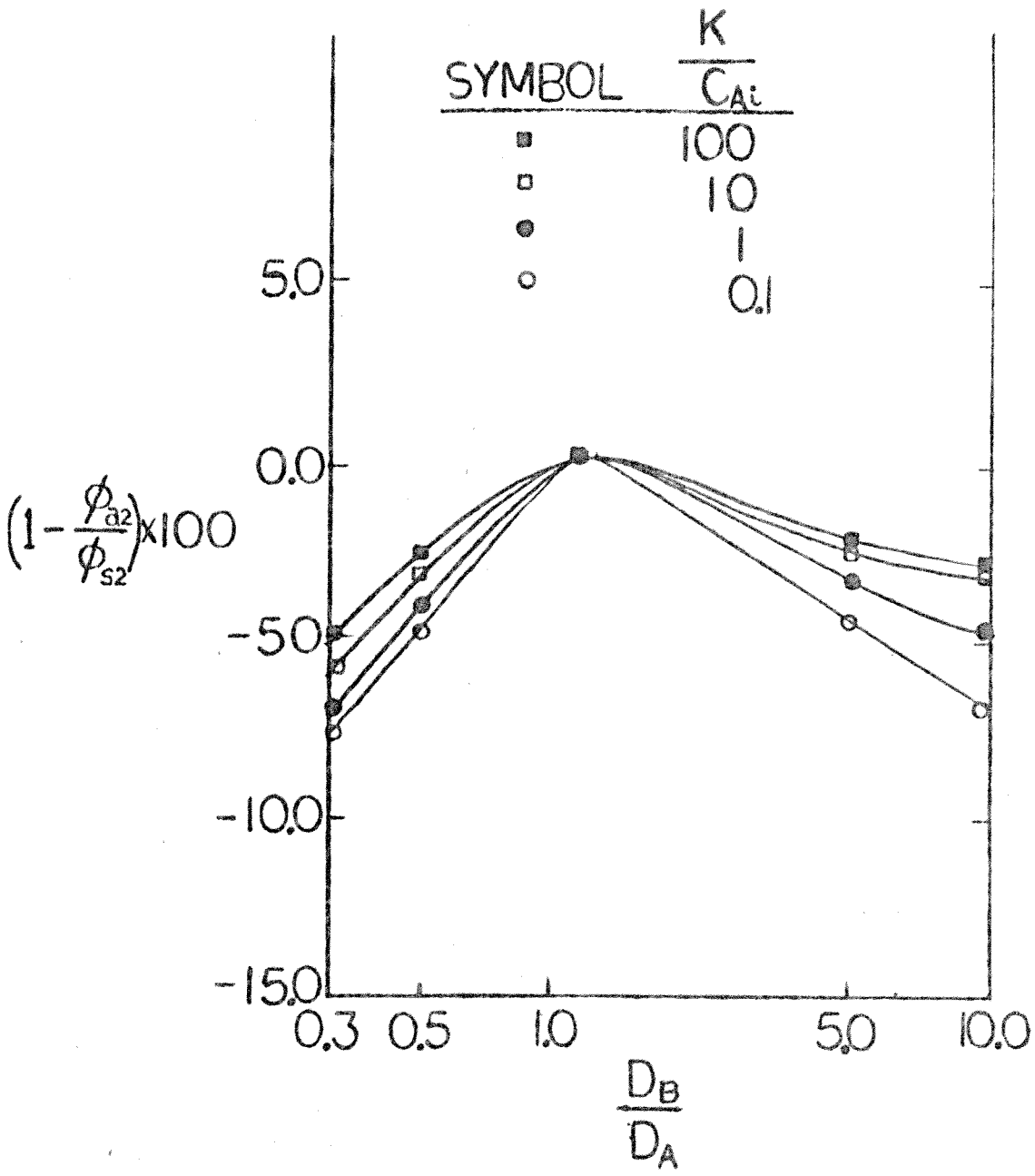

Figure 2-8. Deviation of ϕ_{a2} from ϕ_{s2} for $A \rightleftharpoons B + C$ ($D_C = \sqrt{D_B}$, $C_{Ao} = C_{Bo} = C_{Co} = 0$).

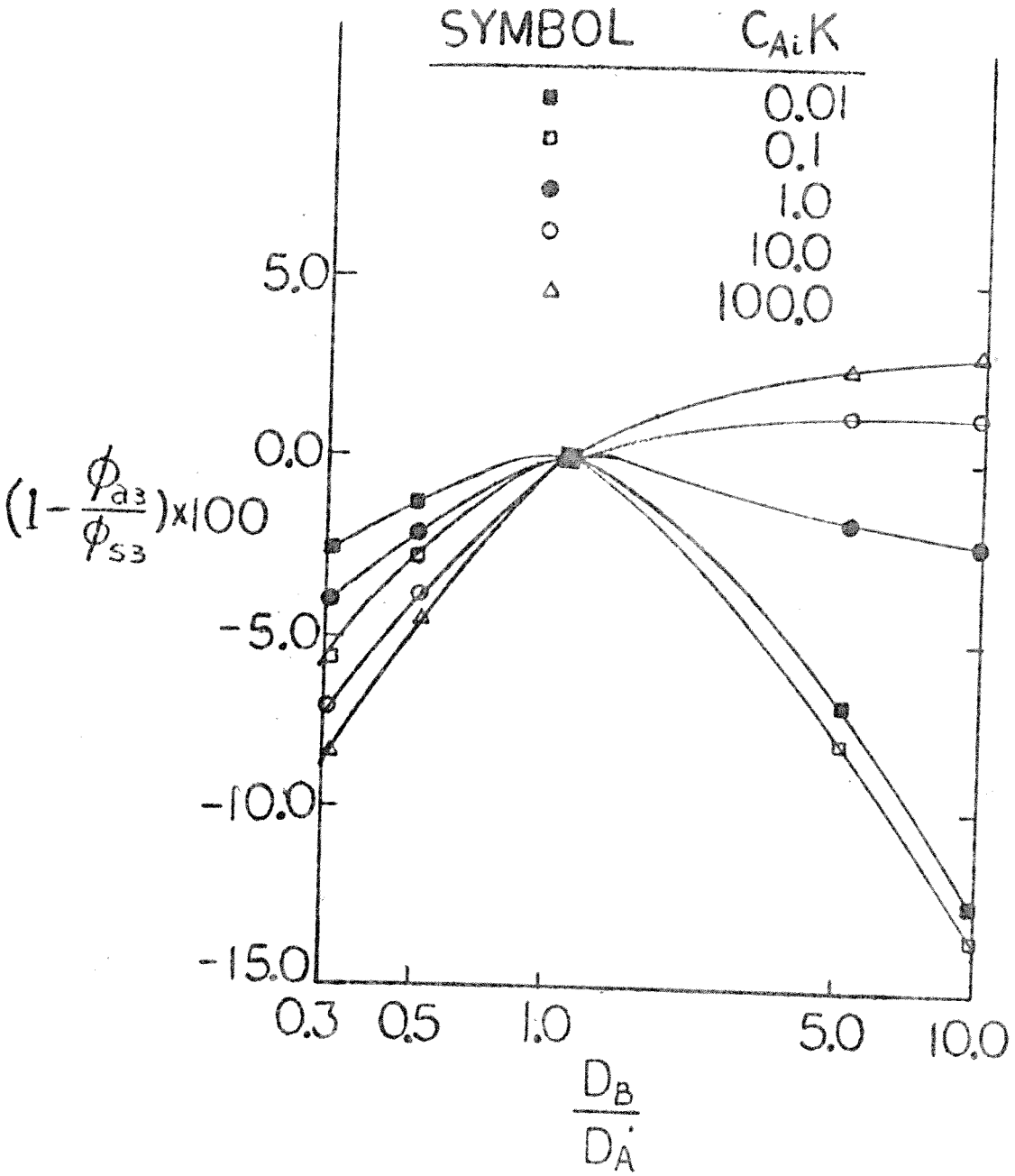

Figure 2-9. Deviation of ϕ_{a3} from ϕ_{s3} for A + B $\rightleftharpoons$ C.
($D_B = D_C$, $C_{Co} = 0$, $C_{Bo}/C_{Ao} = 10$).

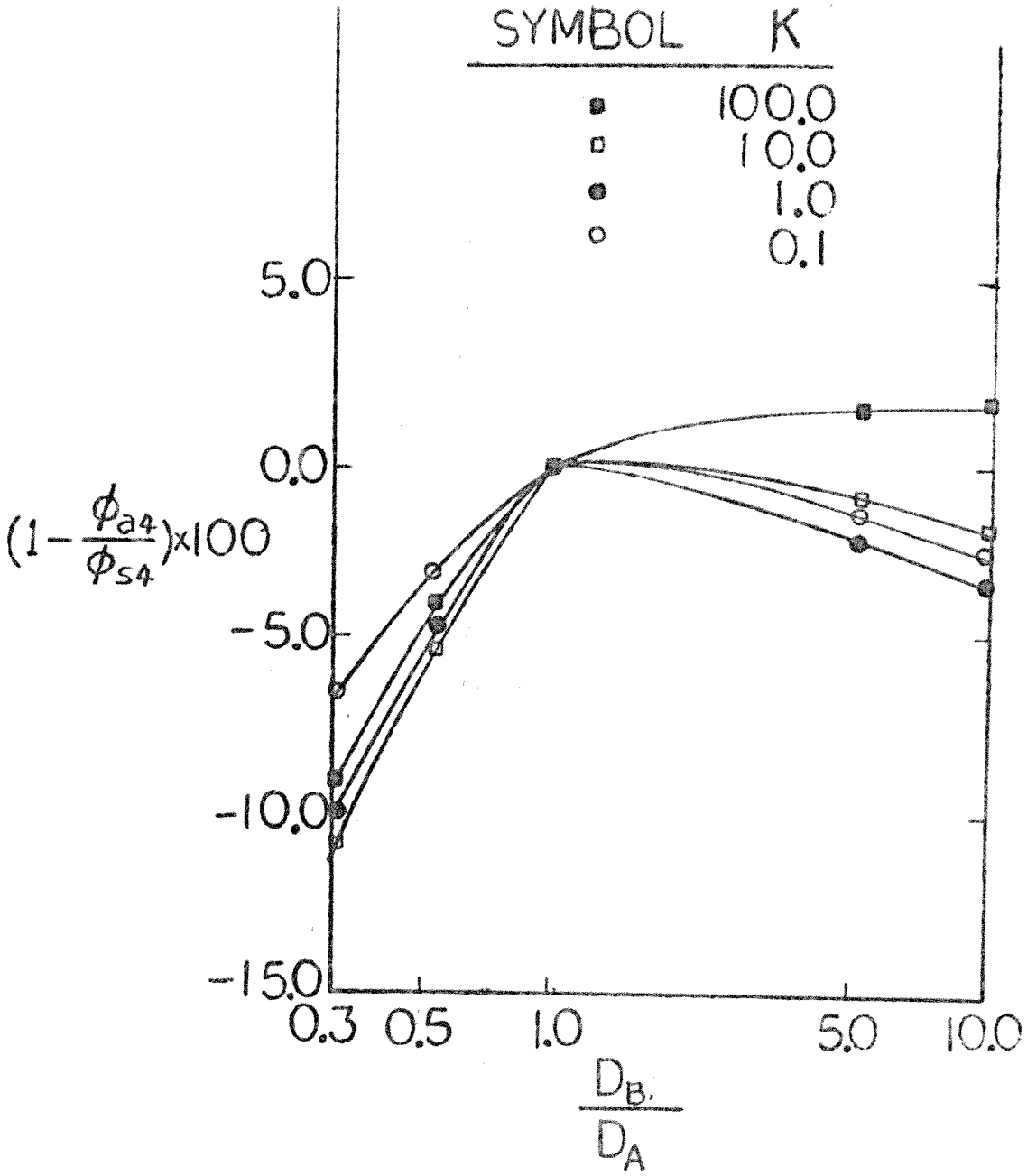

Figure 2-10. Deviation of ϕ_{a4} from ϕ_{s4} for $A + B \rightleftharpoons C + D$ ($D_B = D_C$, $D_D = \sqrt{D_C}$, $C_{Ao} = C_{Co} = C_{Do} = 0$, $C_{Bo}/C_{A1} = 10$).

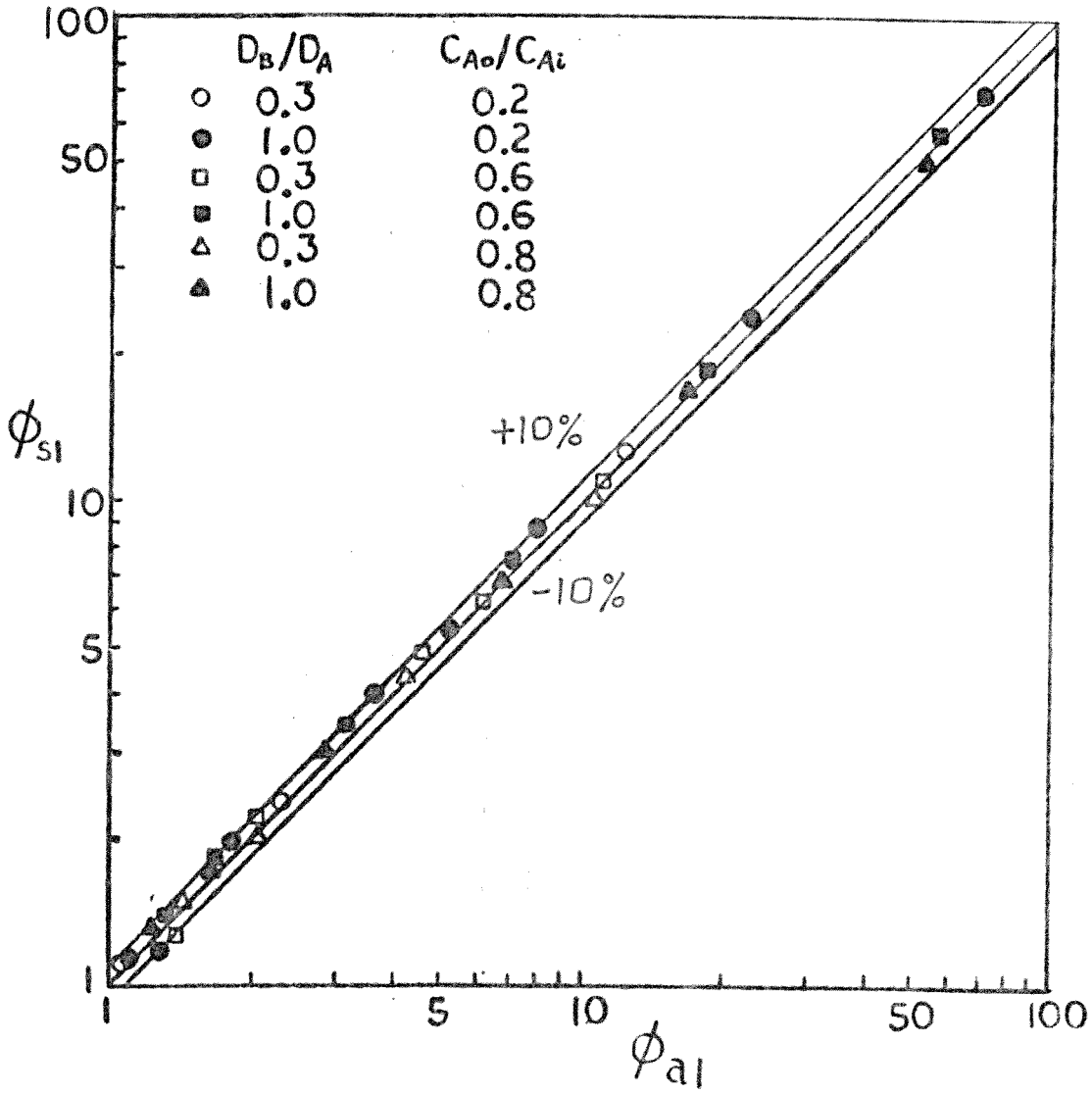

Figure 2-11. Comparison of ϕ_{sl} and ϕ_{al} for $A \rightleftharpoons 2B$ (K_1/C_{Ai} varies from 0.01 to 1000)

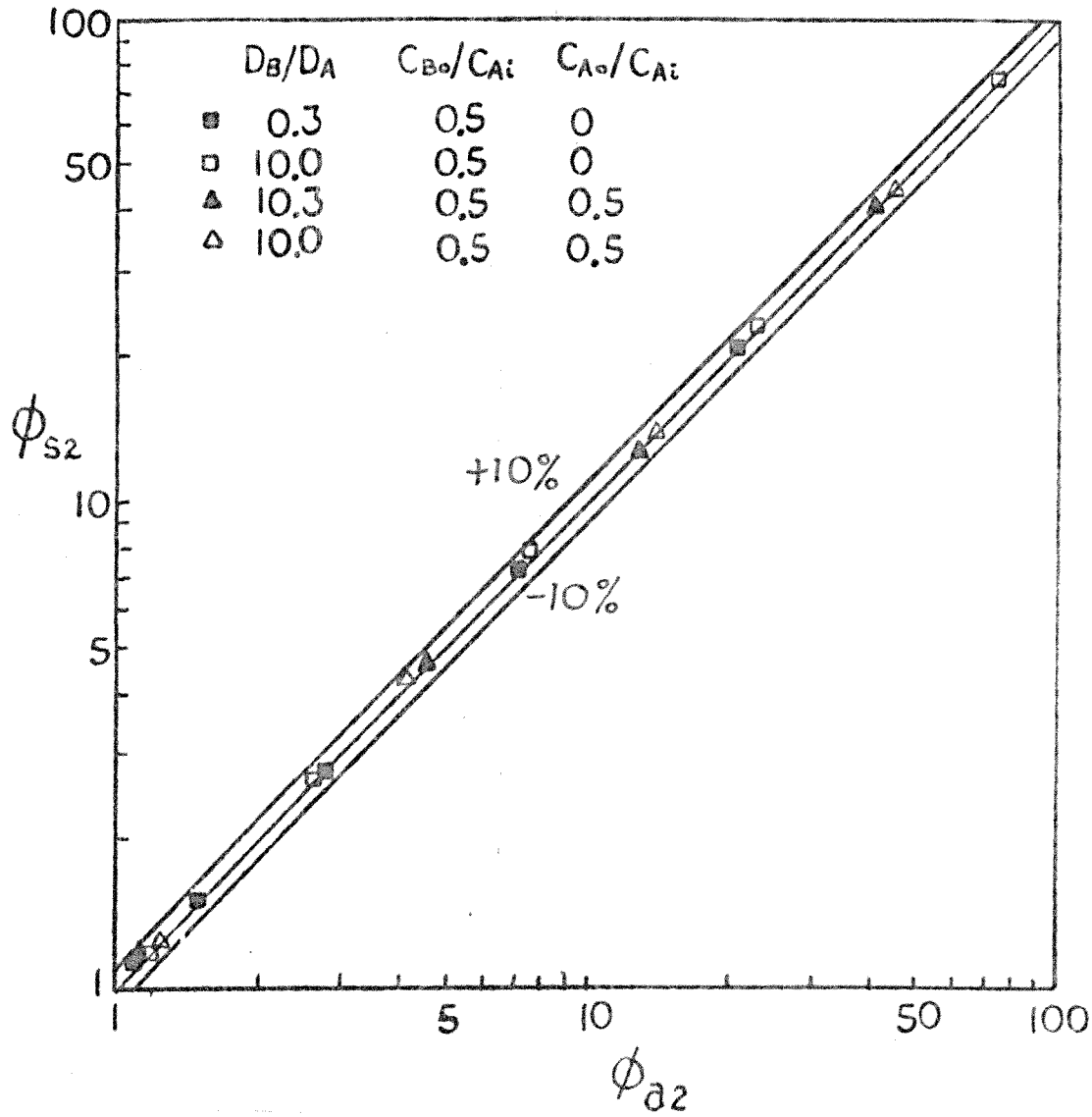

Figure 2-12. Comparison of ϕ_{s2} and ϕ_{a2} for $A \rightleftharpoons B + C$ ($D_C = \sqrt{D_B}$, K_2/C_{Ai} varies from 0.01 to 1000).

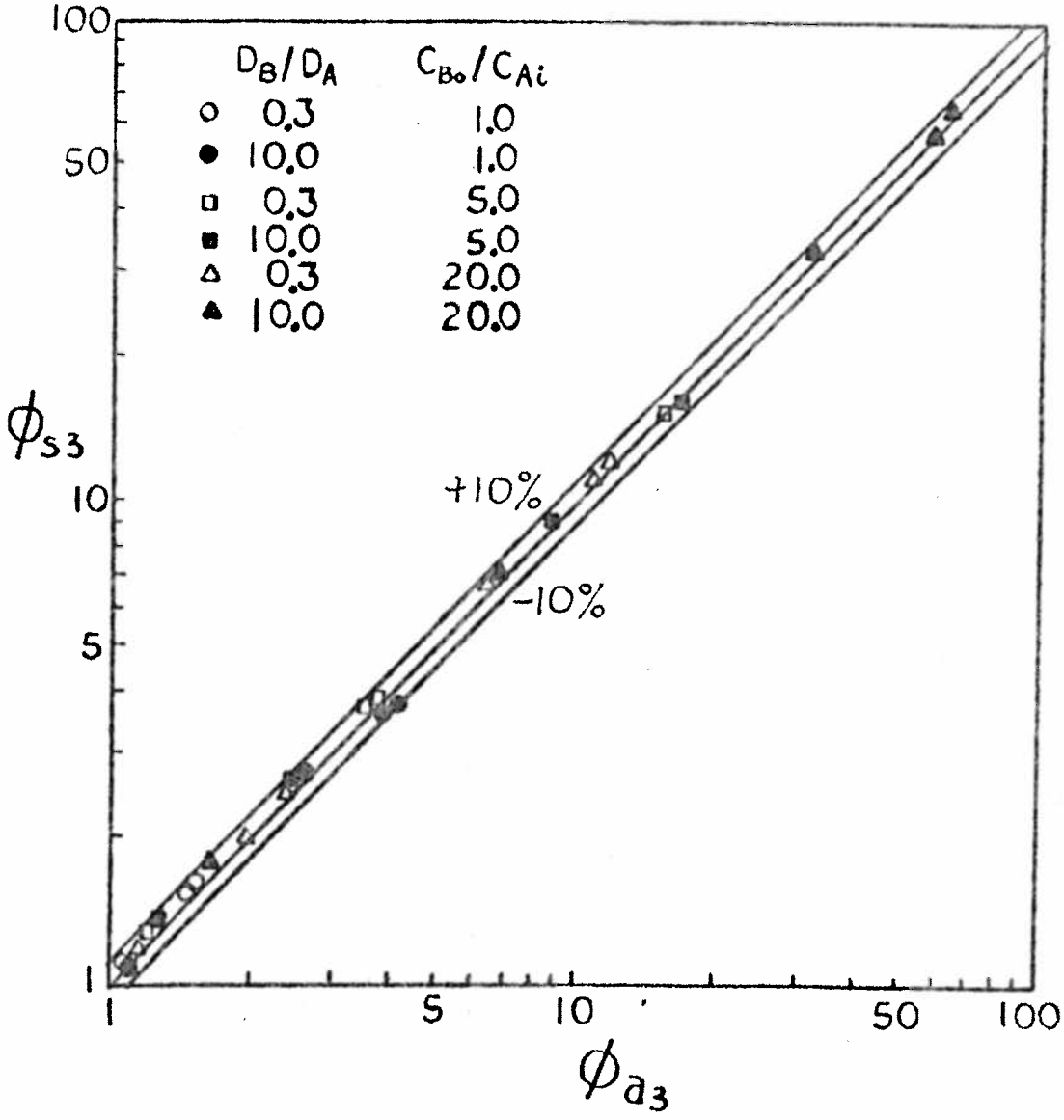

Figure 2-13. Comparison of ϕ_{s3} and ϕ_{a3} for A + B $\rightleftharpoons$ C ($D_B = D_C$, $C_{Ao} = 0$, $C_{Ai}K_3$ varies from 0.01 to 100)

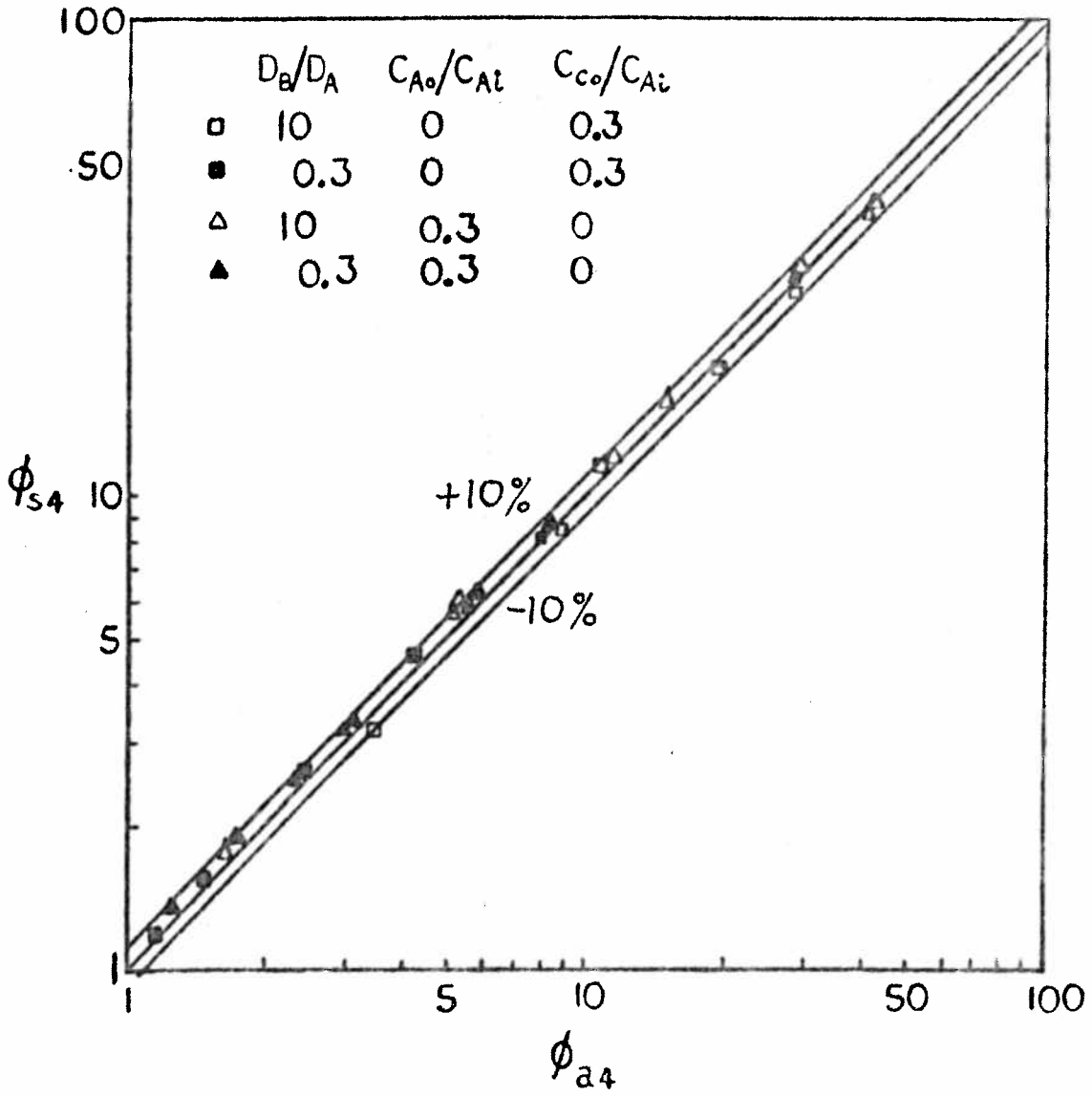

Figure 2-14. Comparison of ϕ_{s4} and ϕ_{a4} for $A + B \rightleftharpoons C + D$.

($D_B = D_C$, $D_D = \sqrt{D_C}$, $C_{Bo}/C_{Ai} = 10$, K_4 varies from 0.1 to 100).

was a good approximation method at high value of ϕ and at values of D_B/D_A near 1.0. Rochelle and King (1977) utilized this kind of approximation to construct a mass transfer model to describe the scrubber behavior for the absorption of sulfur dioxide from stack gas by lime/limestone slurries.

Notation

A^*, B^*, C^*, = dimensionless concentrations for species A, B, and C

A', B', C', = dimensionless concentration gradients for species A, B, and C defined by Equations (39), (11), and (26)

b_1, b_2, b_3, = dimensionless groups defined by Equations (29), (39), and (46)

C_A, C_B, C_C, C_D = concentrations of species A, B, C, and D, g-mole/liter

C_{Ai}, C_{Bi}, C_{Ci}, C_{Di} = concentrations of species A, B, C, and D at interface, g-mole/liter

C_{Ao}, C_{Bo}, C_{Co}, C_{Do} = concentrations of species A, B, C, and D at bulk, g-mole/liter

d_1, d_2, d_3, d_4 = dimensionless groups defined by Equations (8) and (25)

K_1, K_2 = equilibrium constants defined by Equations (6) and (24), g-mole/liter

K_3 = equilibrium constant defined by Equation (38), liter/g-mole

K_4 = equilibrium constant defined by Equation (44)

N = instantaneous flux of A across the interface, g-moles/sec-cm^2

N_{ave} = average flux of A across the interface, g-mole/sec-cm^2

N_{phy} = average flux of A across the interface without chemical reaction, g-mole/sec-cm^2

s = fractional rate of surface renewal, sec

t = time, sec

v = defined by Equation (9)

w = defined by Equation (7)

x = distance, cm

ϕ_{a1}, ϕ_{a2}, ϕ_{a3}, ϕ_{a4} = mass transfer enhancement factors predicted by approximation method for case 1, 2, 3, and 4

ϕ_{f1}, ϕ_{f2}, ϕ_{f4} = mass transfer enhancement factors predicted by film theory for case 1, 2, and 4

ϕ_{s1}, ϕ_{s2}, ϕ_{s3}, ϕ_{s4} = mass transfer enhancement factors predicted by surface renewal model for case 1, 2, 3, and 4

ϕ_{D1} = mass transfer enhancement factor predicted by Danckwerts' model for Case 1

ΔC_A, ΔC_B, ΔC_C, ΔC_D = concentration differences between the interface and the bulk for species A, B, C, and D, g-mole/liter

ΔC_{At} = total concentration difference for species A defined by Equation (18), g-mole/liter

δ = film thickness, cm

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Chapter 3

MASS TRANSFER WITH MULTIPLE EQUILIBRIUM REACTIONS

ABSTRACT

The effects on mass transfer of multiple instantaneous reversible reactions are modeled by film theory and surface renewal theory. Film theory mass transfer enhancement factors are solved directly for simple reaction systems. More complicated systems require numerical solution of higher order algebraic equations.

Non-interacting systems of reactions can be solved as a linear sum of contributions from each constituting reaction. Interacting systems each require a unique solution. Only the simplest reaction system is easily solved for surface renewal theory. The solution of surface renewal theory for more complicated systems is approximated by replacing diffusivity ratios by their square roots in the solution of film theory.

SCOPE

Multiple reactions are frequently more representative than single reactions when considering gas absorption with chemical reactions. However, the analysis is often avoided because of its complexity. Analytical solutions have been obtained for first and second-order, irreversible reactions with finite rates. (Kuo and

Huang, 1970, Kubota and Lee, 1973, Kuo et al, 1974, Seda et al, 1977) Either numerical methods or approximation methods have been used for multiple, irreversible reactions with kinetic order higher than two (Brian and Beaverstock, 1965, Teramoto et al, 1973, Kuo and Huang, 1973). Hikita et al (1972 and 1976) discussed the case of gas absorption accompanied by a two-step instantaneous irreversible reactions in which the gas absorption rate is totally mass transfer controlled.

Experimental studies on gas absorption accompanied by multiple chemical reactions in the liquid phase have been carried out for the systems Cl_2-NaOH, (Hikita et al, 1973), SO_2-NaOH and SO_2-Na_2SO_3, (Hikita et al, 1977); CO_2-NaOH and CO_2-Na_2CO_3-$NaHCO_3$, (Rehm et al, 1963, Hikita et al, 1976); and $CO_2^=$ aqueous amine solutions, (Sada et al, 1976).

However, very few studies have been presented in the literature on the case of mass transfer with multiple instantaneous reversible reactions. Danckwerts (1960) suggested a model for a single equilibrium reaction which considers the equilibrium relation only at the gas-liquid interphase and liquid bulk. This model can be extended to multiple instantaneous reversible reactions. However, its application is restricted to systems with components of equal diffusivities. Olander (1960) presented solutions of film theory for single equilibrium reactions with unequal diffusivities. Chang and Rochelle (1979) considered single equilibrium reactions with surface renewal theory and

approximated surface renewal by a simple modification of the solution to film theory. The objective of this work is to solve film theory and approximate surface renewal theory for systems of multiple instantaneous reversible reactions with components of unequal diffusivities.

Conclusions

The multiple equilibrium reaction systems can be divided into two categories, non-interacting and interacting systems. The former one requires that there are no common components except the one penetrating through the phase boundary. The characteristics of the constituting single reactions can be directly applied to the multiple reaction system. The effects of multiple reactions on mass transfer rate are the sum of the effects of the constituting single reactions.

The interacting systems have more than one common component and all the properties of the components can affect the concentration profiles and mass transfer rates. Therefore, each interacting system results in a unique form of mass transfer enhancement factor.

The film theory of mass transfer with multiple equilibrium reactions can be solved for most cases. Numerical techniques may be required for complicated reaction systems because they involve high order algebraic equations.

Only the simplest reaction system can be solved by surface renewal theory. However, the film theory solutions can be employed to estimate the surface renewal theory mass transfer enhancement factor with the approximation method suggested by Chang and Rochelle (1979).

Introduction

The problem to be considered is a transport process between two phases, for example, gas and liquid phases. As the reactant A diffuses from the gas phase into interface, it is assumed that several instantaneous reversible reactions take place along the path of diffusion in the liquid phase. The main feature of this system is that chemical equilibrium is maintained throughout the diffusion path. The concentration of A at the phase interface is assumed to be constant. Other assumptions and basic approaches of the authors' previous paper on the effect of single equilibrium reactions (Chang and Rochelle, 1979) will also be used as the basis of the present analysis.

Multiple and Single Reactions

Systems of reactions with finite rates can be represented as a combination of two primary reaction types, competing or parallel reactions and consecutive or series reactions. The relative positions of the reactants, intermediate products,and final products are not changeable. However, for the case of instantaneous reversible reactions, the multiple reactions are more versatile and convertible. This is because, first, we do not have to deal with the kinetic behavior of the reactions and,second, there are equilibrium relations between all the reactants and products, for example:

$$A \rightleftharpoons C + D \ , \qquad C_A K_1 = C_C C_D \tag{3-1}$$

$$A \rightleftharpoons E + F \ , \qquad C_A K_2 = C_E C_F \tag{3-2}$$

These two parallel reactions could also be expressed as consecutive reactions:

$$A \rightleftharpoons C + D \rightleftharpoons E + F \,, \qquad C_A K_1 = C_C C_D \qquad (3\text{-}3)$$
$$C_C C_D K_3 = C_E C_F$$

where $K_3 = K_2/K_1$. Furthermore reaction 3-3 can be represented by the combination of the following reaction with either reaction 3-1 or 3-2.

$$C + D \rightleftharpoons E + F \qquad (3\text{-}4)$$

All multiple reactions can be expressed by the parallel combination of single reactions. However, not all the multiple reactions can be represented as a series of single reactions, for example:

$$A + B \rightleftharpoons C + D \qquad (3\text{-}5)$$

$$A + E \rightleftharpoons F \qquad (3\text{-}6)$$

Thus, systems of consecutive reactions are special cases of multiple reactions.

The distinction between a single reaction and multiple reactions is in stoichiometry. If we compare reactions 1 and 2 with a single reaction having the equivalent equilibrium relations,

$$2A \rightleftharpoons C + D + E + F \,, \qquad C_A^2 K_7 = C_C C_D C_E C_F \qquad (3\text{-}7)$$

where $K_7 = K_1 K_2$, the stoichiometry of reaction 3-7 requires that one half mole of each product C, D, E, and F is produced when one mole of A is consumed. However, this is not true for multiple reactions 3-1 and 3-2. The distribution of the reacted A depends on the relative o order of magnitude of the equilibrium constants of reactions 3-1 and 3-2.

Film theory with non-interacting multiple reactions

A system of reactions is non-interacting if the component A is the only common component in each reaction. For this system, only the distribution of reacted A between the products has to be considered. The stoichiometry relations between all of the species other than A are fixed.

The generalized non-interacting system can be expressed as

$$A + \sum_{j=1}^{J_1} \gamma_{1,j} R_{1,j} \rightleftharpoons \sum_{j=1}^{J_1'} p_{1,j} P_{1,j}$$

$$A + \sum_{j=1}^{J_2} \gamma_{2,j} R_{2,j} \rightleftharpoons \sum_{j=1}^{J_2'} p_{2,j} P_{2,j}$$

$$\vdots \qquad\qquad \vdots$$

$$A + \sum_{j=1}^{J_m} \gamma_{m,j} R_{m,j} \rightleftharpoons \sum_{j=1}^{J_m'} p_{m,j} P_{m,j}$$

The total steady-state material balance for component A in terms of the first product of each single reaction gives

$$D_A \frac{d^2 C_A}{dx^2} + \sum_{e=1}^{m} \frac{D_{e,1}}{p_{e,1}} \frac{d^2 C_{e,1}}{dx^2} = 0 \qquad (3\text{-}8)$$

The general solution of Equation 3-8 is

$$D_A C_A + \sum_{e=1}^{m} \frac{D_{e,1}}{p_{e,1}} C_{e,1} = b_1 x + b_2 \qquad (3\text{-}9)$$

where b_1 and b_2 are integration constants. The flux of species A across the interface is

$$N_f = -(D_A \frac{dC_A}{dx} + \sum_{e=1}^{m} \frac{D_{e,1}}{p_{e,1}} \frac{dC_{e,1}}{dx}) \Big|_{x=0} \qquad (3\text{-}10)$$

Combination of Equations 3-9 and 3-10 gives N_f in terms of the boundary conditions C_{Ai}, C_{Ao}, $C_{e,1i}$ and $C_{e,1o}$:

$$N_f = b_1 = \frac{D_A}{\delta} (C_{Ai} - C_{Ao}) + \sum_{e=1}^{m} \frac{D_{e,1}}{p_{e,1}\delta} (C_{e,1i} - C_{e,1o}) \qquad (3\text{-}11)$$

The definition of the mass transfer enhancement factor, ϕ_f, is given by

$$N_f = \phi_f \frac{D_A}{\delta} (C_{Ai} - C_{Ao}) \qquad (3\text{-}12)$$

According to this definition and Equation 3-11, the mass transfer enhancement factor for a system with only one single reaction e can be expressed as

$$\phi_e = 1 + \frac{D_{e,1}}{D_A p_{e,1}} \frac{(C_{e,1i} - C_{e,1o})}{(C_{Ai} - C_{Ao})}$$

Comparison of Equation 3-12 with 3-11 shows that the overall mass transfer enhancement factor for a system of m reactions can be expressed as

$$\phi_f = 1 + \sum_{e=1}^{m} (\phi_e - 1) \qquad (3\text{-}13)$$

Therefore, for a system of non-interacting multiple reactions, each constituting single reaction contributes one additive term to the overall mass transfer enhancement factor. This term is derived from

the mass transfer enhancement factor of the individual single reaction by itself. That is, there is no interaction among the constituting reactions and those single reactions affect the mass transfer rate independently.

Mass transfer enhancement factors of several typical single reactions are listed in Table 3-1. (Olander, 1960, Danckwerts, 1970, Chang and Rochelle, 1979) For example, by the use of Equation 3-13, the mass transfer enhancement factor of the system

$$A + B \rightleftharpoons C \quad , \qquad C_A C_B K_{14} = C_C \tag{3-14}$$

$$A \rightleftharpoons D \quad , \qquad C_A K_{15} = C_D \tag{3-15}$$

can be obtained from Table 1 as

$$\phi_f = 1 + \frac{D_B C_{Bo}}{D_A (C_{Ai} + K_{14} D_B / D_C)} + \frac{D_D K_{15}}{D_A}$$

Film theory with interacting multiple reactions

For a system of interacting multiple reactions, there is more than one common component in all the constituting single reactions. Therefore, the distribution of those common components must be considered in the material balances. Furthermore, the constituting single reactions no longer contribute independently to the mass transfer enhancement factor. All the reactants and products affect each other both in concentration distribution and mass transfer rate.

For example, consider the system:

$$A + B \rightleftharpoons C \tag{3-14}$$

$$A + B \rightleftharpoons D \tag{3-16}$$

Table 3-1. Film theory enhancement factors for single reactions (Olander, 1960, Danckwerts, 1970, Chang and Rochelle, 1979)

Reaction type	$\phi_f - 1$
$A \rightleftharpoons B$ $(C_A K = C_B)$	$\frac{D_B K}{D_A}$
$A \rightleftharpoons 2B$ $(C_A K = C_B^2)$	$\frac{D_B \sqrt{K/4}}{D_A(\sqrt{C_{Ai}} + \sqrt{C_{Ao}})}$
$A + B \rightleftharpoons C$ $(C_A C_B K = C_C)$	$\frac{D_B K C_{Bo}}{D_A (K C_{Ai} + D_B/D_c)}$
$A + B \rightleftharpoons 2C$ $(C_A C_B K = C_C^2)$	$\frac{D_C(C_{Ci}-C_{Co})}{2D_A(C_{Ai}-C_{Ao})}$, $C_{Ci} = \frac{1}{2}\left\{ - \frac{D_C C_{Ai} K}{2D_B} + \left[\left(\frac{D_C C_{Ai} K}{2D_B}\right)^2 + \frac{4C_{Ai}K}{D_C}\left(D_B C_{Bo} + \frac{D_C C_{Co}}{2}\right)\right]^{\frac{1}{2}} \right\}$
$A \rightleftharpoons B + C$ $(C_A K = C_B C_C)$	$\frac{D_B(C_{Bi}-C_{Bo})}{D_A(C_{Ai}-C_{Ao})}$, $C_{Bi} = \frac{1}{2}\left\{ C_{Bo} - \frac{D_C}{D_B}C_{Co} + \left[\left(C_{Bo} - \frac{D_C}{D_B}C_{Co}\right)^2 + \frac{4D_C C_{Ai} K}{D_B}\right]^{\frac{1}{2}} \right\}$
$2A \rightleftharpoons B + C$ $(C_A^2 K = C_B C_C)$	$\frac{2D_B(C_{Bi}-C_{Bo})}{D_A(C_{Ai}-C_{Ao})}$, $C_{Bi} = \frac{1}{2}\left\{ C_{Bo} - \frac{D_C}{D_C}C_{Co} + \left[\left(C_{Bo} - \frac{D_C}{D_B}C_{Co}\right)^2 + \frac{4D_C C_{Ai} K}{D_B}\right]^{\frac{1}{2}} \right\}$

$A + B \rightleftharpoons C + D$

$(C_A C_B K = C_C C_D)$

$$\frac{D_C(C_{Ci}-C_{Co})}{D_A(C_{Ai}-C_{Ao})}$$

$$C_{Ci} = \frac{1}{2}\left\{\left[\left(\frac{D_D}{D_C} C_{Do} + \frac{D_D}{D_B} KC_{Ai} - C_{Co}\right)^2 + 4C_{Ai}K\left(\frac{D_D}{D_C} C_{Bo} + \frac{D_D}{D_B} C_{Co}\right)\right]^{\frac{1}{2}} - \left(\frac{D_D}{D_C} C_{Do} + \frac{D_D}{D_B} KC_{Ai} - C_{Co}\right)\right\}$$

This is an interacting multiple reaction system because those two reactions have two common components, A and B. The total A component material balance is

$$D_A \frac{d^2C_A}{dx^2} - D_B \frac{d^2C_B}{dx^2} = 0 \qquad (3\text{-}17)$$

The total B component material balance is

$$D_B \frac{d^2C_B}{dx^2} + D_C \frac{d^2C_C}{dx^2} + D_D \frac{d^2C_D}{dx^2} = 0 \qquad (3\text{-}18)$$

The equilibrium relations are

$$C_A C_B K_{14} = C_C$$

$$C_A C_B K_{16} = C_D$$

The boundary conditions are

$$\text{at } x = 0 \quad , \quad C_A = C_{Ai}$$

$$\text{at } x = \delta \quad , \quad C_A = C_{Ao} \quad , \quad C_B = C_{Bo}$$

The final boundary condition is:

$$\text{at } x = 0 \quad , \quad D_B \frac{dC_B}{dx} + D_C \frac{dC_C}{dx} + D_D \frac{dC_D}{dx} = 0$$

Substituting the boundary conditions and the equilibrium relations into Equations 3-17 and 3-18, we can obtain the interface concentration of species B:

$$C_{Bi} = \frac{D_B C_{Bo} + D_C C_{Co} + D_D C_{Do}}{D_B + D_C C_{Ai} K_{14} + D_D C_{Ai} K_{16}} \qquad (3\text{-}19)$$

Equation 3-19 shows C_{Bi} is a function of bulk concentrations,

diffusivities, and equilibrium constants of all the components and reactions of this system.

The mass transfer rate of A across the interface can be obtained as

$$N_f = \left(\frac{D_A}{\delta}\right)(C_{Ai} - C_{Ao})\ \phi_f \qquad (3\text{-}20)$$

where

$$\phi_f = 1 + \frac{D_B C_{Bo}\left(1 + \frac{D_D K_{16}}{D_C K_{14}}\right)}{D_A\left[\frac{D_B}{D_C K_{14}} + C_{Ai}\left(1 + \frac{D_D K_{16}}{D_C K_{14}}\right)\right]}$$

The mass transfer enhancement factor, ϕ_f, is quite different from those of non-interacting systems in the previous section. There is no obvious relation between the mass transfer enhancement factor of the system of interacting multiple reactions and of the constituting single reactions.

Not all multiple reaction systems have analytical solutions for mass transfer rates. When there are more than three products, the algebraic equation which relates the interface concentration and other known properties becomes a complicated form with order higher than three. Numerical techniques, such as Newton Rapson's method, must be used to solve the algebraic equation. Once the interface concentration is obtained, the mass transfer rate can also be calculated.

Surface Renewal Theory with Multiple Reactions

First, consider the simplest case of multiple reactions:

$$\begin{aligned} A &\rightleftharpoons B_1 & C_A K_{21,1} &= C_{B,1} \\ A &\rightleftharpoons B_2 & C_A K_{21,2} &= C_{B,2} \\ &\vdots & &\vdots \\ A &\rightleftharpoons B_m & C_A K_{21,m} &= C_{B,m} \end{aligned} \qquad (3\text{-}21)$$

The total unsteady-state material balance for component A gives

$$D_A \frac{\partial^2 C_A}{\partial x^2} + \sum_{e=1}^{m} D_{B,e} \frac{\partial^2 C_{B,e}}{\partial x^2} = \frac{\partial}{\partial t}\left(C_A + \sum_{e=1}^{m} C_{B,e}\right) \qquad (3\text{-}22)$$

The initial and boundary conditions are

$$\begin{aligned} \text{at } t = 0, \quad & C_A = C_{Ao} \\ t > 0 \text{ and } x = 0, \quad & C_A = C_{Ai} \\ t > 0 \text{ and } x \to \infty, \quad & C_A = C_{Ao} \end{aligned}$$

The boundary conditions of species B_e can be obtained from the equilibrium relations. Equation 3-22 can be solved for the instantaneous flux of A across the phase boundary defined by

$$N_s = -\left[D_A \frac{\partial C_A}{\partial x} + \sum_{e=1}^{m} D_{Be} \left(\frac{\partial C_{B,e}}{\partial x}\right)\right]_{x=0} \qquad (3\text{-}23)$$

to yield the time-average flux:

$$N_{ave} = \int_0^\infty N_s \, s e^{-st} \, dt = \sqrt{D_A s}\,(C_{Ai} - C_{Ao})\,\phi_s \qquad (3\text{-}24)$$

where the enhancement factor, ϕ_s, is given by

$$\phi_s = \left[(1 + \sum_{e=1}^{m} K_{21,e})(1 + \sum_{e=1}^{m} \frac{D_{B,e}}{D_A} K_{21,e})\right]^{\frac{1}{2}}$$

For comparison, the film theory solution obtained from Table 3-1 and Equation 3-13 gives:

$$\phi_f = 1 + \sum_{e=1}^{m} \frac{D_{B,e} K_{21,e}}{D_A} \qquad (3\text{-}25)$$

Danckwerts (1968) proposed a simple concept which simplified this case into purely physical mass transfer taking $(C_{Ati} - C_{Ato})$ as the driving force. The concentration of total A component, C_{At}, is

$$C_{At} = C_A + \sum_{e=1}^{m} C_{B,e} \qquad (3\text{-}26)$$

Then, Equation 3-24 can be written as

$$N_{ave} = \sqrt{D_A s}\,(C_{Ati} - C_{Ato}) \frac{\left(1 + \sum_{e=1}^{m} \frac{D_{B,e}}{D_A} K_{21,e}\right)^{\frac{1}{2}}}{1 + \sum_{e=1}^{m} K_{21,e}} \qquad (3\text{-}27)$$

Equation 3-27 is equivalent to Danckwerts' model when all the diffusivity ratios are equal to one.

Because of the non-linear equilibrium relations, no analytical solutions are expected for multiple reaction systems other than reaction 3-21. An approximation method which can estimate the surface renewal mass transfer enhancement factor by the use of film theory solutions was tested by Chang and Rochelle (1979) for single equilibrium reaction systems. This method suggests that the mass transfer enhancement factors derived from surface renewal theory can be estimated by replacing all the diffusivity ratios in film theory solutions by their square roots. Figure 3-1 shows the comparison of mass transfer enhancement factors predicted by surface renewal theory and approximation method for reaction 3-21. It is seen that the approximation

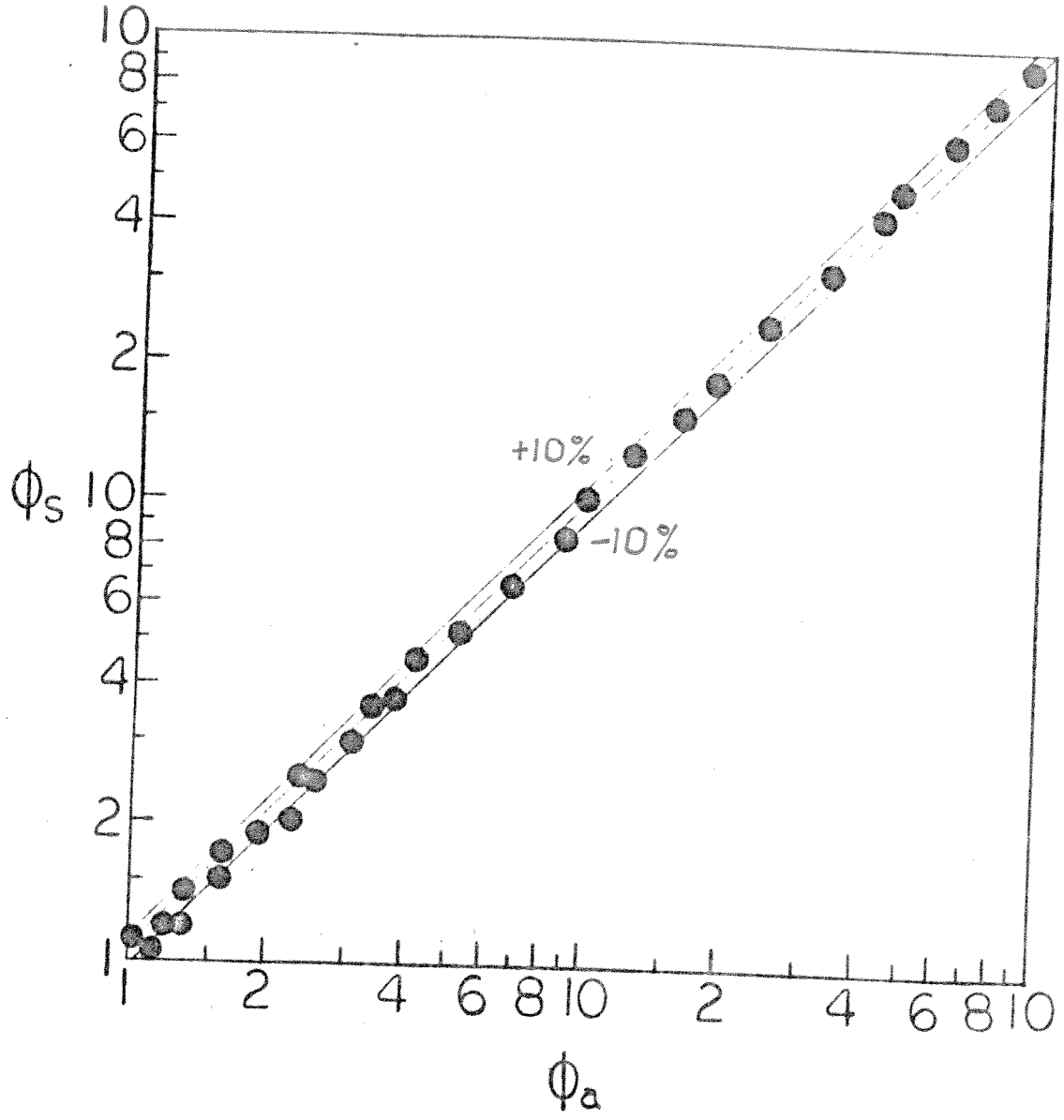

Figure 3-1. Comparison of mass transfer enhancement factors predicted by rigorous and approximate surface renewal theory for reaction 21 with $D_{B,e}/D_A$ = 0.3 to 10, $K_{21,e}$ = 0.1 to 10, m = 2 to 10.

method can estimate the surface renewal theory solutions within 10% error for a wide range of all the parameters. Since film theory solution, either analytical or numerical, can usually be obtained for other multiple reactions, this approximation method should be very useful for the estimation of the surface renewal theory solutions for the more complicated and practical multiple reaction systems.

For example, material balance for the surface renewal theory of the interacting system with reactions 3-14 and 3-16 gives two second-order nonlinear partial differential equations. Solution of those equations involves complicated numerical methods and tedious trial and error procedures. However, surface renewal theory can be easily approximated by replacing diffusivities by their square roots in the corresponding film theory solution as shown in Equation 3-20 to give:

$$\phi_a = 1 + \sqrt{\frac{D_B}{D_A}} \; \frac{C_{Bo}\left(1 + \sqrt{\frac{D_D}{D_c}}\,\frac{K_{16}}{K_{14}}\right)}{\sqrt{\frac{D_B}{D_C}}\,\frac{1}{K_{14}} + C_{Ai}\left(1 + \sqrt{\frac{D_D}{D_C}}\,\frac{K_{16}}{K_{14}}\right)} \qquad (3\text{-}28)$$

Notation

b_1, b_2	=	constants, see Equation (9)
C	=	concentration, g-mole/liter
D	=	diffusivity, cm^2/sec
J,J'	=	number of reactants and products
K	=	equilibrium constant
m	=	number of reactions
N	=	absorption rate, g-mole/sec
p,Y	=	stoichiometric coefficient
s	=	fractional rate of surface renewal, sec.
t	=	time, sec.
x	=	distance, cm.
ϕ	=	mass transfer enhancement factor
δ	=	film thickness, cm.

Subscripts

a	=	approximation method
e	=	reaction e
f	=	film theory
i	=	interface
j	=	component number
o	=	bulk
s	=	surface renewal theory

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Chapter 4

SO_2 ABSORPTION INTO AQUEOUS SOLUTIONS

ABSTRACT

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. Gas-phase mass transfer resistance was determined by absorption into 0.7 to 1.0 molar NaOH solution. 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.

Because H^+ and HSO_3^- diffuse at the same rate, pure water results in the reaction type, $A \rightleftharpoons 2B$. The enhancement factor varies from 1.1 with pure SO_2 to 12 with 200 ppm SO_2 in the gas. HCl solutions give the reaction type, $A \rightleftharpoons B$. The enhancement factor with dilute SO_2 varies from 2.5 in 0.01 molar HCl to 1.0 in 1 molar HCl. In NaCl solutions, H^+ and HSO_3^- diffuse at different rates and the reaction is given by $A \rightleftharpoons B + C$. The enhancement factor with 1250 ppm SO_2 increases by 20 to 25% in going from pure water to 0.4 molar NaCl.

SCOPE

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

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.

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 diffusiviteis. 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 used to interpret the absorption data. However, the rigorous surface renewal model has been solved numerically by Chang and Rochelle (1979). Their results will be employed to analyze the experimental data of this work.

Most previous experimental studies used pure sulfur dioxide as 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%. It is very difficult to discuss the absorption mechanism with such a small rate change. 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 atm to 0.98 atm. Thes results show a greater effect of the hydrolysis reaction and are of greater practical significance.

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.

CONCLUSIONS

Experiments have been carried out on the absorption of sulfur dioside, 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.

For the sulfur dioxide-water system, the gas absorption mechanism can be modeled by mass transfer with an instantaneous reversible reaction of the type $A \rightleftharpoons 2B$. 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 $A \rightleftharpoons B$. 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 $A \rightleftharpoons B + C$. The presence of the relatively high concentration of sodium chloride releases the hydrogen ion from the force of electrical potential gradient in the system. 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:

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^- \qquad (4\text{-}1)$$

The forward reaction rate constant at $20^{\circ}C$ was estimated to be 3.4×10^6 $(s)^{-1}$ (Eigen et al., 1961) and this reaction can be considered to be instantaneous. The value of the equilibrium constant of reaction 4-1 is

$$K_a = \frac{a_{H^+} a_{HSO_3^-}}{a_{SO_2}} = 1.3 \times 10^{-2} \qquad (4\text{-}2)$$

at $25^{\circ}C$ 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 (1979) 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 $A \rightleftharpoons 2B$. 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, 1979):

$$\phi_a = 1 + \sqrt{\frac{D_B}{D_A}} \cdot \frac{\sqrt{K_C}}{\sqrt{C_{Ai}} + \sqrt{C_{Ao}}} \qquad (4\text{-}3)$$

where D_A and D_B represent the diffusivities of species A and B, K_C the effective equilibrium constant of reaction 4-1, 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

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

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 become a gas absorption process accompanied by an equilibrium reaction of the form $A \rightleftharpoons B$, where B represents the bisulfite ion only. The exact surface renewal theory solution for the mass transfer enhancement factor was given by (Olander, 1960):

$$\phi_s = \sqrt{(1 + \frac{D_B}{D_A} K_C')(1 + K_C')} \qquad (4\text{-}5)$$

and the film theory solution was given:

$$\phi_f = 1 + \frac{D_B}{D_A} K_C' \qquad (4\text{-}6)$$

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 $A \rightleftharpoons B + C$. The numerical solution of the surface renewal model can be approximated by (Chang and Rochelle, 1979):

$$\phi_a = 1 + \sqrt{\frac{D_C}{D_A}} \frac{C_{Ci} - C_{Co}}{C_{Ai} - C_{Ao}} \qquad (4\text{-}7)$$

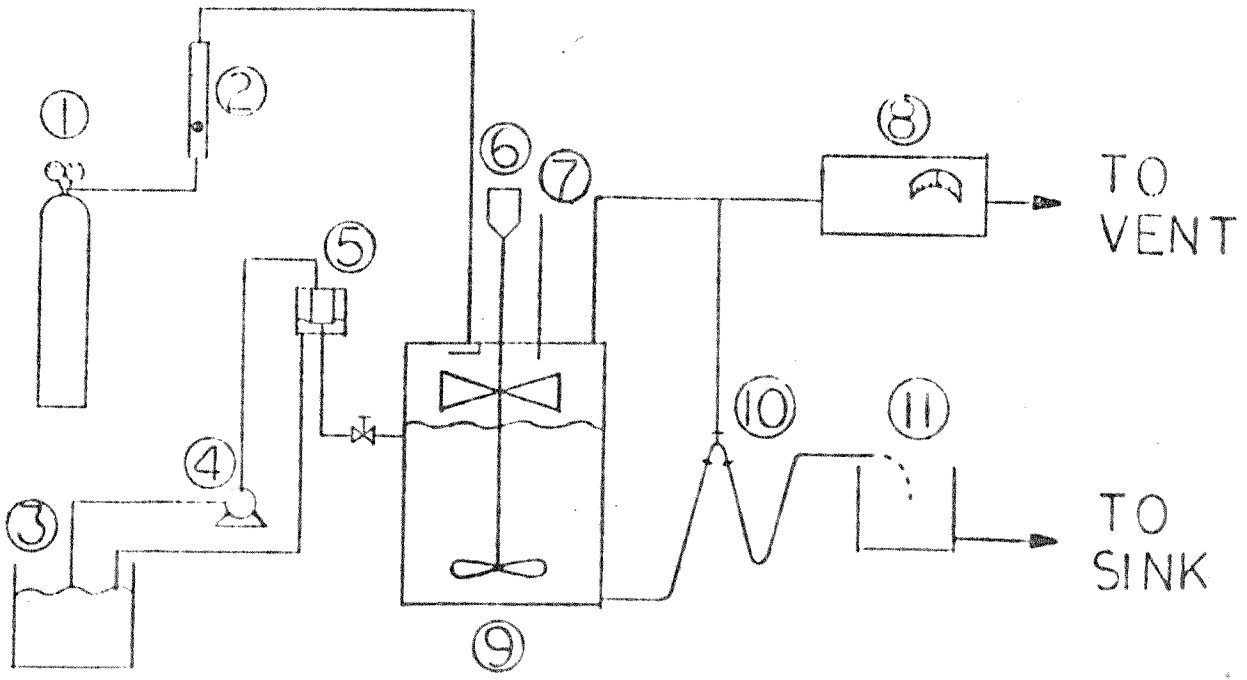
in which

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

EXPERIMENTAL

Apparatus and procedure

Figure 4-1 shows a schematic diagram of the experimental apparatus. The agitated vessel, shown in Figure 4-2, 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 4-2(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.



1. SO_2/N_2 mixture
2. Gas rotameter
3. Liquid storage tank
4. Pump
5. Overflow system
6. Varible speed motor
7. Thermometer
8. SO_2 analyzer
9. Agitated vessel
10. Liquid trap
11. Sampling

Figure 4-1. Experimental apparatus.

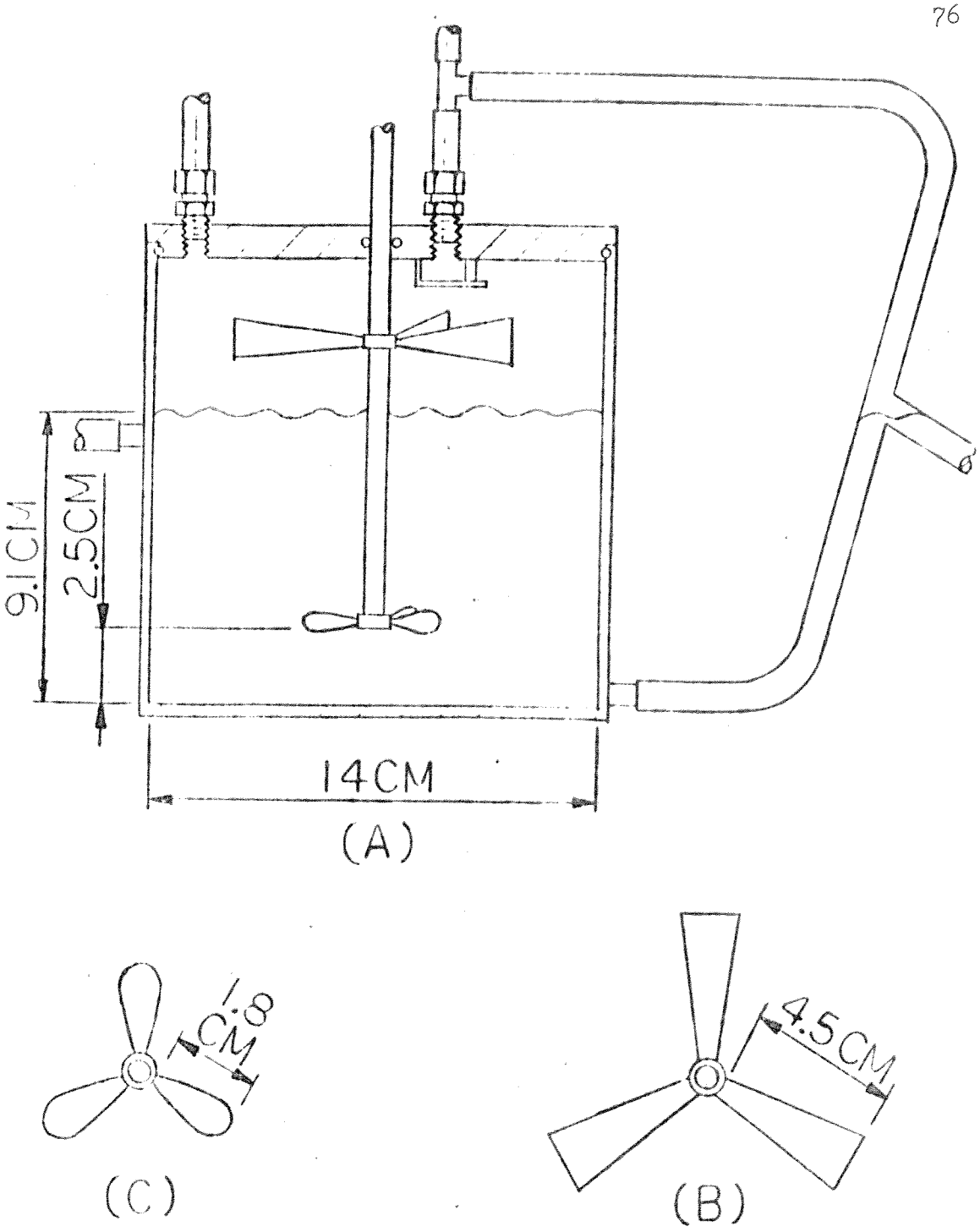


Figure 4-2. Agitated vessel and stirrers.
(a) Agitated vessel (b) Gas stirrer
(c) Liquid stirrer.

The gas phase stirrer, shown in Figure 4-2 (b), was a propeller with three flat blades and was placed in the center of the gas phase. The liquid stirrer, shown in Figure 4-2(c), was a propeller with three blades smaller than those of 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 h.p. 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 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 atm. The absorbing liquids used were pure water and aqueous solutions of HCl, NaOH, or NaCl of concentration varying from 0.01 to 1 g-mole/liter.

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 ml/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

$$H = \exp (2851.1/T - 9.3795) \qquad (4\text{-}8)$$

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

$$C_{Aiw} = P_{SO_2} \cdot H \qquad (4\text{-}9)$$

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, 1949):

$$\log (C_{Ai}/C_{Aiw}) = -K_s I \qquad (4\text{-}10)$$

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 4-1 was calculated from the correlation (Rabe and Harris, 1963)

$$K_a = \exp (1972.5/T - 10.9670) \qquad (4\text{-}11)$$

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,

$$a_j = \gamma_j \cdot C_j \qquad (4\text{-}12)$$

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

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

where n_j is the charge on the jth ion, and C_{3j} and C_{4j} are characteristic parameters for each ion species. Table 4-1 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):

$$\log \gamma = 0.076\ I \qquad (4\text{-}14)$$

Figure 4-3 shows the values of effective equilibrium constant K_c in concentration units, calculated from Eq. 4-11, 4-12, 4-13 and 4-14, versus ionic strength.

The liquid phase diffusivity D_{Aw} of sulfur dioxide in pure water was taken as 2.00×10^{-5} cm^2/sec 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 Stokes-Einstein relation.

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

Table 4-1. 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

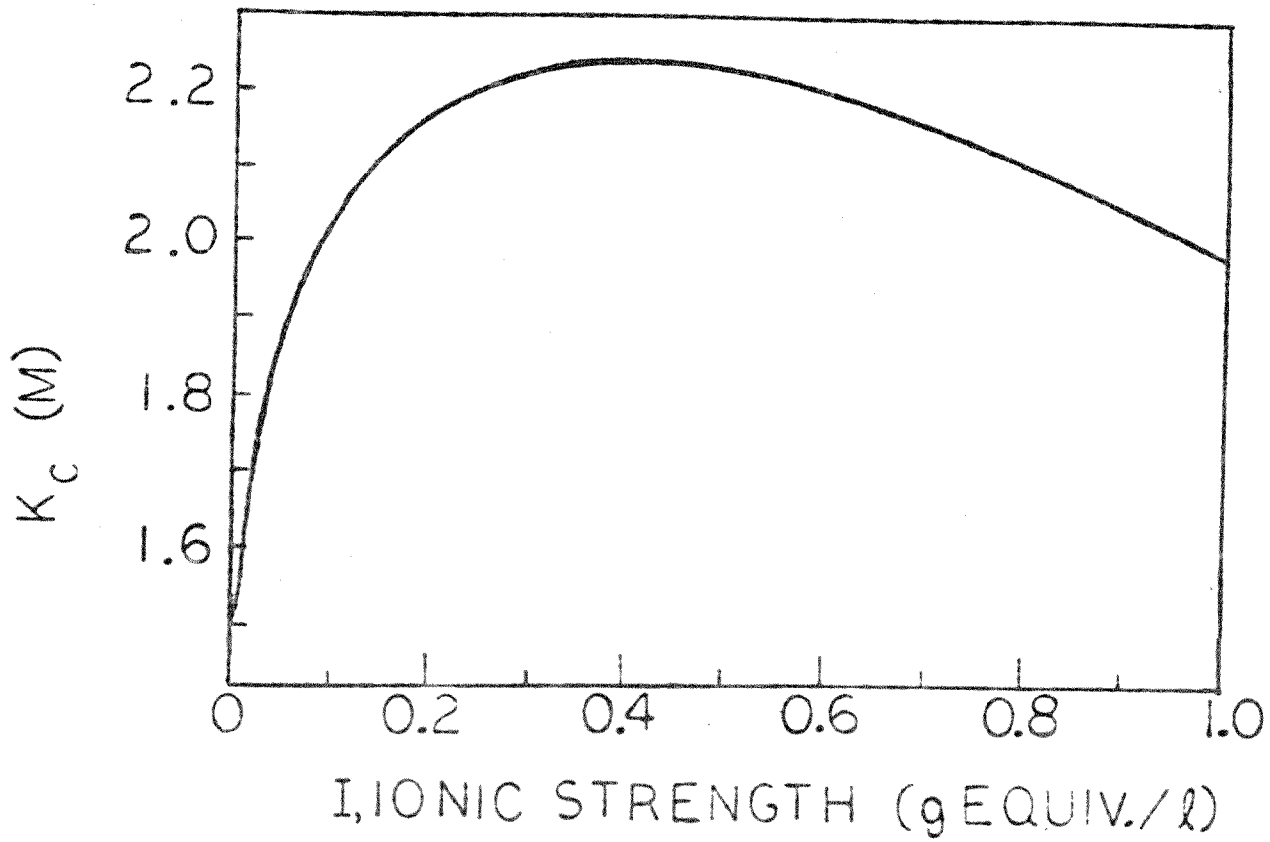


Figure 4-3. Effect of ionic strength on equilibrium constant of reaction (1) at 25°C.

$$D\pm = \frac{RT\gamma^{\circ}\pm}{(Fa)^2} \qquad (4\text{-}15)$$

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 cm^2/mole-ohm, respectively (Landolt - Bornstein, 1960). Therefore, H^+ tends to move six 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):

$$D_{eff} = \frac{RT(1/n^+ + 1/n^-)}{(Fa)^2(1/\lambda^{\circ}+ + 1/\lambda^{\circ}-)} \qquad (4\text{-}16)$$

The value of D_{eff} for H^+ and HSO_3^- in pure water at 25°C is 2.33 cm^2/sec.

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 and 1.33 cm^2/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 coefficient

The gas 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 the liquid phase reactant at the gas-liquid interphase. 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 completely mixed.

The effect of gas flow rate on the value of $k_g a$ is shown in Figure 4-4. It can be seen that the $k_g a$ values are independent of

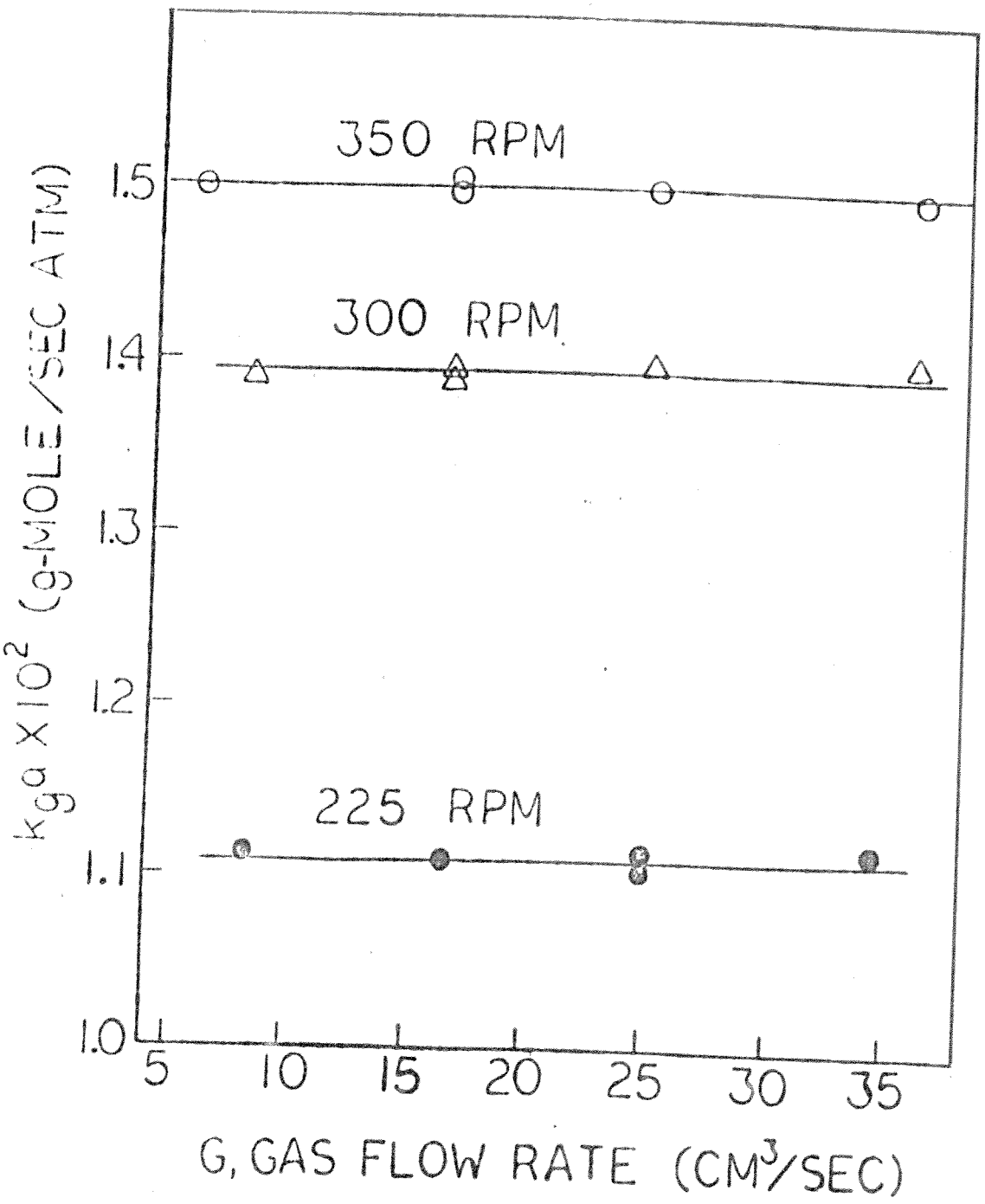


Figure 4-4. Effect of gas flow rate on gas-phase mass transfer coefficient (absorption of SO_2 into aqueous NaOH

the gas flow rate, indicating that the above assumption of complete mixing in the gas phase is valid. 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, $k_L^o a$, 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. 4-5, the chemical reaction effect on the mass transfer rate is negligible in 1 M HCl solution and only physical gas absorption of SO_2 occurred in liquid phase. Experimental results for the liquid-side mass transfer coefficient are shown in Figure 4-5 as a plot of $k_L^o a$ vs temperature. It was found that $Hk_L^o a$ is about forty times greater than $k_g a$. Therefore, in most experiments the mass transfer rates were controlled by liquid phase resistance and the chemical reaction effect on liquid phase resistance and the chemical reaction effect on liquid phase mass transfer can be easily detected.

SO_2 - H_2O system

Experimental results obtained with pure SO_2 and pure H_2O at different temperatuers are listed in Table 4-2. 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,

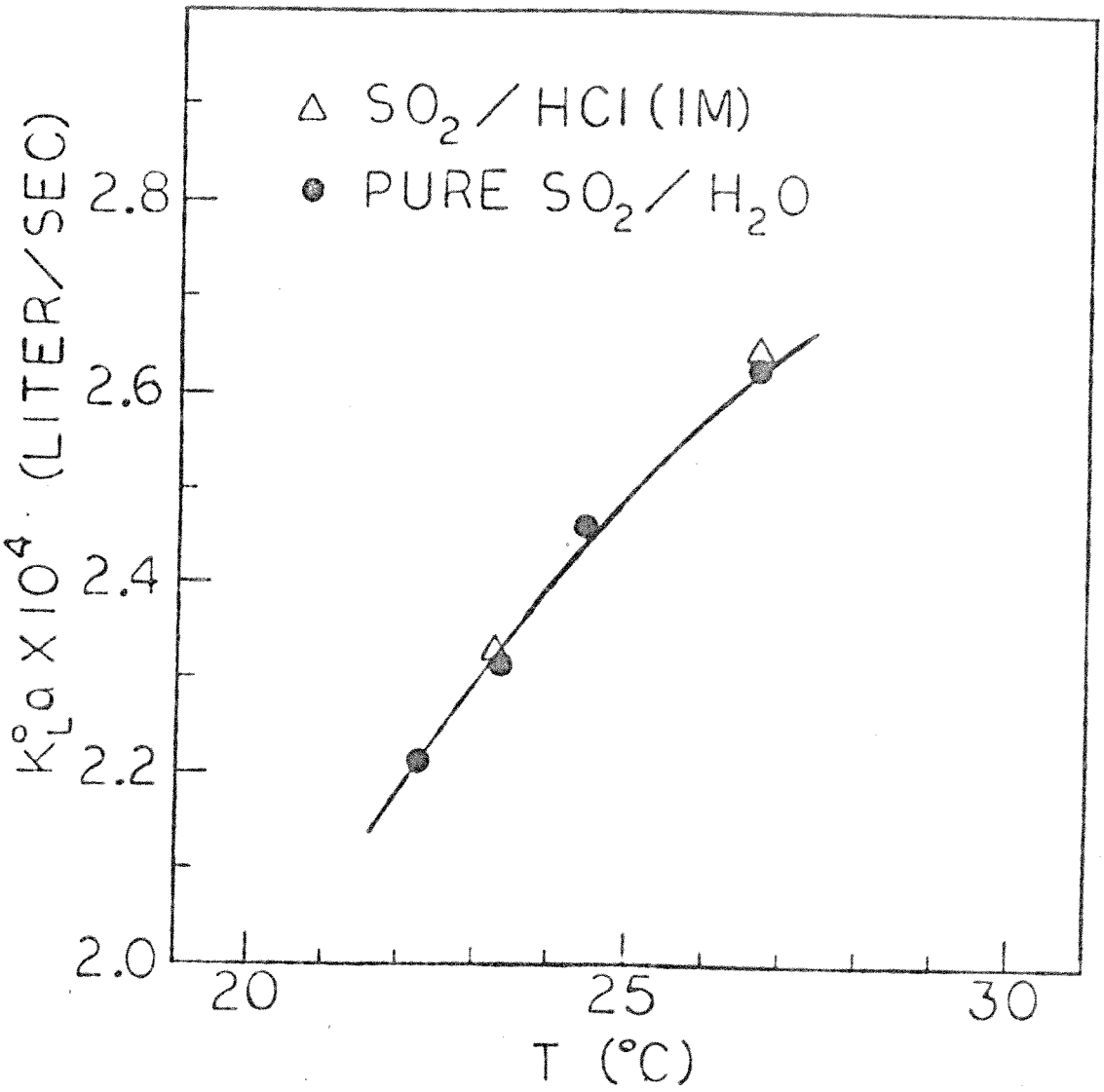


Figure 4-5. Liquid-phase physical mass transfer coefficient of sulfur dioxide into water at 300 rpm.

Table 4-2. Experimental conditions and absorption rate data of pure SO_2 - H_2O

Run	T (°C)	L (cm^3/sec)	C_{Ai} (M)	C_{Ao} (M)	$\phi k_L^\circ a$ (liter/sec)	$k_L^\circ a$ (liter/sec)
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}

the mass transfer enhancement factors calculated from Eq. 4-3 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 coused by SO_2 hydrolysis. The black dots in Figure 4-5 represent the $k_L^o a$ 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 4-6 represents the experimental data obtained for the dilute SO_2 - H_2O system at 25°C. The experimental value of the mass transfer enhancement factors are shown in Figure 4-6 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 4-6 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 $A \rightleftharpoons 2B$ 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.

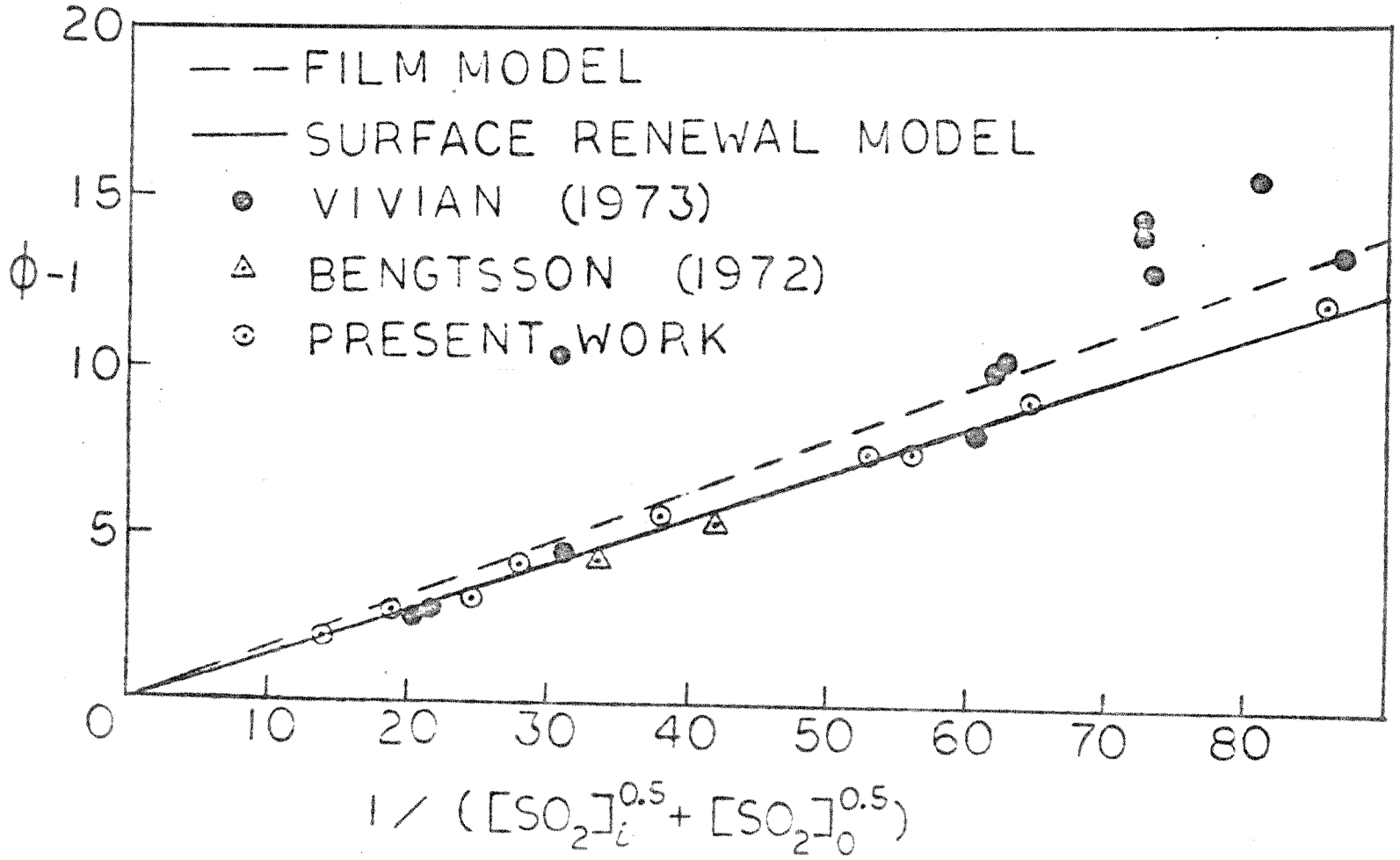


Figure 4-6. Comparison of theoretical mass transfer enhancement factor with experimental data for SO_2/N_2 - H_2O system at 25°C.

SO_2 - HCl system

Experimental results on the absorption of SO_2 into HCl solutions are shown in Figure 4-7, 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 $A \rightleftharpoons B$ takes place instantaneously along the diffusion path, while the broken curve shows the corresponding film theory predictions.

Eq. 4-5 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 4-8 show that the change of gas phase SO_2 concentration dose not affect the value of ϕ, as long as the temperature and the HCl concentration remain the same.

SO_2 - NaCl system

Figure 4-9 present 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

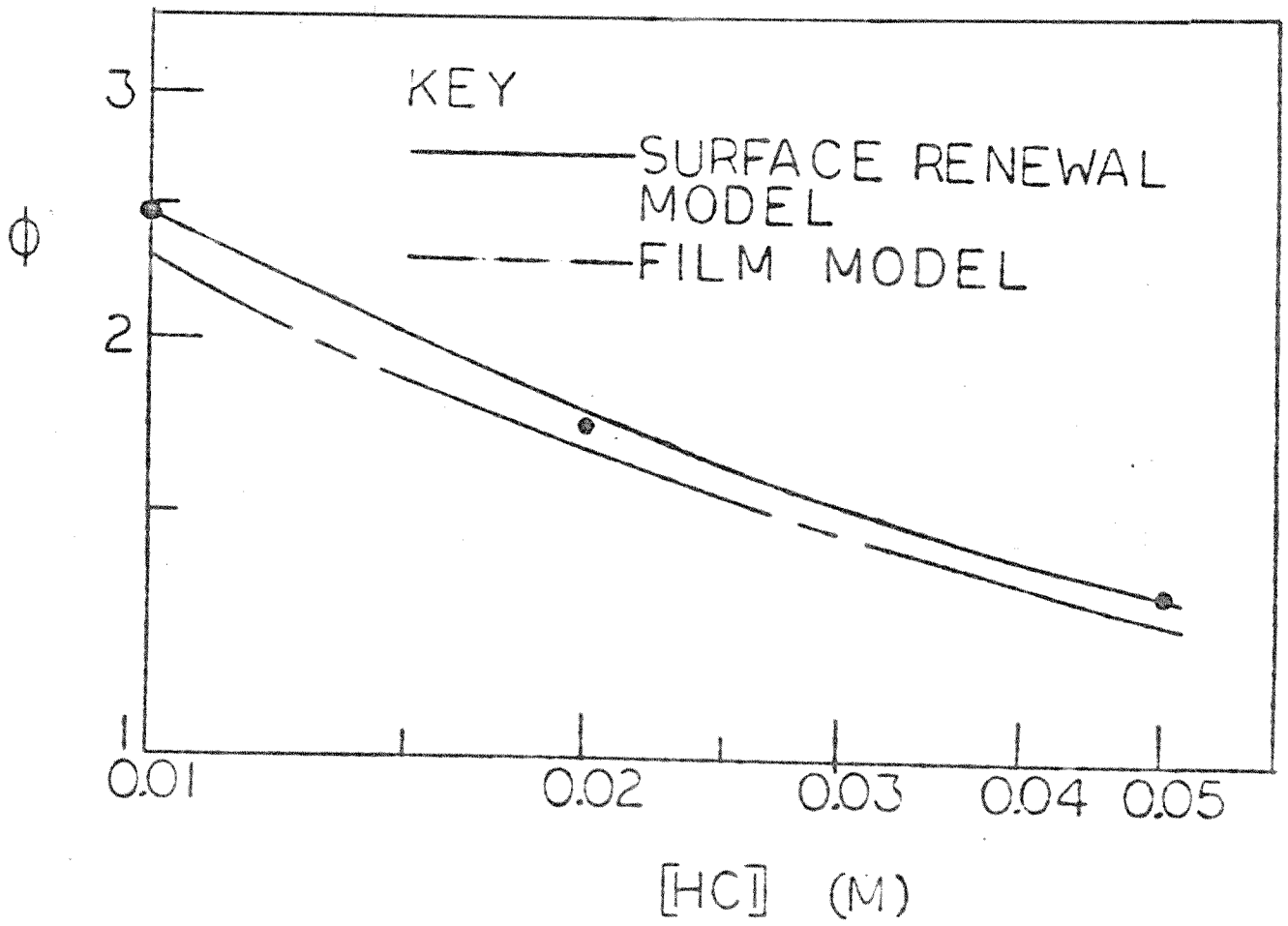


Figure 4-7. Comparison of theoretical mass transfer enhancement factor with experimental data for SO_2/N_2 - HCl system at 23.5°C.

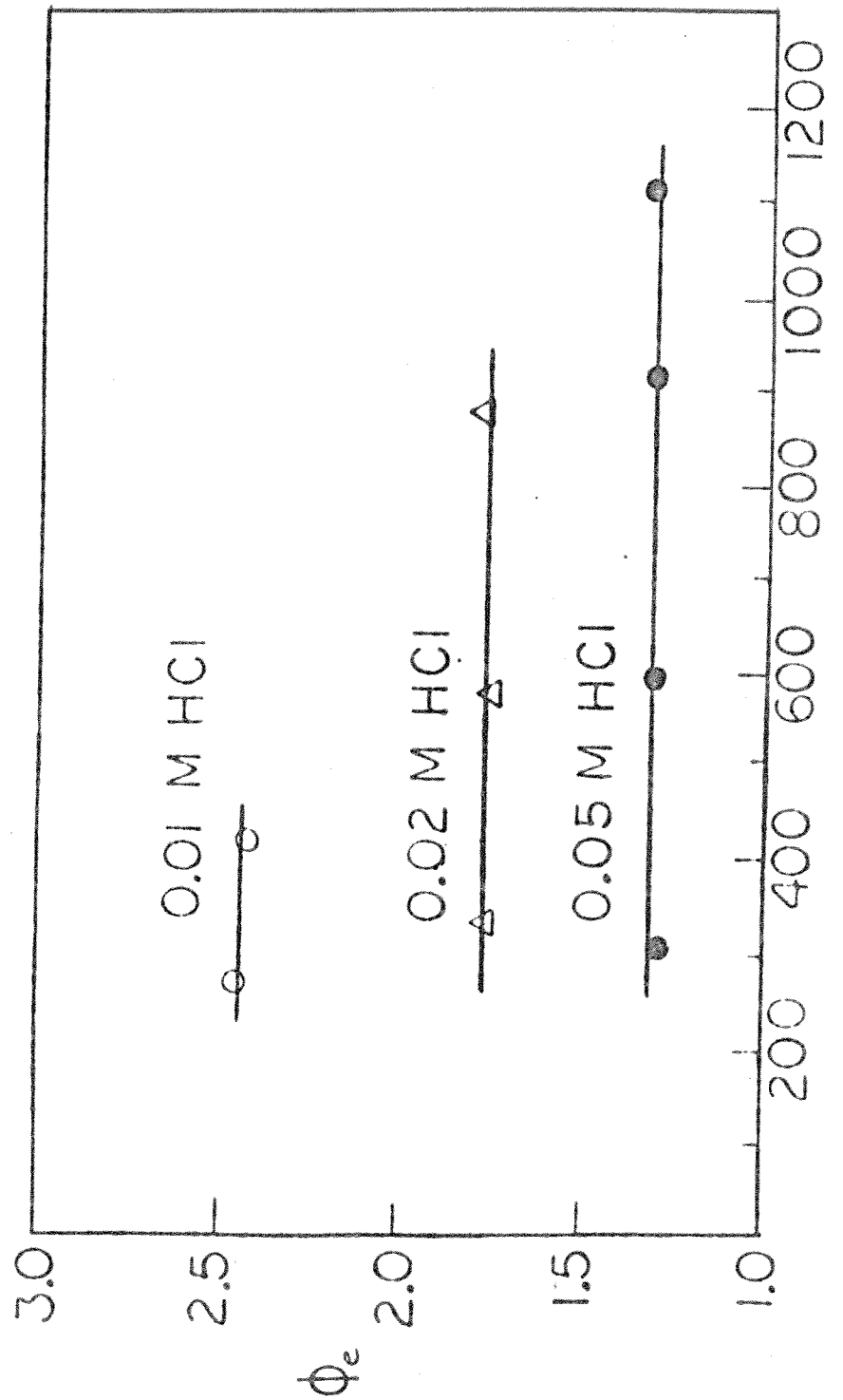


Figure 4-8. Effect of SO_2 partial pressure on liquid phase mass transfer enhancement factor at 23.5°C.

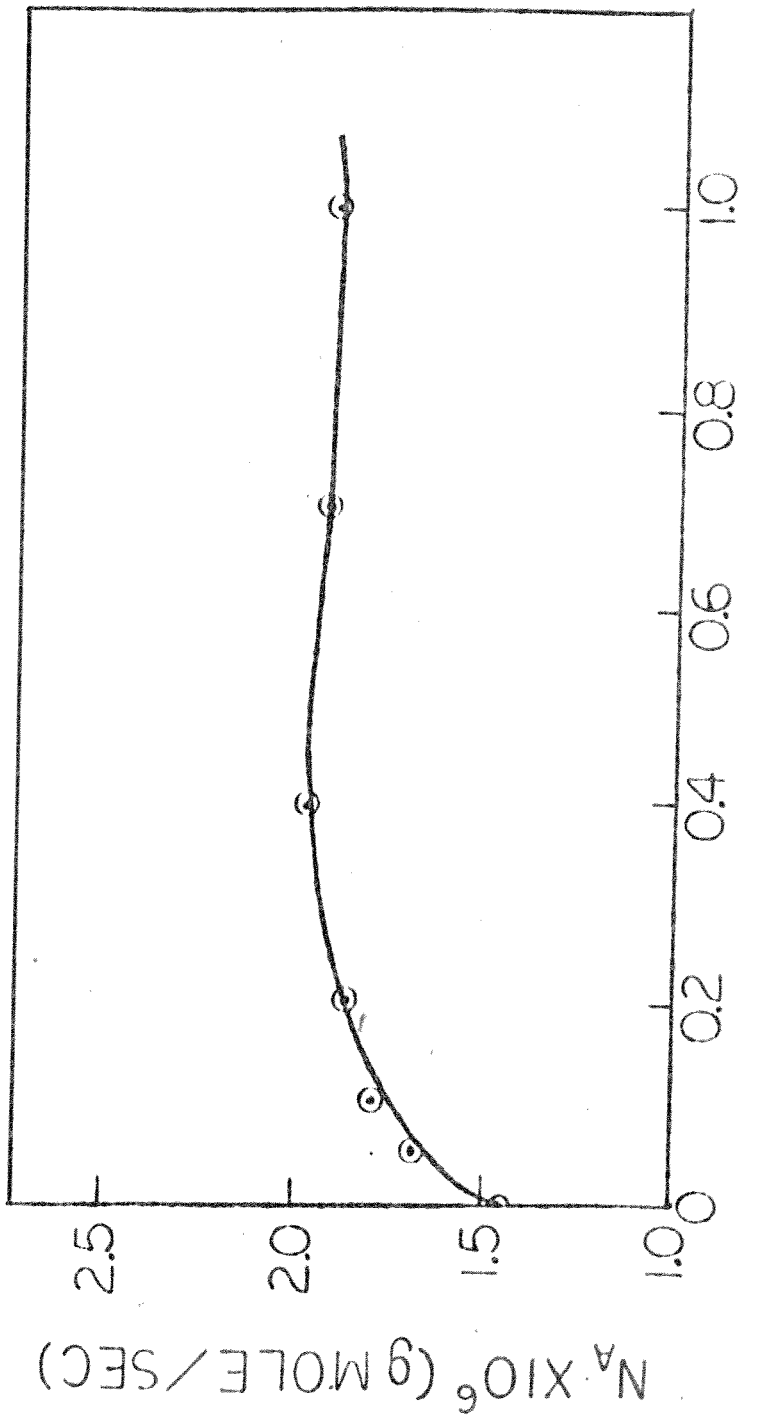


Figure 4-9. Absorption rate of SO_2 into aqueous NaCl solutions at 24°C with 1250 ppm SO_2 in N_2.

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 which affects the effective equilibrium constant K_c as shown in Figure 4-3. The similarity between the shape of the curve in Figures 4-3 and 4-9 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 4-10 as a plot of enhancement factor vs interphase equilibrium concentration of sulfur

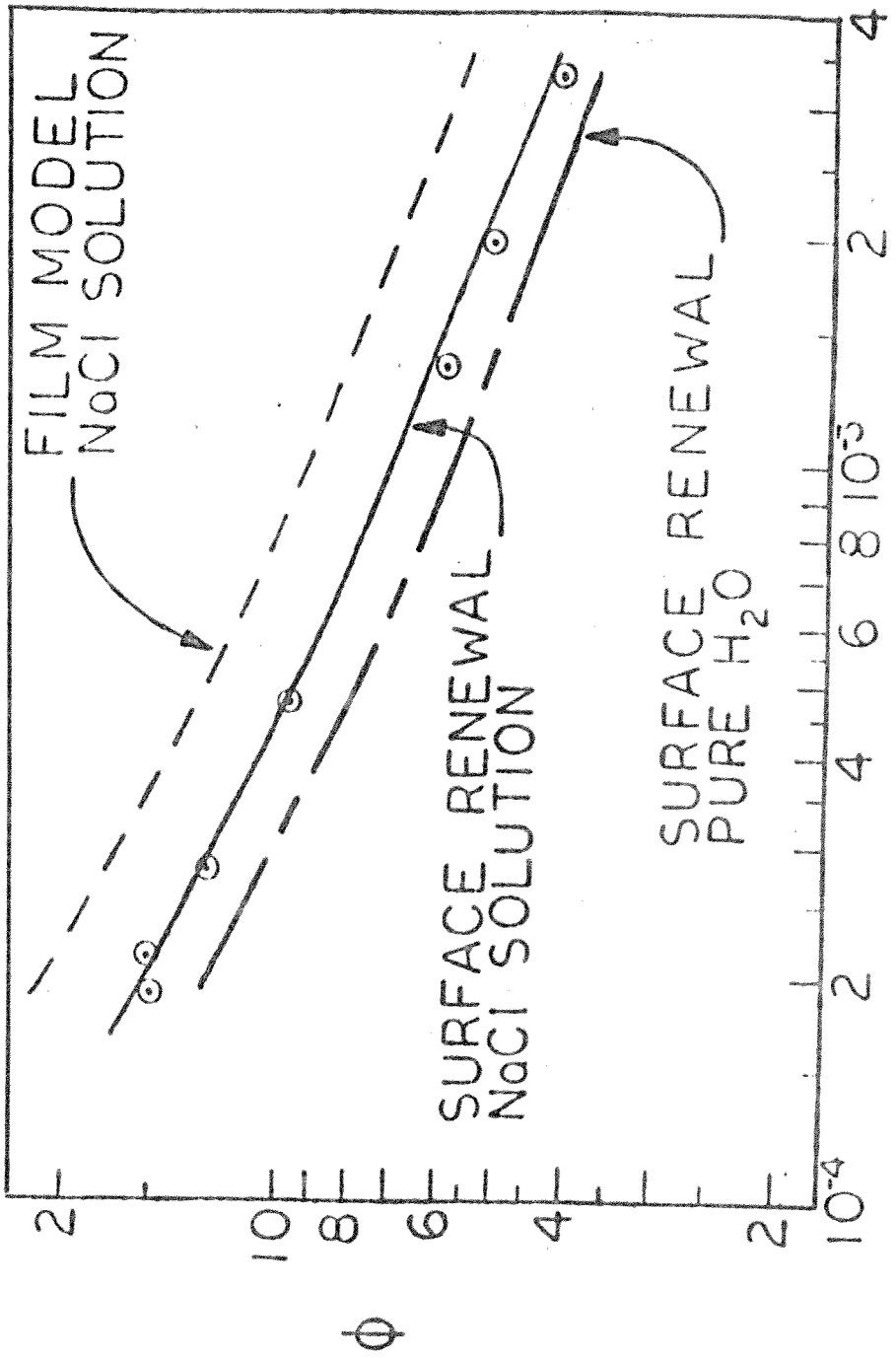


Figure 4-10. Comparison of theoretical mass transfer enhancement factor with experimental data for SO_2 (1200 ppm) - NaCl (0.4 M) system at 25°C.

dioxide. The solid curve gives the surface renewal theory solution for gas absorption with an instantaneous reversible reaction of the type A B + C and can reasonably represent the data. The chain curve (—·—·—) shows the predictions of surface renewal model with reaction of the type A 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-mole/liter
C	concentration	g-mole/liter
C_{3j}, C_{4j}	parameter in Eq (13)	
D	diffusivity of component	cm^2/sec
D_{eff}	effective diffusivity defined by by Eq (16)	cm^2/sec
$D\pm$	effective diffusivity of ions defined by Eq (15)	cm^2/sec
Fa	Faraday = 96488 coulumbs/g-equivalent	
G	gas flow rate	cm^3/sec
H	Henry's law constant	g-mole/atm
I	ionic strength	g-mole/liter
K_a	thermodynamic equilibrium constant	g-mole/liter
K_c	effective equilibrium constant in concentration units	g-mole/liter
$K_{c'}$	equilibrium constant defined by Eq (6)	
$k_g^{\circ}a$	gas-phass mass transfer coefficient	
$k_L^{\circ}a$	liquid-phase mass transfer coefficient	liter/sec
K_s	salting out parameter	liter/g-mole
L	liquid flow rate	cm^3/sec
N_A	absorption rate	g-mole/sec
$n\pm$, n_j	valence	
P_{SO_2}	SO_2 partial pressure	atm
R	gas constant = 8.315 J/°K-g-mole	

T	temperature	°K
$\phi_a, \phi_s, \phi_f, \phi_e$	mass transfer enhancement factor obtained from approximation method, penetration model, film model and experiment	
γ_j	activity coefficient of component j	
$\lambda^{\circ}_{\pm}$	equivalent ion conductance	cm^2/g-mole/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-mole/l

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Chapter 5

ABSORPTION OF SO_2 INTO AQUEOUS NaOH AND Na_2SO_3 SULFITE SOLUTIONS

Abstract

The chemical absorption of sulfur dioxide into aqueous sodium sulfite and sodium hydroxide solutions is modelled by simultaneous mass transfer and multiple instantaneous reversible reactions. Experiments on the absorption of dilute sulfur dioxide into aqueous sodium hydroxide solutions were carried out in a stirred vessel with a plain gas-liquid interface. An approximation method based on film theory is used to estimate surface renewal theory solutions for mass transfer enhancement factors. Predictions by the present model are compared with those by a previous irreversible model over a wide range of SO_2 partial pressure in the gas phase.

Scope

Because of its relevance to pollution abatement, SO_2 absorption into NaOH or Na_2SO_3 solution has been studied by several investigators. Goettler (1967) investigated the simultaneous absorption of SO_2 and CO_2 into NaOH solution flowing over a single sphere. The absorption rates were modelled by the film theory with the assumption that dissolved sulfur dioxide and OH^- partici-

pate in a two-step instantaneous irreversible reaction and two reaction planes are formed within the liquid phase. Hikita et al (1972) derived the solution of the penetration theory using the model of two reaction planes. Onda et al (1971) studied the behavior of the reaction plane movement by absorbing sulfur dioxide into agar-agar gel containing sodium hydroxide or sodium sulfite solution. The experimental results for sulfur dioxide-sodium hydroxide system were found to agree with penetration theory based on the two reaction plane model. Hikita et al (1977) measured the absorption rate of pure sulfur dioxide into aqueous sodium bisulfite, sodium hydroxide and sodium sulfite solutions in a liquid jet column. The absorption rates obtained with no interfacial turbulence were in good agreement with the theoretical prediction based on the penetration theory.

The two reaction plane model used by previous investigators neglects the reversible hydrolysis of the absorbed sulfur dioxide. Most previous studies used either pure or concentrated sulfur dioxide in gas phase under which the sulfur dioxide hydrolysis reaction is highly depressed (Teramoto et al, 1978). However, the stack gas sulfur dioxide concentration in SO_2 scrubbers is normally very dilute (100 ~ 4000 ppm) and under these conditions the sulfur dioxide hydrolysis reaction can have a significant effect on the absorption rate.

This paper develops an approximation of the surface renewal theory with instantaneous, reversible chemical reactions representative of SO_2 absorption into NaOH or Na_2SO_3 solution. The theory

is tested by experimental absorption of SO_2 at low partial pressure in a well-stirred vessel.

Conclusions

1. The experimental data on the absorption of dilute sulfur dioxide into NaOH solutions agree well with the approximate solutions of surface renewal theory with instantaneous reversible reactions.

2. This chemical absorption model shows that the reversible SO_2 hydrolysis reaction is significant and H^+ plays an important role in the absorption mechanism when SO_2 partial pressure is much lower than 0.05 atm. When the SO_2 partial pressure is higher than 0.05 atm, the hydrolysis of dissolved SO_2 is negligible and the present model gives the same prediction of mass transfer enhancement factor as the irreversible two-reaction plane model.

Chemical Absorption Mechanism

When dilute sulfur dioxide is absorbed into aqueous alkaline solutions, the following three reactions should be considered.

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^- \qquad (5\text{-}1)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^= \qquad (5\text{-}2)$$

$$H^+ + OH^- \rightleftarrows H_2O \qquad (5\text{-}3)$$

The values of the three equilibrium constants for reactions 5-1, 5-2, and 5-3 are designated as K_{a1}, K_{a2}, and K_{a3} and they are given, respectively, as:

$$K_{a1} = \frac{a_{H^+}\, a_{HSO_3^-}}{a_{SO_2}} = 1.3 \times 10^{-2} \qquad \text{(Johnstone and Leppla, 1934)}$$

$$K_{a2} = \frac{a_{H^+}\, a_{SO_3^-}}{a_{HSO_3^-}} = 6.2 \times 10^{-8} \qquad \text{(Tartar and Garretson, 1941)}$$

$$K_{a3} = a_{H^+}\, a_{OH^-} = 1.0 \times 10^{-14} \qquad \text{(Harned and Owen, 1958)}$$

at 25°C and infinite dilution. Reaction 5-1 is very fast, with a forward rate constant estimated to be 3.4×10^6 $(s)^{-1}$, (Eigen et al, 1961). Reaction 5-2 and 5-3 are even faster than reaction 5-1 since they are proton transfer reactions. Therefore, the absorption of sulfur dioxide into aqueous alkaline solutions can be regarded as a process of gas absorption accompanied by multiple instantaneous reversible reactions in the liquid phase.

The differential equations describing the diffusion of all species in the liquid phase, based on surface renewal theory and total-component material balance, can be written as:

$$SO_2 : D_{SO_2} \frac{\partial^2[SO_2]}{\partial x^2} + D_{HSO_3^-} \frac{\partial^2[HSO_3^-]}{\partial x^2} + D_{SO_3^=} \frac{\partial^2[SO_3^=]}{\partial x^2}$$

$$= \frac{\partial[SO_2]}{\partial t} + \frac{\partial[HSO_3^-]}{\partial t} + \frac{\partial[SO_3^=]}{\partial t} \qquad (5\text{-}4)$$

$$\text{Acidity: } D_{H^+} \frac{\partial^2[H^+]}{\partial x^2} - D_{HSO_3^-} \frac{\partial^2[HSO_3]}{\partial x^2} - 2D_{SO_3^=} \frac{\partial^2[SO_3^=]}{\partial x^2} - D_{OH^-} \frac{\partial^2[OH^-]}{\partial x^2}$$

$$= \frac{\partial[H^+]}{\partial t} - \frac{\partial[HSO_3^-]}{\partial t} - 2 \frac{\partial^2[SO_3^=]}{\partial t} - \frac{\partial[OH^-]}{\partial t} \qquad (5\text{-}5)$$

Furthermore, the chemical equilibrium relations of reactions 5-1, 5-2, and 5-3 also apply at all points in liquid phase. The substitution of the equilibrium relations into Equations 5-4 and 5-5 results in two non-linear second-order partial differential equations. Therefore, there are no analytical solutions for the above differential equations. However, an approximate analytical solution for surface renewal theory can be obtained by replacing all the diffusivity ratios in the exact solution based on film theory by their square roots, (Chang and Rochelle, 1979a, 1979 b).

The general solutions of the film theory material balance equations are:

$$D_{SO_2}[SO_2] + D_{HSO_3^-}[HSO_3^-] + D_{SO_3^=}[SO_3^=] = b_1 x + b_2 \qquad (5\text{-}6)$$

$$D_{H^+}[H^+] - D_{HSO_3^-}[HSO_3^-] - 2D_{SO_3^=}[SO_3^=] - D_{OH^-}[OH^-] = b_3x + b_4 \quad (5\text{-}7)$$

Concentrations of all the species are subject to the equilibrium relations of reaction 5-1, 5-2 and 5-3. The boundary conditions are

at $x = 0$, $[SO_2] = [SO_2]_i$,

$$D_{H^+}\frac{d[H^+]}{dx} - D_{HSO_3^-}\frac{d[HSO_3^-]}{dx} - 2D_{SO_3^=}\frac{d[SO_3^=]}{dx} - D_{OH^-}\frac{d[OH^-]}{dx} = 0$$

at $x = \infty$, $[SO_2] = [SO_2]_o$, $[OH^-] = [OH^-]_o$, $[SO_3^=] = [SO_3^=]_o$

The SO_2 absorption rate is given by

$$N_{SO_2} = \phi k_L^o a ([SO_2]_i - [SO_2]_o) \quad (5\text{-}8)$$

where ϕ is the mass transfer enhancement factor. Solution of Equations 5-6 and 5-7 with appropriate boundary conditions followed by substitution for diffusivity ratios by their square roots gives the approximate enhancement factor from surface renewal theory:

$$\phi_a = 1 + \sqrt{\frac{D_{HSO_3^-}}{D_{SO_2}}}\left(\frac{[HSO_3^-]_i - [HSO_3^-]_o}{[SO_2]_i - [SO_2]_o}\right) + \sqrt{\frac{D_{SO_3^=}}{D_{SO_2}}}\left(\frac{[SO_3^=]_i - [SO_3^=]_o}{[SO_2]_i - [SO_2]_o}\right) \quad (5\text{-}9)$$

The values of $[HSO_3^-]_i$ and $[SO_3^=]_i$ are related to $[H^+]_i$ and $[SO_2]_i$ by the equilibrium relations:

$$[HSO_3^-]_i = K_{c1}[SO_2]_i/[H^+]_i$$

$$[SO_3^=]_i = K_{c1}K_{c2}[SO_2]_i/[H^+]_i^2$$

where K_{c1}, K_{c2} and K_{c3} are the effective equilibrium constants of reactions 5-1, 5-2, and 5-3 expressed in concentration units. Furthermore, the value of $[H^+]_i$ can be obtained from the following equation derived from Equations 5-6 and 5-7.

$$\sqrt{D_{H^+}}[H^+]_i^3 + [H^+]_i^2(\sqrt{D_{HSO_3^-}}[HSO_3^-]_o - \sqrt{D_{H^+}}[H^+]_o + 2\sqrt{D_{SO_3^=}}[SO_3^=]_o + \sqrt{D_{OH^-}}[OH^-]_o) - [H^+]_i(\sqrt{D_{HSO_3^-}}[SO_2]_i K_{c1} + \sqrt{D_{OH^-}}K_{c3}) - 2\sqrt{D_{SO_3^=}}[SO_2]_i K_{c1}K_{c2} = 0 \qquad (5\text{-}10)$$

Experimental

Apparatus and Procedures

Experiments on the absorption of sulfur dioxide by aqueous sodium hydroxide solutions were carried out in an agitated vessel with an unbroken gas-liquid interface which was used by Chang and Rochelle (1979c) in a previous work. The absorber uses continuous flow for both gas and liquid phases and is suitable for steady-state operation. Sulfur dioxide diluted by nitrogen was fed into the stirred vessel at constant flow rate. Sufficient sodium chloride (0.5 molar) was added to the aqueous sodium hydroxide solutions to eliminate the effect of electric potential gradient on the diffusivities of ionic species (Vinograd and McBain, 1941). All the experimental runs were performed at about atmospheric pressure and 25±1°C. The sulfur dioxide partial pressure of the

outlet gas stream was measured by a pulsed fluorescent SO_2 analyzer (Thermoelectrom model 40). At steady-state, samples of the outlet liquid were acidified by HCl and oxidized by hydrogen peroxide. Total sulfate concentration was determined by an ion chromatograph. The sulfur dioxide absorption rate was calculated from the liquid phase material balance.

Physical Properties

The physical solubility of sulfur dioxide in water was obtained from the following equation based on the measurement of Rabe and Harris (1963).

$$[SO_2]_i = P_{SO_{2i}} \exp (2851.1/T - 9.3 + 95) \qquad (5\text{-}11)$$

since the equilibrium constants of reactions 5-1, 5-2, and 5-3 are in thermodynamic units, an appropriate activity coefficient must be incorporated with the concentration of each component to estimate the effective equilibrium constants in concentration units for equation 5-10. For example

$$K_{c1} = K_{a1} \cdot \frac{\gamma_{SO_2}}{\gamma_{H^+}\gamma_{HSO_3^-}} \qquad (5\text{-}12)$$

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

$$\log \gamma_j = 0.512\, n_j^2 \left[\frac{-I^{1/2}}{1 + 0.312\, C_{3j} I^{1/2}} + C_{4j} I\right] \qquad (5\text{-}13)$$

where n_j is the charge on the jth ion, I represents the ionic strength, and C_{3j} and C_{4j} are the characteristic parameters for each ion species. Table 5-1 lists the values of those two parameters on a molar

Table 5-1. Parameters for the estimation of activity coefficient at 25°C

	C_{3j}	C_{4j}
H^+	6.0	0.4
OH^-	3.0	0.3
HSO_3^-	4.5	0.0
$SO_3^=$	4.5	0.0

concentration basis. The activity coefficient of the hydrated sulfur dioxide was estimated by Harned and Owen, (1958)

$$\log \gamma_{SO_2} = 0.076I \qquad (5\text{-}14)$$

The liquid phase diffusivity, D_{SO_2}, of sulfur dioxide in water was taken as 2.00×10^{-5} cm^2/sec at 30°C (Peaceman, 1951). The value of D_{SO_2} at 25°C was predicted by correcting for the temperature and viscosity of water according to Sakes-Einstein relation.

One half mole of sodium chloride was added to each liter of sodium hydroxide solution for all the experimental runs to avoid the interference of electrical potential gradient with the diffusion of ionic species (Chang and Rochelle, 1979c). Therefore, the effective diffusivities of all the ionic species were assumed to be equal to their true diffusivities as determined from equivalent ionic conductivities:

$$D_{\pm} = \frac{RT \lambda_{\pm}^{o}}{N_j (Fa)^2} \qquad (5\text{-}15)$$

where Fa is the Faraday number and $\lambda_{\pm}^{o}$ the equivalent ionic conductivity. The values of $\lambda_{\pm}^{o}$ for H^+, OH^-, HSO_3^- and $SO_3^=$ at 25°C and infinite dilution are given in Landolt-Börnstein (1960). The diffusivities used in the model calculations are listed in Table 5-2.

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.

Table 5-2. Effective diffusivities at 25°C and infinite dilution

	$D \times 10^5$ (cm^2/sec)
H^+	9.31
OH^-	5.25
HSO_3^-	1.33
$SO_3^=$	0.958
SO_2	1.76
NaOH	2.122
$NaHSO_3$	1.33
Na_2SO_3	1.18

Experimental Results and Discussion

Experimental results for the absorption of dilute sulfur dioxide into aqueous sodium hydroxide solutions are shown in Figure 5-1 as a plot of mass transfer enhancement factor versus NaOH concentration. The data are in good agreement with the approximate surface renewal theory.

Hikita et al (1977) conducted a series of experiments with pure sulfur dioxide as gas phase and concentrated NaOH or Na_2SO_3 solutions as liquid phase with a laminar liquid jet. Because no excess sodium salt was added to liquid phase, the ionic diffusivities were affected by the electric potential developed by the diffusing ions. However, it is shown in Figures 5-2 and 5-3 that the present model can fit their experimental data if sodium salt diffusivities were used as the average effective diffusivities of the diffusing ions. For example, the average effective diffusivity of sodium hydroxide can be calculated from Vinograd and McBain, (1941).

$$D_{NaOH} = \frac{RT\left(\frac{1}{n_{Na^+}} + \frac{1}{n_{OH^-}}\right)}{(Fa)^2\left(\frac{1}{\lambda_{Na^+}} + \frac{1}{\lambda_{OH^-}}\right)}$$

The values of those average diffusivities used in the model calculation are listed in Table 5-2.

Hikita et al (1972) proposed a model using a two-step instantaneous reaction which considered the following reactions to occur irreversibly as sulfur dioxide is absorbed into aqueous alkaline solutions

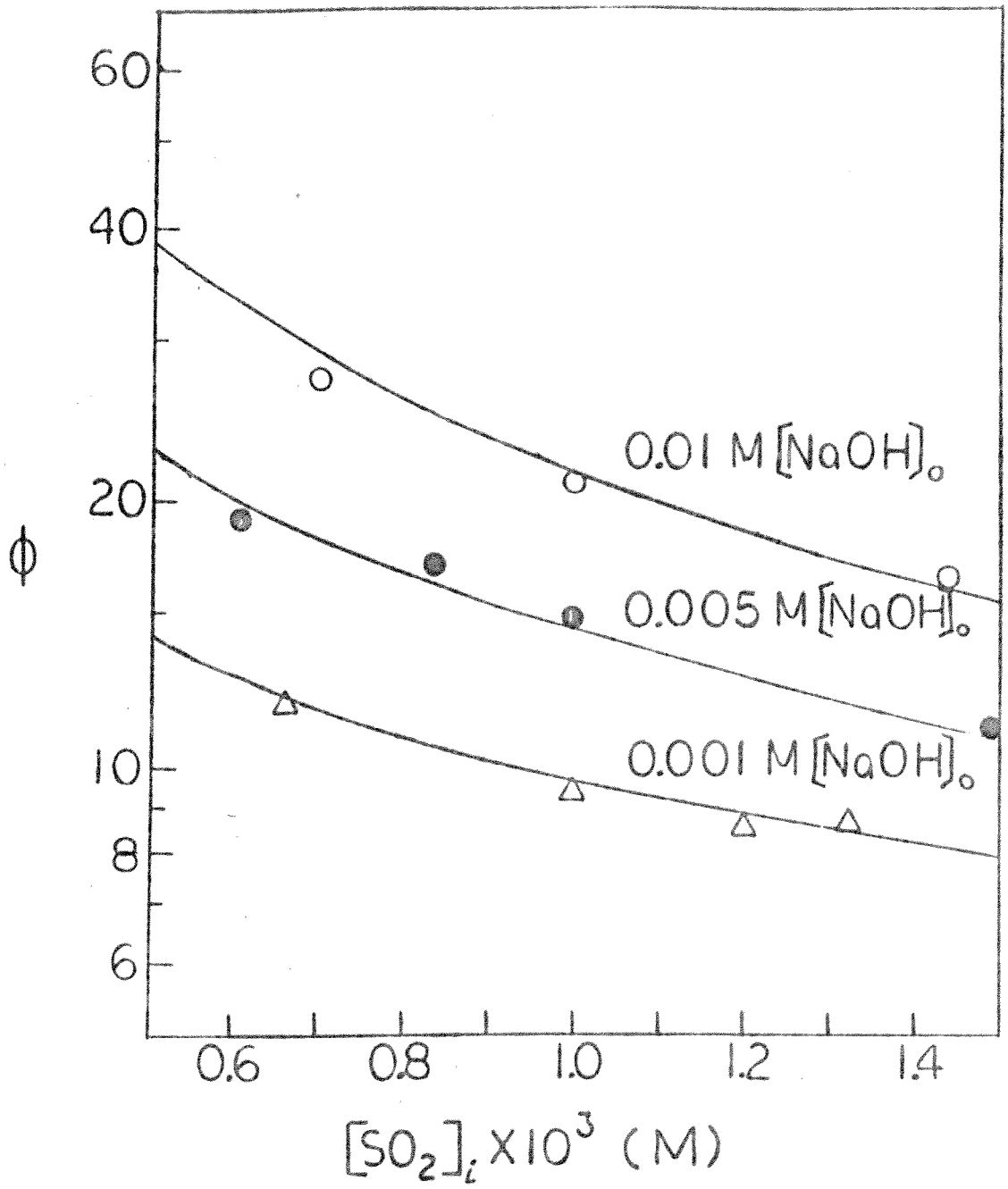

Figure 5-1. Comparison of surface renewal theory with experimental data for SO_2/N_2 - NaOH system at 25°C.

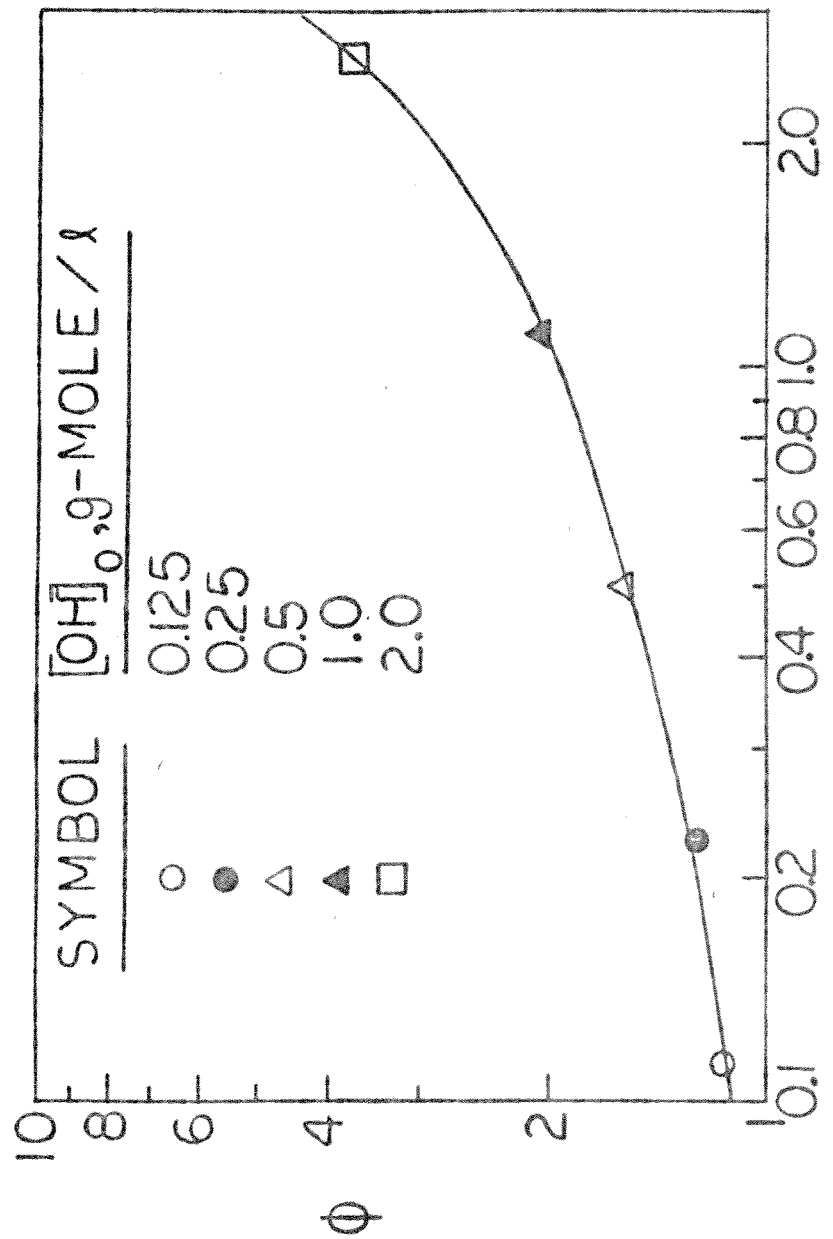

Figure 5-2. Comparison of approximate surface renewal theory with Hikita's data (1977) for pure SO_2 - NaOH solution.

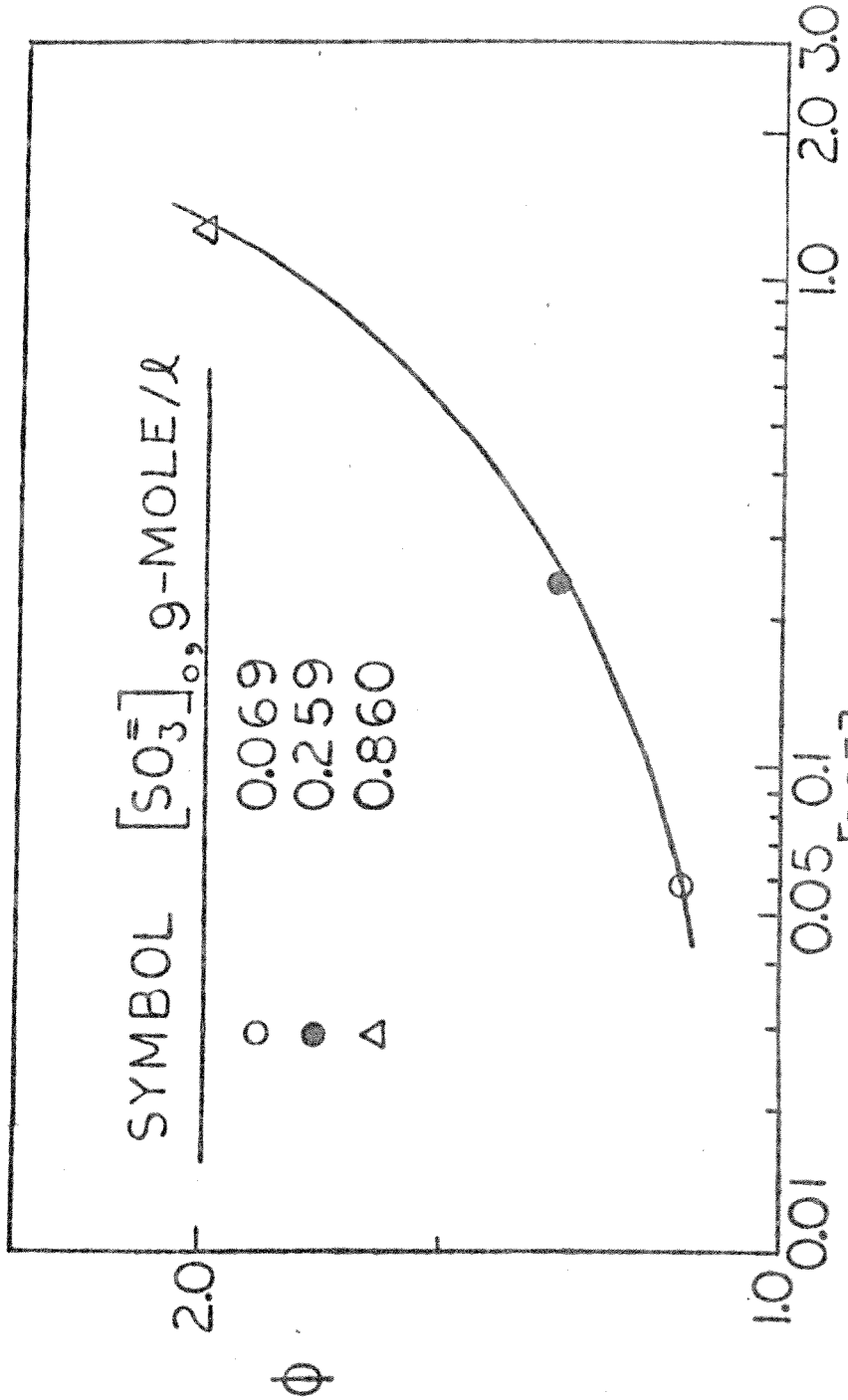

Figure 5-3. Comparison of approximate surface renewal theory with Hikita's data (1977) for pure SO_2 - Na_2SO_3 solution.

$$SO_2 + SO_3^{=} \rightarrow 2HSO_3^{-} \qquad (5\text{-}16)$$

$$HSO_3^{-} + OH^{-} \rightarrow SO_3^{-} + H_2O \qquad (5\text{-}17)$$

When only sulfite ion is present in significant amount in liquid bulk, reaction 5-17 is not important and only reaction 5-16 proceeds irreversibly at a single reaction plane. When hydroxide ion is the major alkaline species in liquid bulk, two reaction planes were formed within the liquid. Reaction 5-16 and reaction 5-17 take place irreversibly at the first and the second reaction planes, respectively.

The main differences between Hikita's model and the present model are the reversible feature of reaction 5-1 and the role of hydrogen ion in the absorption mechanism. The concentration profiles of impo important species predicted by the present reversible model are shown in Figures 5-4 and 5-5 for SO_2 - Na_2SO_3 and SO_2 - NaOH systems, respectively. It can be seen that when the SO_2 partial pressure in gas phase is high ($P_{SO_2} \gg$ 0.05 atm), the hydrogen ion concentration, relative to the concentrations of the other species, is negligible throughout the system. Therefore, the reversibility of reaction 5-1 is not important. But when SO_2 partial pressure in gas phase is much less than 0.05 atm, the hydrogen ion concentration is comparable to the concentrations of SO_2 and HSO_3^{-} near the gas-liquid interface. Therefore, the reversible SO_2 hydrolysis reaction has a significant effect on the sulfur dioxide absorption rate.

Figure 5-6 compares the mass transfer enhancement factors predicted for the SO_2 - $NaSO_3$ system by film theory with reversible

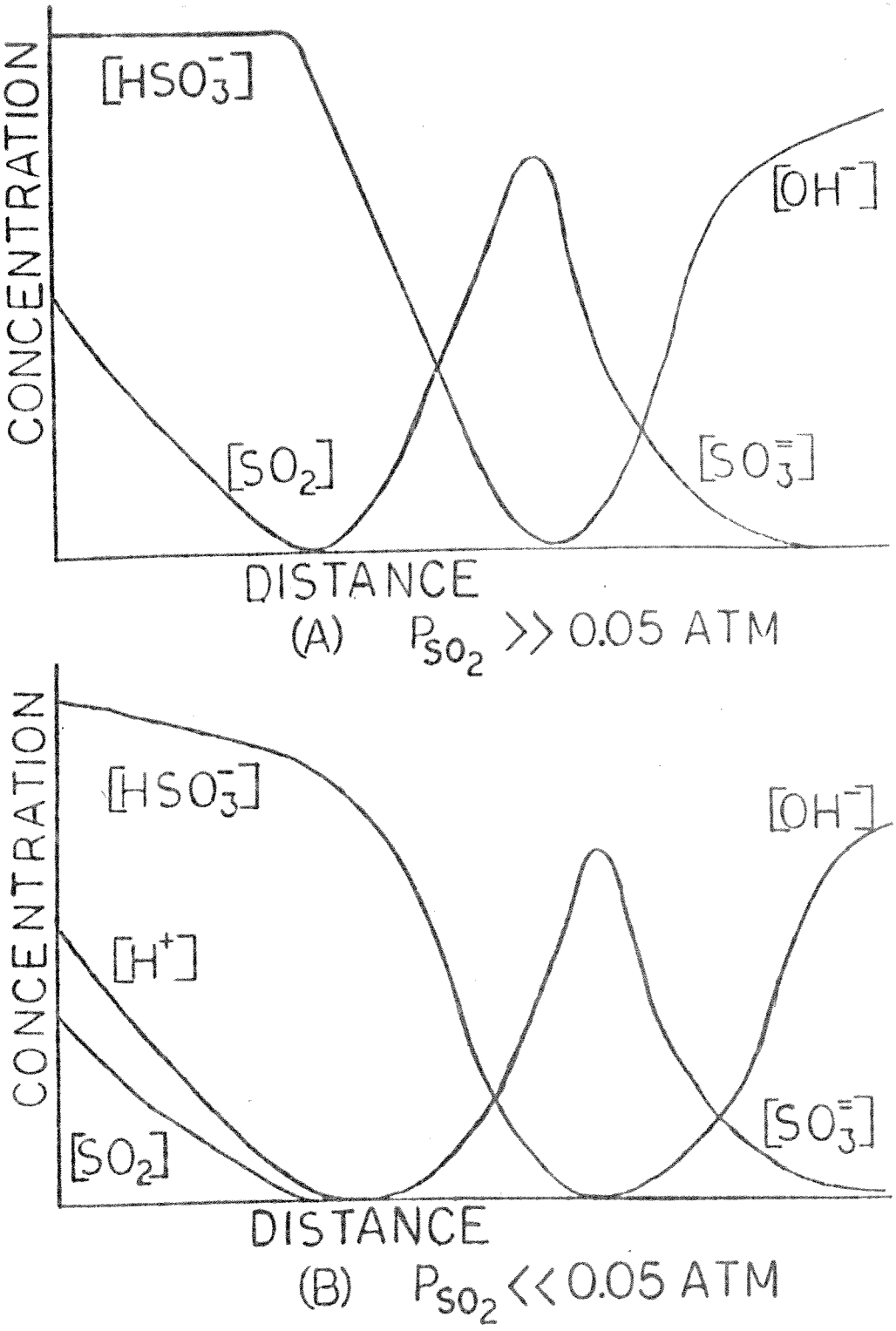

Figure 5-4. Schematic diagram of concentration profiles for the absorption of sulfur dioxide into aqueous sodium hydroxide solutions:

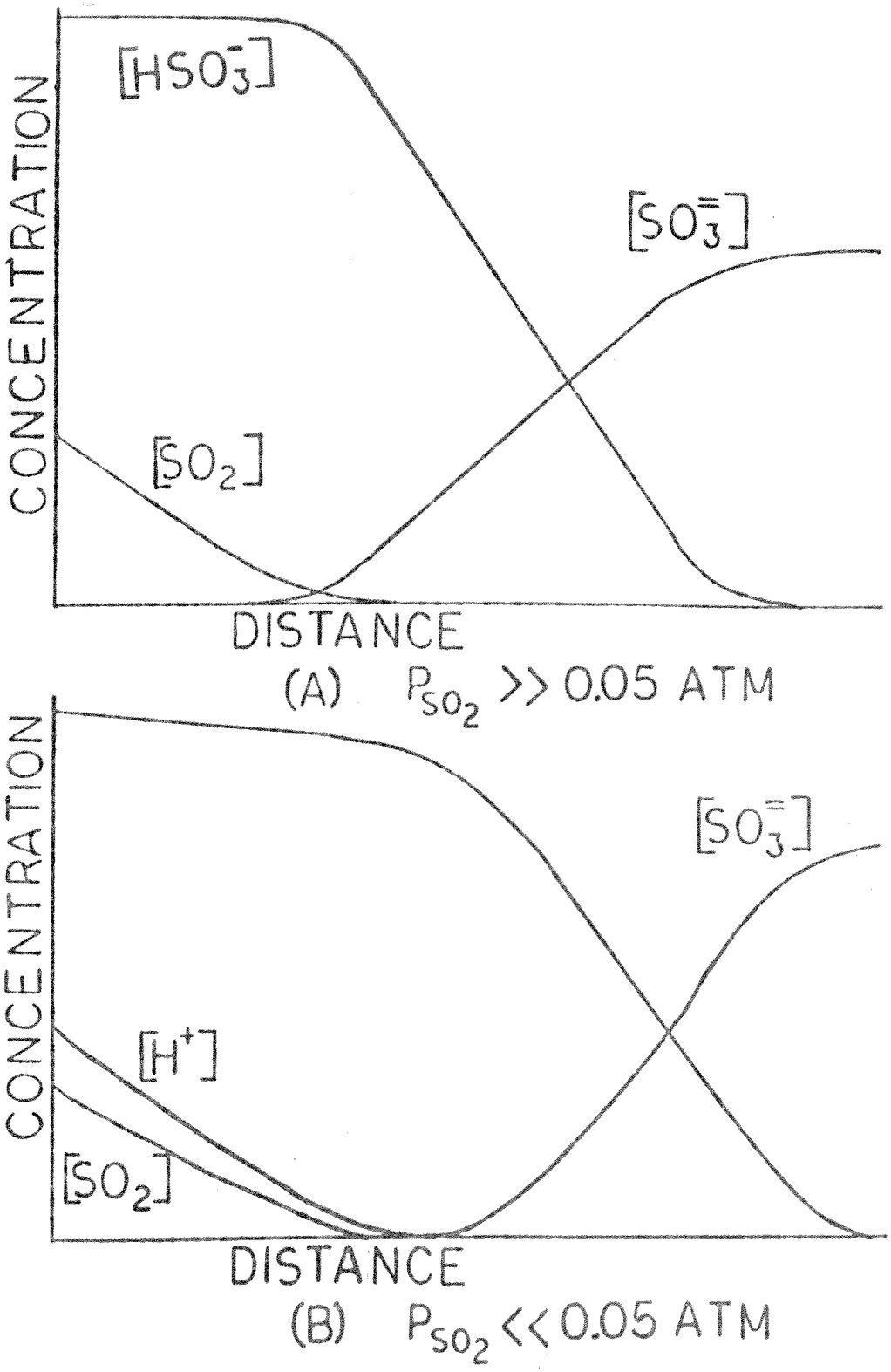

Figure 5-5. Schematic diagram of concentration profiles for the absorption of sulfur dioxide into aqueous sodium sulfite solutions:

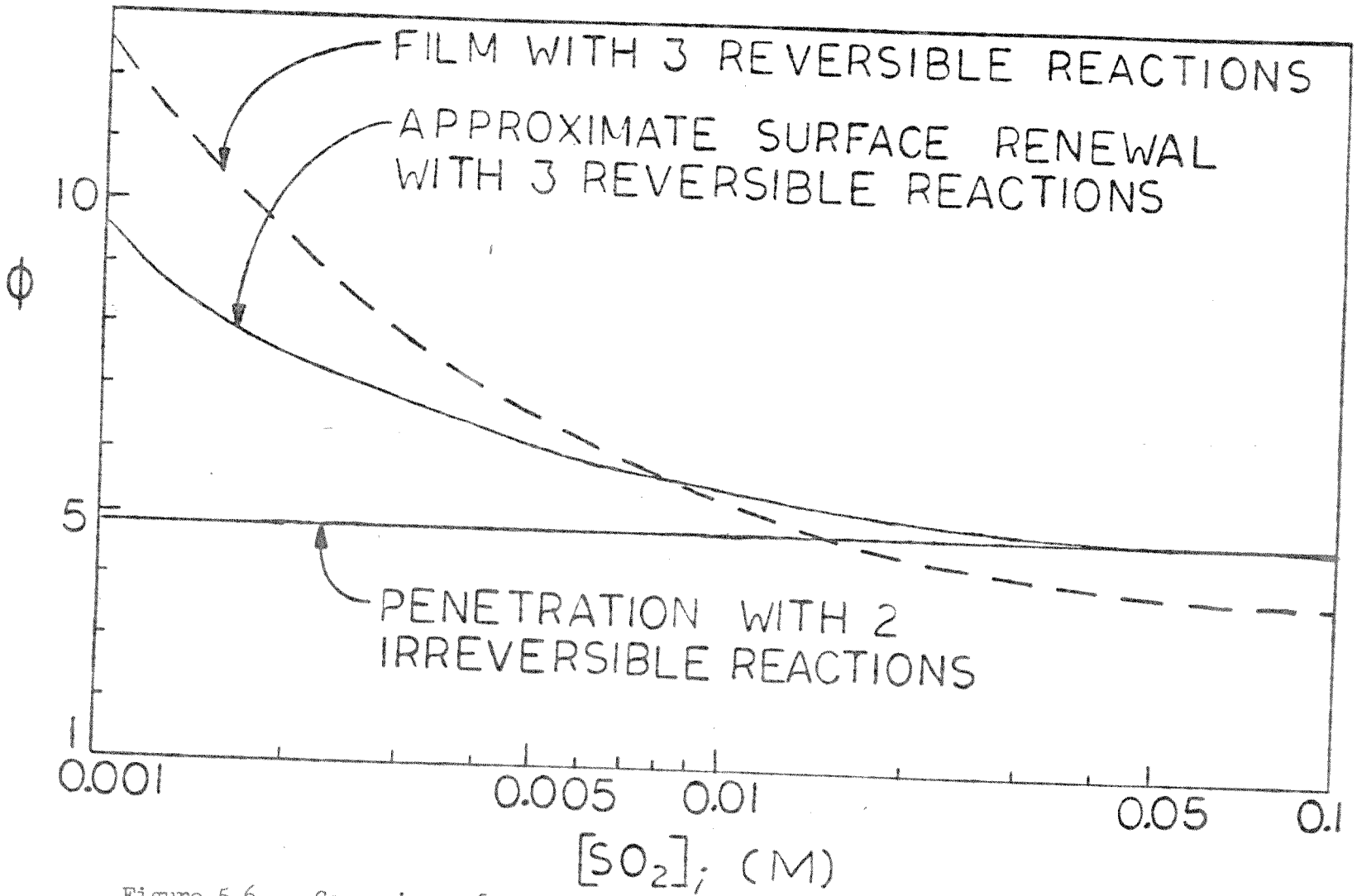

Figure 5-6. Comparison of mass transfer enhancement factors predicted from three different models for SO_2 - Na_2SO_3 system.

reactions 5-1, 5-2 and 5-3, by approximate surface renewal theory with reversible reactions 5-1, 5-2, and 5-3 and by penetration theory with irreversible reaction 5-16 and 5-17. With a constant ratio of $[SO_3^{=}]_o$ to $[SO_2]_i$, Hikita's irreversible model predicts a mass transfer enhancement factor which is independent of sulfur dioxide partial pressure. However, the present reversible model shows that the mass transfer enhancement factor increases with the decrease of gas phase SO_2 partial pressure. This is because the hydrolysis reaction 5-1 gradually becomes more important as the SO_2 partial pressure decreases. decreases.

Since the hydrogen ion diffusivity is much higher than that of dissolved sulfur dioxide, the film theory prediction of ϕ is higher than that of surface renewal theory at low SO_2 partial pressure where the diffusion of hydrogen ion has a significant effect on SO_2 absorption rate. However, when the SO_2 partial pressure is greater than 0.05 atm, the hydrogen ion is no longer important, and the major species which influence the SO_2 absorption rate are HSO_3^{-} and $SO_3^{=}$. Their diffusivities are both lower than that of absorbed SO_2. Therefore, the film theory prediction of ϕ is less than surface renewal theory at higher SO_2 partial pressure. These phenomena comply with the observation of Chang and Rochelle (1979a) on the effect of diffusivity ratios on mass transfer with general equilibrium reactions.

Figure 5-7 shows the comparison of experimental data with the predictions of the present reversible model and Hikita's irreversible model for the dilute SO_2 - NaOH system. The approximation solution

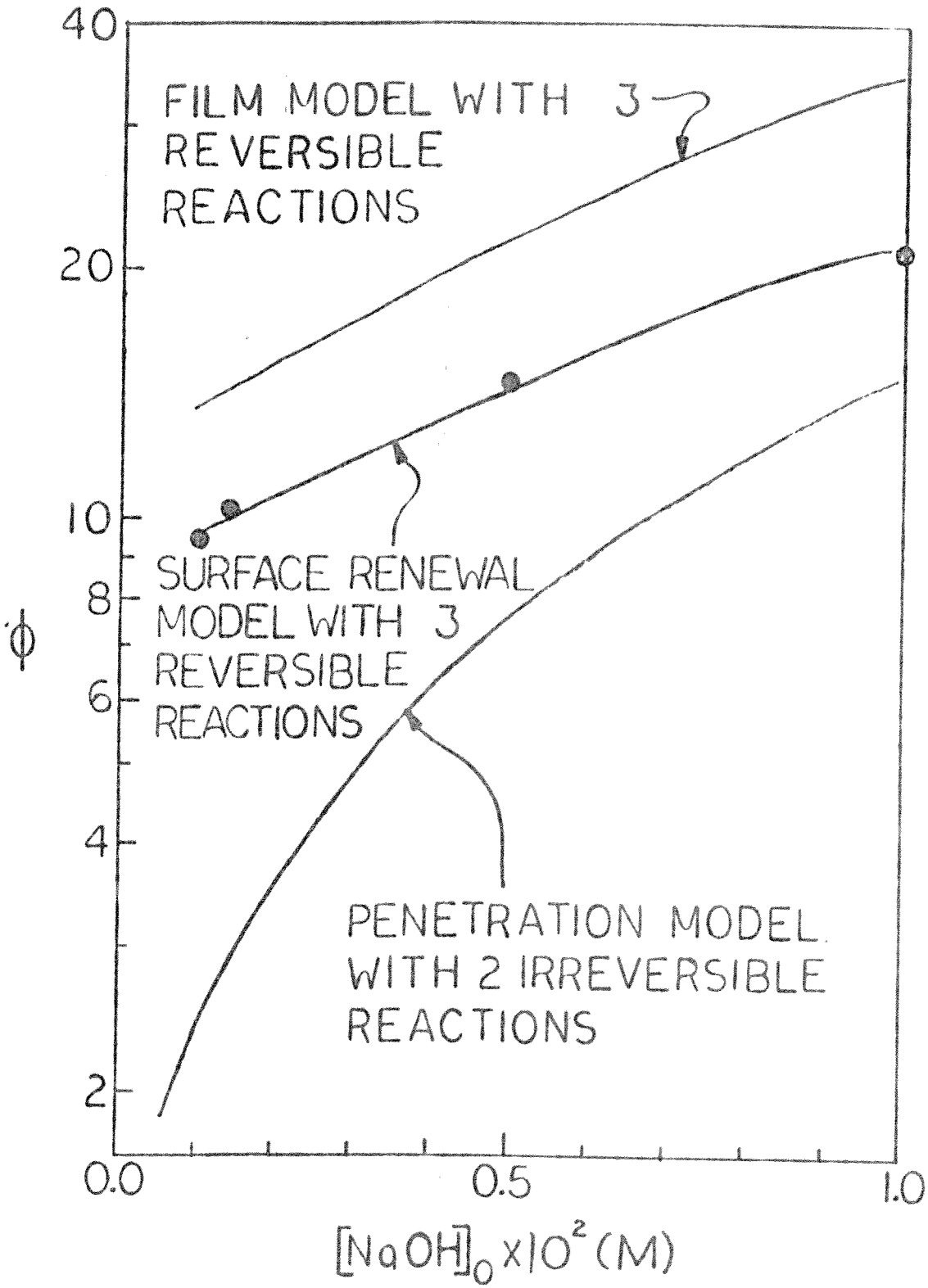

Figure 5-7. Comparison of mass transfer enhancement factors predicted from three different models for SO_2 - NaOH system.

of surface renewal theory with multiple instantaneous reversible rea reactions fits the data well. The difference between the reversible model and Hikita's irreversible model represents the effect of reversible SO_2 hydrolysis reaction on the absorption rate.

Notation

a	=	component activity, g-mole/liter
C_{3j}, C_{4j}	=	parameter in Eq. (13)
D	=	diffusivity of component, cm^2/sec
$D_{\pm}$	=	effective diffusivity defined by Eq. (15), cm^2/sec
Fa	=	Faraday = 96488 columbs/g-equivalent
I	=	ionic strength, g-mole/liter
K_a	=	thermodynamic equilibrium constant
K_c	=	effective equilibrium constant in concentration units
$k_L^o a$	=	liquid phase mass transfer coefficient, liter/sec
N_{SO_2}	=	absorption rate, g-mole/sec
n	=	valence
P_{SO_2}	=	SO_2 partial pressure, atm
R	=	gas constant = 8.315 $J/^oK$-g-mole
T	=	temperature, ^oK
t	=	time, sec
x	=	distance, cm
ϕ_a	=	mass transfer enhancement factor obtained from approximation method
γ	=	activity coefficient
$\lambda_{\pm}$	=	equivalent ion conductance, cm^2/g-mole/ohm
δ	=	film thickness, cm
[ ]	=	concentration, g-mole/liter

Subscript

1, 2, 3	=	reaction (1), (2), and (3)
i	=	concentration at gas-liquid interface
j	=	component j
o	=	concentration in bulk liquid

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Chapter 6

EFFECT OF ORGANIC ACID ADDITIVES ON SO_2 ABSORPTION INTO $CaO/CaCO_3$ SLURRIES

Abstract

The absorption rate of sulfur dioxide from a gas mixture of SO_2 and N_2 into aqueous acetic acid and adipic acid solutions at pH 4 to 6 has been measured at 25°C in a continuous stirred vessel with an unbroken gas-liquid interface. Experimental data are interpreted by approximate surface renewal theory with multiple equilibrium reactions.

The model of gas/liquid mass transfer with simultaneous equilibrium reactions is further applied to the absorption of SO_2 from waste gases into lime or limestone slurries with the following objectives:

1. to describe the SO_2 absorption mechanism in scrubbers.
2. to model novel processes such as intentional oxidation and buffer additives.
3. to evaluate the effectiveness of eleven organic-acid buffer additives.

Scope

SO_2 absorption from waste gases by lime/limestone slurries is frequently limited by liquid-phase mass transfer resistance.

Experimental results have shown that buffer additives such as organic acids can effectively enhance the mass transfer rate (Hatfield and Potts, 1971, Hatfield et al, 1972, Hollinden et al, 1974, Wasag et al, 1975, Borgwardt, 1977, Bechtel, 1979). Several investigators (Rochelle and King, 1977, Cavanaugh, 1978) have extensively evaluated the available carboxylic acids on the basis of cost, buffer capacity, solubility, and other factors. The combined use of buffer additives and forced oxidation have been tested as a means of dewatering waste solids more easily, thereby minimizing loss of the soluble additive (Rochelle and King, 1978, Head, 1979). In this paper, a mass transfer model is developed for the SO_2 absorption with or without buffer additives and forced oxidation.

Film theory mass transfer with equilibrium reactions was first discussed by Olander (1960). Danckwerts (1968) proposed a simple physical mass transfer concept for equal diffusivity systems. Chang and Rochelle (1979a, 1979b) studied the equilibrium reaction effect on mass transfer rate by surface renewal theory with unequal diffusivities. This mass transfer model is suitable for SO_2 absorption processes because the dissolved SO_2 is hydrolyzed instantaneously and reversibly. Chang and Rochelle (1979c, 1979d) have employed the model to interpret experimental data of SO_2 absorption into pure water and several other aqueous solutions.

The major objective of this work is to use surface renewal theory with equilibrium reactions to model the SO_2 absorption by aqueous solutions buffered with organic acids. Experimental data are presented with adipic acid and acetic acid solutions for 25°C, 0.5 M NaCl, and pH 4.5 to 5.5. The mass transfer model will be further employed to evaluate appropriate buffer additives under SO_2 scrubbing conditions at 55°C with 0.1 M $CaCl_2$. The amount of adipic acid needed for a typical SO_2 scrubber will be estimated.

Conclusions

1. The absorption rate of SO_2 into buffered solutions of acetic or adipic acid can be modeled by approximate surface renewal theory with multiple equilibrium chemical reactions.
2. Forced oxidation in the scrubber loop results in better SO_2 removal because the SO_2 hydrolysis reaction contributes more to mass transfer enhancement in the absence of bisulfite.
3. Adipic, sulfopropionic, sulfosuccinic and β-hydroxypropionic acids are the most promising buffer additives for lime/limestone slurry scrubbing of SO_2 from flue gas. Formic acid and acetic acid are nominally the least expensive buffer additives. However, losses by volatilization in the scrubber may be economically and environmentally significant.
4. 10 to 20 mM adipic acid should be adequate to provide most of the benefit from buffer additives on mass transfer enhancement for a typical lime/limestone slurry scrubber for stack gas

desulfurization with high-sulfur coal.

Chemical absorption mechanism

When sulfur dioxide is absorbed into aqueous solution of difunctional buffer like adipic acid in the pH range from 4 to 7, the following four reactions should be considered:

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^- \qquad (6\text{-}1)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^= \qquad (6\text{-}2)$$

$$H_2Ad \rightleftharpoons H^+ + HAd^- \qquad (6\text{-}3)$$

$$HAd^- \rightleftharpoons H^+ + Ad^= \qquad (6\text{-}4)$$

where H_2Ad represents adipic acid and HAd^-, $Ad^=$ its ions. The first reaction corresponds to the hydrolysis of absorbed SO_2. Its forward reaction rate constant was estimated to be 3.4×10^6 sec^{-1} (Eigen et al, 1961) at 20°C. Reactions 6-2, 6-3 and 6-4 are proton transfer reactions and have much higher reaction rates than that of reaction 6-1. Therefore, all four reactions can be regarded as instantaneous.

The values of the equilibrium constants, K_1, K_2, K_3 and K_4 of reactions 6-1, 6-2, 6-3 and 6-4, respectively, are:

$$K_1 = \frac{a_{H^+}\, a_{HSO_3^-}}{a_{SO_2}} = 1.3 \times 10^{-2}$$ (Johnstone and Leppla, 1934)

$$K_2 = \frac{a_{H^+}\, a_{SO_3^=}}{a_{HSO_3^-}} = 6.2 \times 10^{-8}$$ (Tartar and Garretson, 1941)

$$K_3 = \frac{a_{H^+}\, a_{HAd^-}}{a_{H_2Ad}} = 3.82 \times 10^{-5}$$ (Gane and Ingold, 1931)

$$K_4 = \frac{a_{H^+}\, a_{Ad^=}}{a_{HAd^-}} = 3.87 \times 10^{-6}$$ (Gane and Ingold, 1931)

at 25°C and infinite dilution. Under typical conditions of CaO/$CaCO_3$ slurry scrubbing reaction 1 must be treated as a reversible reaction. Therefore, SO_2 absorption becomes a process of simultaneous mass transfer with multiple equilibrium reactions.

According to surface renewal theory , the total componenent material balance gives:

For SO_2 species:

$$D_{SO_2}\frac{\partial^2[SO_2]}{\partial x^2} + D_{H^+}\frac{\partial^2[H^+]}{\partial x^2} - D_{SO_3^=}\frac{\partial^2[SO_3^=]}{\partial x^2} - D_{Ad^=}\frac{\partial^2[Ad^=]}{\partial x^2} + D_{H_2Ad}\frac{\partial^2[H_2Ad]}{\partial x^2} = \frac{\partial[SO_2]}{\partial t} + \frac{\partial[H^+]}{\partial t} - \frac{\partial[SO_3^=]}{\partial t} - \frac{\partial[Ad^=]}{\partial t} + \frac{\partial[H_2Ad]}{\partial t} \qquad (6\text{-}5)$$

For H^+ species:

$$D_{H^+}\frac{\partial^2[H^+]}{\partial x^2} - D_{HSO_3^-}\frac{\partial^2[HSO_3^-]}{\partial x^2} - 2D_{SO_3^=}\frac{\partial^2[SO_3^=]}{\partial x^2} + D_{H_2Ad}\frac{\partial^2[H_2Ad]}{\partial x^2} - D_{Ad^=}\frac{\partial^2[Ad^=]}{\partial x^2} = \frac{\partial[H^+]}{\partial t} - \frac{\partial[HSO_3^-]}{\partial t} - 2\frac{\partial[SO_3^=]}{\partial t} + \frac{\partial[H_2Ad]}{\partial t} -$$

$$\frac{\partial [Ad^{=}]}{\partial t} \qquad (6\text{-}6)$$

For H_2Ad species:

$$D_{H_2Ad}\frac{\partial^2[H_2Ad]}{\partial x^2} + D_{HAd^-}\frac{\partial^2[HAd^-]}{\partial x^2} + D_{Ad^=}\frac{\partial^2[Ad^{=}]}{\partial x^2} = \frac{\partial[H_2Ad]}{\partial t} + \frac{\partial[HAd^-]}{\partial t} + \frac{\partial[Ad^{=}]}{\partial t} \qquad (6\text{-}7)$$

Furthermore, the chemical equilibrium relations of reactions 6-1, 6-2, 6-3 and 6-4 are effective at every point in the liquid phase. Three non-linear second order partial differential equations with three unknowns can be obtained by substituting the equilibrium relations into Equations 6-5, 6-6 and 6-7. There is no analytical solution for this set of equations, however, an approximate analytical solution can be obtained by replacing the diffusivity ratios in the solution of film theory by their square roots (Chang and Rochelle, 1979a, 1979b). The general solutions of the film theory material balance equations are:

$$D_{SO_2}[SO_2] + D_{H^+}[H^+] - D_{SO_3^=}[SO_3^{=}] - D_{Ad^=}[Ad^{=}] + D_{H_2Ad}[H_2Ad] = b_1x + b_2 \qquad (6\text{-}8)$$

$$D_{H^+}[H^+] - D_{HSO_3^-}[HSO_3^-] - 2D_{SO_3^=}[SO_3^{=}] + D_{H_2Ad}[H_2Ad] - D_{Ad^=}[Ad^{=}] = b_3x + b_4 \qquad (6\text{-}9)$$

$$D_{H_2Ad}[H_2Ad] + D_{HAd^-}[HAd^-] + D_{Ad^=}[Ad^=] = b_5x + b_6 \qquad (6\text{-}10)$$

All the concentrations are subject to the equilibrium relations of reactions 6-1, 6-2, 6-3 and 6-4. The boundary conditions are:

$$\text{at } x = 0,\ [SO_2] = [SO_2]_i$$

$$D_{H^+}\frac{d[H^+]}{dx} - D_{HSO_3^-}\frac{d[HSO_3^-]}{dx} - 2D_{SO_3^=}\frac{d[SO_3^=]}{dx} + D_{H_2Ad}\frac{d[H_2Ad]}{dx} - D_{Ad^=}\frac{d[Ad^=]}{dx} = 0$$

$$D_{H_2Ad}\frac{d[H_2Ad]}{dx} + D_{HAd^-}\frac{d[HAd^-]}{dx} + D_{Ad^=}\frac{d[Ad^=]}{dx} = 0$$

$$\text{at } x = \delta,\ [SO_2] = [SO_2]_o,\ [H^+] = [H^+]_o,\ [H_2Ad] = [H_2Ad]_o$$

where $[SO_2]_i$ represents the physical solubility of SO_2. The other two differential equations reflect the inability of other species to penetrate through the gas-liquid interface.

The approximate surface renewal theory mass transfer enhancement factor ϕ can be written as:

$$\phi = 1 + D_{H^+}([H^+]_i - [H^+]_o) - D_{SO_3^=}([SO_3^=]_i - [SO_3^=]_o) - D_{Ad^=}([Ad^=]_i - [Ad^=]_o) + D_{H_2Ad}([H_2Ad]_i - [H_2Ad]_o) / D_{SO_2}([SO_2]_i - [SO_2]_o) \quad (6\text{-}11)$$

The values of all the concentrations at the gas-liquid interface can be estimated by numerical solution of a fifth order algebraic equation derived from Equations 6-8, 6-9 and 6-10 and their boundary conditions with all the diffusivity ratios replaced by their square roots.

This mass transfer model can also be employed with other buffers by the substitution of appropriate equilibrium constants and diffusivities. With monofunctional buffers like acetic acid, the mass transfer enhancement factor can be obtained by using the single buffer K_a value for K_3 and a dummy value for K_4 outside the range of 10^{-4} to 10^{-7}, such as 10^{-13}. The value of K_3 used in the model calculation is 1.75×10^{-5} at 25°C (MacInnes and Sedlovsky, 1932) for acetic acid.

Experimental

Apparatus and procedures

The experiments of the absorption of sulfur dioxide by aqueous acetic acid and adipic acid solutions were carried out in an agitated vessel with a plain gas-liquid interface, as used by

Chang and Rochelle (1979c, 1979d) in previous works. The absorber has continuous flow with respect to both gas and liquid phases, enabling steady-state operation. The physical gas and liquid phase mass transfer coefficients were measured by Chang and Rochelle (1979c) as a function of stirrer rate. The stirrer speed for all runs was kept at 300 rpm.

Sulfur dioxide was diluted by nitrogen and fed into the stirred vessel at a constant flow rate. An appropriate amount of sodium chloride was added to the aqueous solutions to disperse the effect of electrical potential gradient on the diffusivities of ionic species. All the runs were performed at about atmospheric pressure and 25±1°C.

The sulfur dioxide partial pressure of the outlet gas stream was measured by a pulsed fluorescent SO_2 analyzer. (Thermoelectron model 40). The hydrogen ion activity of the outlet liquid stream was measured by a pH meter. Solution samples were collected after the system reached steady state. The absorbed sulfur dioxide was oxidized into sulfate species by the addition of 30% hydrogen peroxide solution to liquid sample. An ion chromatograph was used to analyze the total sulfate concentration. The sulfur dioxide absorption rate was calculated from the liquid phase material balance.

Physical properties

The concentration of molecular sulfur dioxide at the gas-liquid interface was obtained from the following equation given by Rabe and Harris (1963):

$$[SO_2]_i = P_{SO_2,i} \exp(2851.1/T - 9.3795) \qquad (6\text{-}12)$$

Since all the equilibrium constants are in thermodynamic units, appropriate activity coefficients must be incorporated with the concentration of each component to estimate the effective equilibrium constant in concentration units. For example,

$$K_{c,1} = K_1 \cdot \frac{\gamma_{SO_2}}{\gamma_{H^+} \gamma_{HSO_3^-}} \qquad (6\text{-}13)$$

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

$$\log \gamma_j = 0.512 n_j^2 \left[\frac{-I^{1/2}}{1 + 0.312\, C_{3j}\, I^{1/2}} + C_{4j}\, I \right] \qquad (6\text{-}14)$$

where n_j is the charge on the jth ion, I represents the ionic strength, C_{3j} and C_{4j} are the characteristic parameters for each ion species. The values of those two parameters for H^+, HSO_3^- and $SO_3^=$ were listed in a previous paper (Chang and Rochelle, 1979d). 3.0 and 0.3 were the values used for C_{3j} and C_{4j}, respectively, for all other charged species. The activity coefficients of hydrated sulfur dioxide, acetic acid and adipic acid in solutions were estimated by (Harned and Owen, 1958)

$$\log \gamma = 0.076\ I \qquad (6\text{-}15)$$

The liquid phase diffusivity, D_{SO_2}, of sulfur dioxide in water was taken as $2.00 \times 10^{-5} cm^2/sec$ at 30^oC (Peaceman, 1951). The value of D_{SO_2} at 25^oC was predicted by correcting for the temperature and viscosity of water according to Stokes-Einstein relation. All experimental runs were made with 0.5 M NaCl solutions to disperse the effect of electrical potential gradient on the diffusion of ionic species (Chang and Rochelle, 1979c). Therefore, the effective diffusivities of all the ionic species were assumed to be equal to their true diffusivities, as calculated from equivalent ionic conductivities by

$$D_{\pm} = \frac{RT\lambda_{\pm}}{n_j (Fa)^2} \qquad (6\text{-}16)$$

where Fa is the Faraday number and $\lambda^o_{\pm}$ the equivalent ionic conductivity. The values of $\lambda^o_{\pm}$ for H^+, HSO_3^-, $SO_3^=$ and Ac^- at 25^oC and infinite dilution are 350, 50, 72 and 40.9 cm^2/mole-ohm, respectively (Landolt - Bornstein, 1960).

The value of acetic acid diffusivity in water at 25^oC was taken as 1.19 cm^2/sec (Lewis, 1955). The diffusivities of adipic acid and adipate ion in water at 25^oC was reported to be 0.736 and 0.705 cm^2/sec, respectively (Albery et al, 1967, Jeffery and Vogel, 1935). Since those two values are very close to each other, the diffusivity of HAd^- was taken to be their arithmetic mean.

Experimental results

According to interphase mass transfer theory:

$$N = k_g a\,(P_{SO_2} - P_{SO_{2i}}) = k_L^o a \phi ([SO_2]_i - [SO_2]_o) \qquad (6\text{-}17)$$

Therefore, experimental values of ϕ can be obtained from the measurement of SO_2 absorption rate. Figures 6-1 and 6-2 show the experimental results for acetic acid and adipic acid systems, respectively. The data are in good agreement with the theoretical predictions shown by curves.

Model for slurry scrubbing conditions

Typical conditions in a CaO/CaCO3 slurry scrubber are listed in Table 6-1. In order to evalute the effectiveness of organic acids as buffer additives, the present mass transfer model was modified to include the effects of 0.1 M $CaCl_2$ (rather than 0.5 M NaCl) and higher temperature (55°C).

The presence of dissolved Ca results in formation of the calcium sulfite ion pair:

$$Ca^{++} + SO_3^{=} \rightleftharpoons CaSO_3^{\,o} \qquad (6\text{-}18)$$

$$K_{CaSO_3^{\,o}} = \frac{a_{CaSO_3^{\,o}}}{a_{Ca^{++}}\, a_{SO_3^{=}}}$$

$CaSO_3^{\,o}$ can react with dissolved SO_2 and acts like sulfite ion. Therefore, if $CaSO_3^{\,o}$ is assumed to have the same diffusivity as $SO_3^{=}$, a modified equilibrium constant of reaction 2 can be used to account for $CaSO_3^{\,o}$ in the presence of excess Ca^{++}.

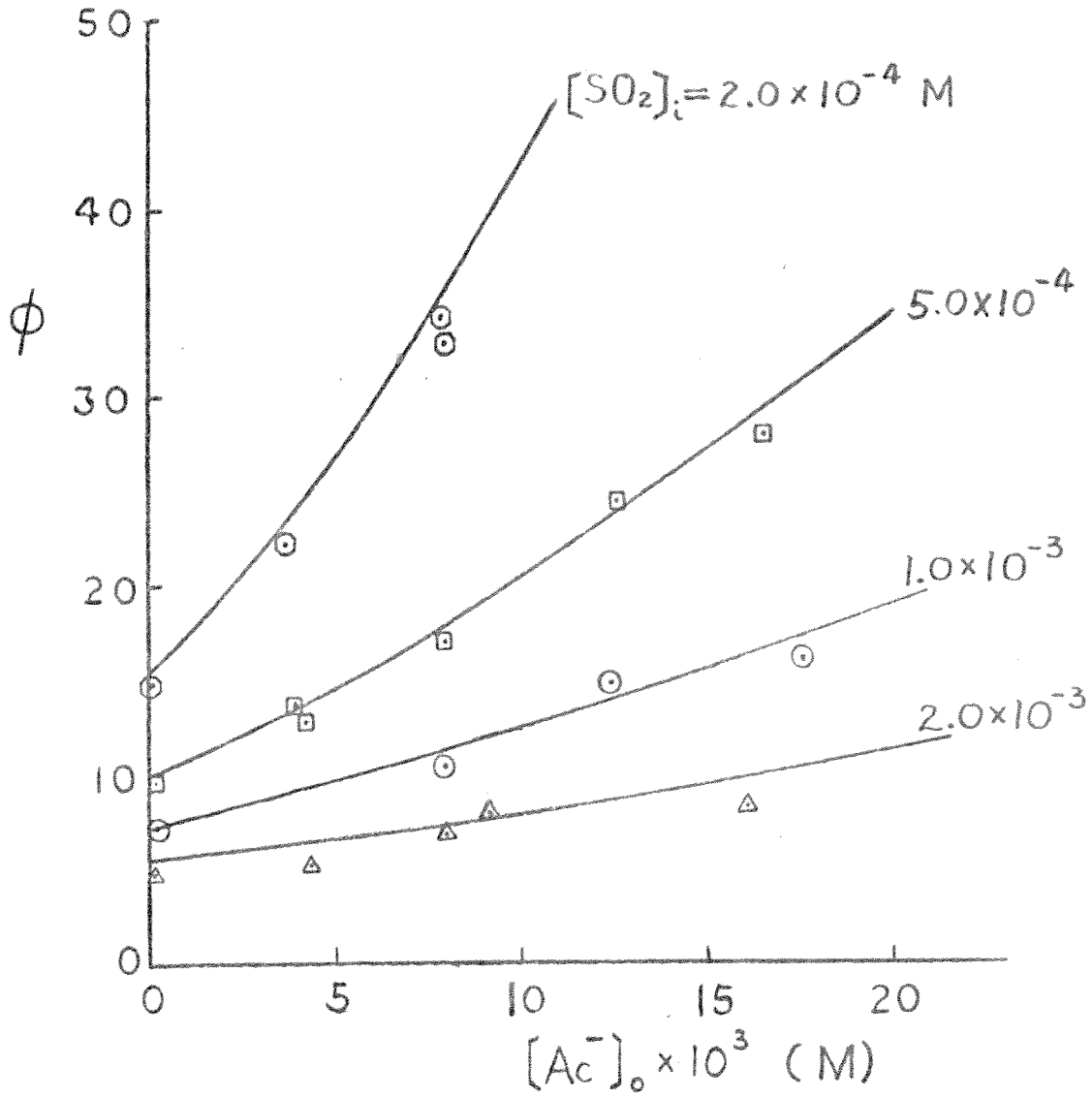

Figure 6-1. Mass transfer enhancement factor with acetic acid, 25°C, 0.5 M NaCl, pH 4 to 6.

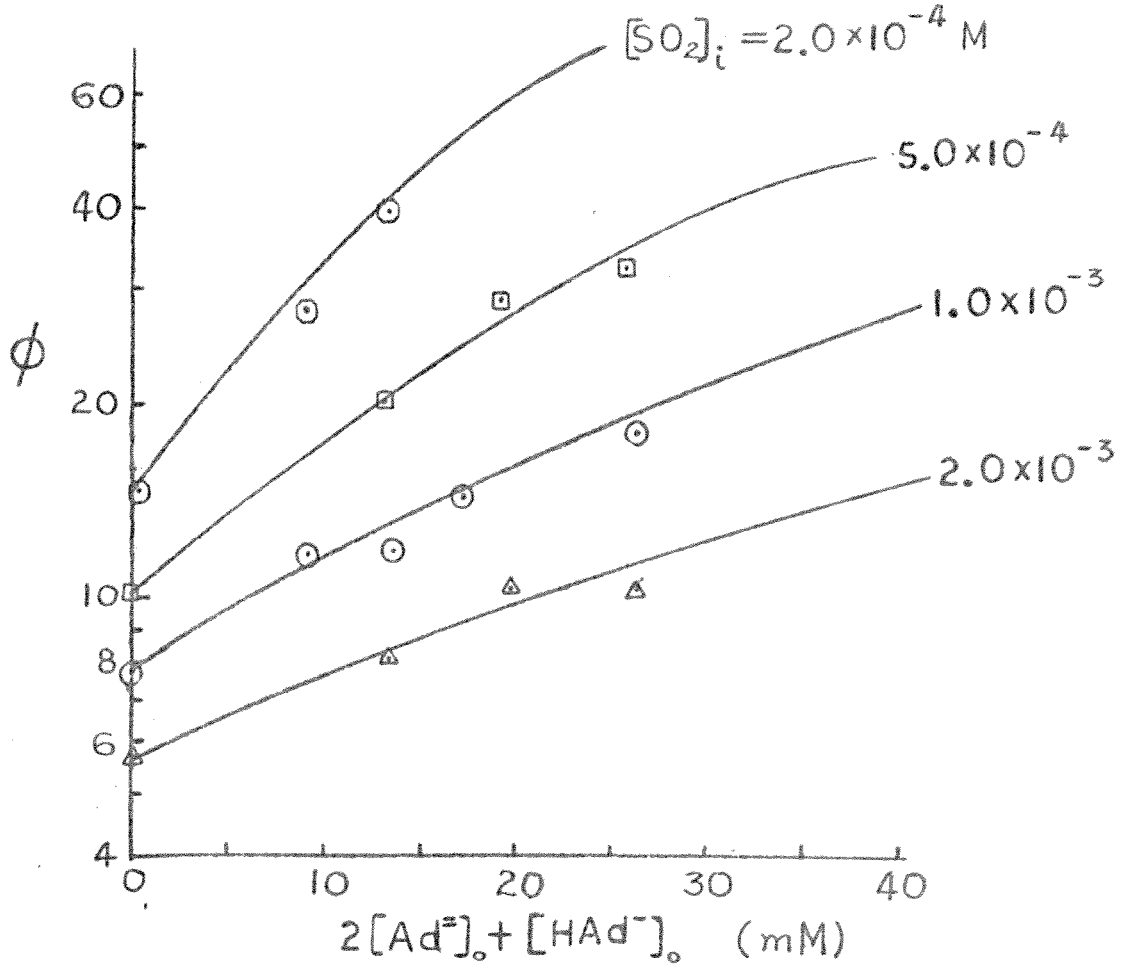

Figure 6-2. Mass transfer enhancement factor with adipic acid, 25°C, 0.5 M NaCl, pH 4 to 6.

Table 6-1. Typical conditions in $CaO/CaCO_3$ slurry scrubber.

Temperature	55°C
$P_{SO_2,in}$	0.005 to 0.0005 atm.
$P_{SO_2,out}$	0.0002 to 0.00002 atm.
pH	4.5 to 5.5
Total dissolved sulfite	0 to 20 mM
Total dissolved calcium	0.05 to 0.2 M

$$K_2' = \frac{a_{H^+} \, a'_{SO_3^=}}{a_{HSO_3^-}} \qquad (6\text{-}19)$$

where $a'_{SO_3^=} = a_{SO_3^=} (1 + a_{Ca^{++}} K_{CaSO_3^o})$

The value of $K'_{c,2}$ at 55°C in 0.1 M $CaCl_2$ was estimated to be 2.02×10^{-6} g-mole/liter (Lowell et al, 1970).

Higher temperature is accounted for by changes and appropriate assumptions for equilibrium constants, activity coefficients and diffusivities. The diffusity ratios and effective equilibrium constants were assumed to be independent of temperature. Minor modifications were made in the computation of activity coefficients for $K_{c,1}$ and $K_{c,2}$ by the method of Lowell et al (1970).

Optimum pK_c of buffer additives

To be effective for mass transfer enhancement, additives should buffer between the pH of the gas/liquid interface and the pH of the bulk liquid. Figure 6-3 shows the optimum pK_c values for a hypothetical monofunctional buffer as predicted by the modified mass transfer model (55°C, 0.1 M $CaCl_2$) for a wide range of scrubber conditions. The optimum pK_c values are very nearly equal to the average of the pH values at the gas/liquid interface and in the bulk liquid.

The pH at the gas/liquid interface is primarily a function of SO_2 gas concentration, but also varies with total dissolved sulfite and buffer concentration. In a typical absorber calculated

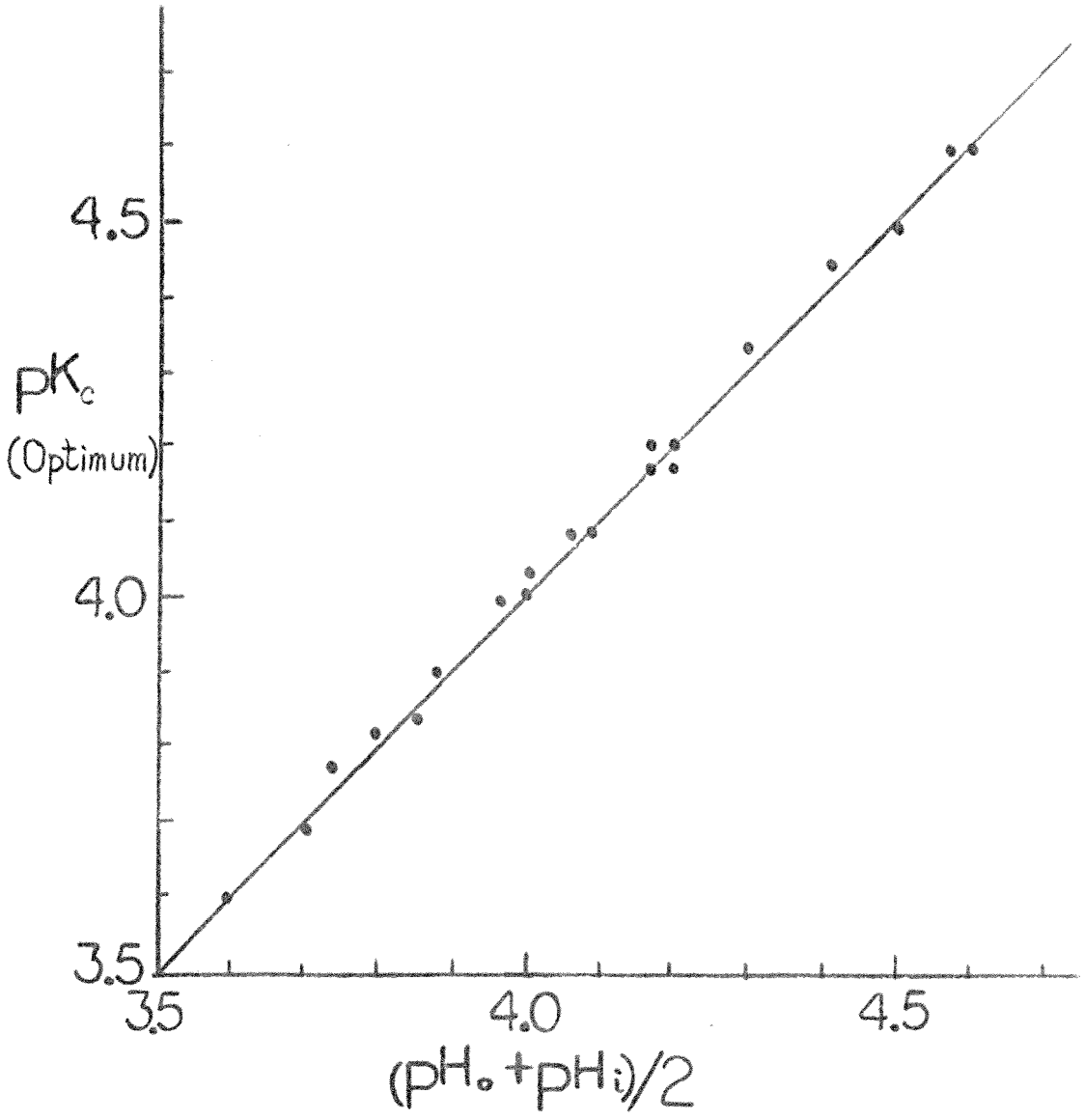

Figure 6-3. Optimum pK_c values for monofunctional buffer.

values of pH at interface decrease from 4.0 in the top of the absorber to 3.0 in the bottom. At more extreme conditions interface pH can be as low as 2.0 or as high as 4.5. Bulk solution pH is typically 4.5 to 5.5. Therefore, the optimum pK_c value of a monofunctional buffer should lie between 3.5 and 4.5. Polyfunctional buffers should also have pK_c values near 3.5 to 4.5 for maximum effectiveness. In concentrated solutions such as 0.1 M $CaCl_2$ pK_c values will be 0.3 to 0.6 units less the true pK_a values.

Evaluation of buffer additives

Eleven buffer additives with appropriate pK_c values have been assessed by the modified mass transfer model. The diffusivities and pK_c values are listed in Table 6-2. For some buffers, the diffusivities were estimated by the following equation for carboxylic acids (Albery, 1967).

$$\log D = -(4.04 + 0.49 \log V') \qquad (6\text{-}20)$$

where V' is the molecular volume of the organic acid estimated by the method of Le Bas (1915). The carboxylic ions were assumed to have the same diffusivities as their molecules. In several cases pK_c values were measured by Cavanaugh (1978) by acid-base titration in 0.1 M $CaCl_2$ at 25°C.

The relative effectiveness and costs of eleven organic acids are given in Table 6-3. Adipic acid was taken as the basis of comparison. The modified mass transfer model was used to determine the buffer concentration required to give an enhancement factor of 20. Sulfopropionic, β-hydroxypropionic,

Table 6-2. Physical properties of organic acid additives at 25°C.

Organic acid	Diffusivity x 10^5 (cm^2/sec) acid species	basic species	pK$_c$	
Formic acid	1.46	1.433	3.45	--
Acetic acid	1.19	1.09	4.45	--
Benzoic acid	1.21	0.862	3.9_b	--
Glycolic acid	0.98	--	3.424_b	--
Lactic acid	0.987_a	--	3.36_b	--
Sulfopropionic acid	0.82_a	--	4.06_b	--
β-hydroxypropionic acid	0.987_a	--	4.26_b	--
Phthalic acid	0.717_a	0.692	2.82_b	4.4_b
Succinic acid	0.86	0.812	3.98	4.6
Sulfosuccinic acid	0.731	--	3.1_b	4.4_b
Adipic acid	0.736	0.705	3.98_b	4.86_b

*(a) estimated values

*(b) measured by Cavanaugh(1978)

*(c) effective pK values in 0.1 M $CaCl_2$

Table 6-3. Organic acid additive costs

Basis: $\phi = 20$

$55^{\circ}C$, pH = 5.0, $C_{CaCl_2} = 0.1$ M

$C_{SO_{2i}} = 0.5$ mM, $C_{SO_{3T}^{=}} = 10$ mM

Organic acid	Concentration (mM)	Price[a] $/ lb-mole	Relative cost
Formic acid	17.7	12.88	0.513
Acetic acid	14.3	11.4	0.367
Adipic acid	7.0	63.51	1.0
Sulfosuccinic acid	7.8	44.1[e]	0.774
Sulfopropionic acid	16.1	28.8[b]	1.04
β-hydroxypropionic acid	14.55	28.8[b]	0.943
Phthalic acid	6.4	58.1[c]	0.836
Succinic acid	7.3	106.0[d]	1.74
Benzoic acid	15.8	36.66	1.302
Glycolic acid	22.4	30.4	1.532
Lactic acid	24.7	73.8	4.10

a Chemical Marketing Reporter, July 2, 1979

b Acrylic acid

c Phthalic anhydride

d Succinic anhydride

e Maleic anhydride

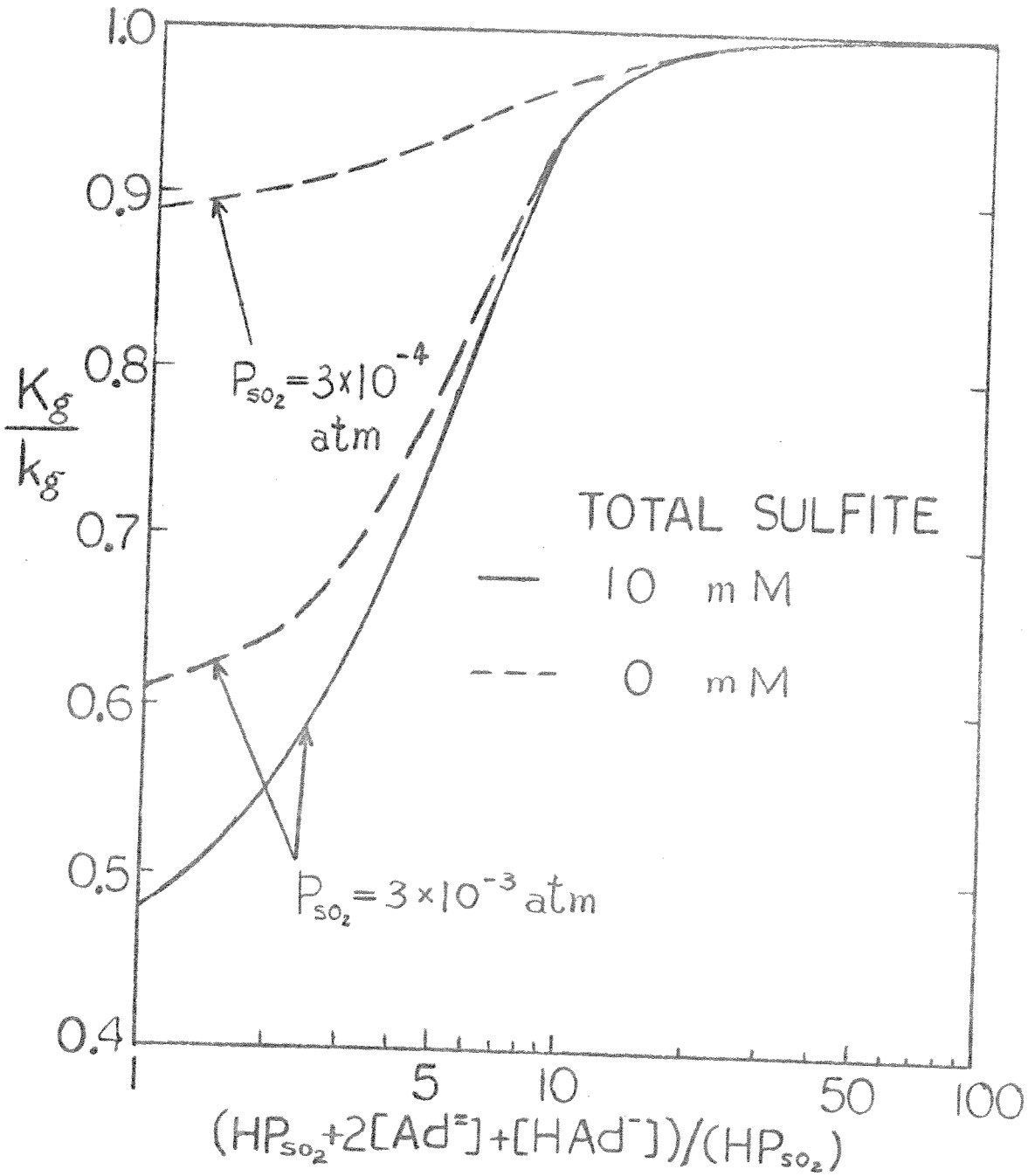

Figure 6-4. Scrubber mass transfer capacity vs. adipic acid addition for SO_2 removal.

$$\frac{K_g}{k_g} = \frac{P_{SO_2} - P_{SO_{2i}}}{P_{SO_2}} \qquad (6\text{-}22)$$

The low value of P_{SO_2} represents scrubber conditions near the gas outlet or for flue gas of low-sulfur coal. The high value of P_{SO_2} represents typical conditions at the gas inlet. It is seen that the SO_2 absorption is more gas-phase controlled with low P_{SO_2}. Therefore, adipic acid is relatively more effective with high P_{SO_2}.

Forced oxidation in the scrubber loop usually results in low total sulfite. Figure 6-4 shows that at pH 5 the overall mass transfer coefficient of slurry without sulfite is greater than that with 10 mM sulfite. In other words, the SO_2 absorption efficiency is improved by forced oxidation as observed by Borgwardt (1978). At pH 5, most of the total dissolved sulfite is present as bisulfite ions which depress the SO_2 hydrolysis. In the absence of bisulfite, increased SO_2 hydrolysis enhances mass transfer.

As adipic acid is added to the system, liquid phase mass transfer rate is enhanced by the buffering couples of H_2Ad/HAd^- and $HAd^-/Ad^=$. Better scrubber performance was shown in Figure 6-4 with the addition of adipic acid under three different operating conditions. Less overall mass transfer enhancement is obtained with low P_{SO_2} because it is more gas-phase controlled. All

three curves approach the asymptotic value of 1.0 at a high concentration of adipic acid, where SO_2 removal is totally controlled by gas phase resistance. Further addition of adipic acid or other buffer will not improve SO_2 removal. Actually, in a typical $CaCO_3$ slurry scrubber 10 to 20 mmole/liter should be adequate to provide most of the benefit from adipic acid addition. This is very close to the experimental results obtained by Bechtel (1979)

Notation

a = component activity, g-mole/liter

b = integration constant in Equation (8), (9) and (10)

D = diffusivity of component, cm^2/sec

$D_{\pm}$ = effective diffusivity of ions defined by Equation (16), cm^2/sec

Fa = Faraday = 96488 coulumbs/g-equivalent

I = ionic strength, g-mole/liter

K = thermodynamic equilibrium constant

K_c = effective equilibrium constant in concentration units

$k_g a$ = gas-phase mass transfer coefficient, g-mole/sec-atm

$k_L^o a$ = liquid-phase mass transfer coefficient, liter/sec

n = valence

N = absorption rate, g-mole/sec

P_{SO_2} = SO_2 partial pressure, atm

t = time, sec

T = temperature, ^oC

V' = molecular volume

x = distance, cm

ϕ = mass transfer enhancement factor

γ = activity coefficient

$\lambda_{\pm}^o$ = equivalent ion conductance, $cm^2/g\text{-mole/ohm}$

δ = film thickness, cm

Subscript

1, 2, 3, 4 = reaction 1, 2, 3, 4

i = at gas-liquid interface

j = component j

o = at liquid bulk

[ ] = concentration, g-mole/liter

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Chapter 7

SUMMARY

The objectives of this work are:

(1) to model the SO_2 absorption mechanism.

(2) to evaluate buffer additives for SO_2 scrubbing

Analysis using the mass transfer model developed elucidates the functions of three major lime/limestone slurry flue gas desulfurization processes: simple slurry, forced oxidation and buffer additive.

Theoretical Development

Mass transfer theory with equilibrium reactions was investigated because the hydrolysis of absorbed SO_2 is an instantaneous reversible reaction.

The solution of surface renewal theory for the effect of instantaneous reversible reaction on the rate of mass transfer has been computed numerically. The material balance equations were transformed into ordinary differential equations by combination of variables. An explicit, finite difference method was employed to solve the differential equations. At every point along the diffusion path, all the species were assumed to be in equilibrium. The analytical solutions derived from film theory are also presented and compared with those surface renewal theory.

An approximation method which can estimate the surface renewal theory solutions by the use of film theory solutions was tested over a wide range of variables. It was found that the approximation method can estimate the surface renewal theory solutions within 10% for most cases.

Multiple reactions are frequently more representative than single reactions when considering gas absorption with chemical reactions. The effects on mass transfer of multiple instantaneous reversible reactions are modeled by film theory and surface renewal theory. Film theory mass transfer enhancement factors are solved directly for simple reaction systems. More complicated systems require numerical solution of higher order algebraic equations.

Non-interacting systems of reactions can be solved as a linear sum of contributions from each constituting reaction. Interacting system each requires a unique solution. Only the simplest reaction system is easily solved for surface renewal theory. The solution of surface renewal theory for more complicated systems is approximated by replacing diffusivity ratios by their square roots in the solution of film theory.

Application of the theories

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 $25^{o}C$ in a continuous stirred vessel with an unbroken gas-liquid interface. Gas-phase mass transfer resistance was determined by

absorption into 0.7 to 1.0 molar NaOH solution. 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.

Because H^+ and HSO_3^- diffuse at the same rate, pure water results in the reaction type, $A \rightleftharpoons 2B$. The enhancement factor varies from 1.1 with pure SO_2 to 12 with 200 ppm SO_2 in the gas. HCl solutions give the reaction type, $A \rightleftharpoons B$. The enhancement factor with dilute SO_2 varies from 2.5 in 0.01 molar HCl to 1.0 in 1 molar HCl. In NaCl solutions, H^+ and HSO_3^- diffuse at different rates and the reaction is given by $A \rightleftharpoons B + C$. The enhancement factor with 1250 ppm SO_2 increases by 20 to 25% in going from pure water to 0.4 molar NaCl.

The chemical absorption of sulfur dioxide into aqueous sodium sulfite and sodium hydroxide solutions is modelled by simultaneous mass transfer and multiple instantaneous reversible reactions. Experiments on the absorption of dilute sulfur dioxide into aqueous sodium hydroxide solutions were carried out in a stirred vessel with a plain gas-liquid interface. An approximation method based on film theory is used to estimate surface renewal theory solutions for mass transfer enhancement factors. Predictions by the present model are compared with those by a previous irreversible model over a wide range of SO_2 partial pressure in the gas phase.

Approximate surface renewal theory with multiple equilibrium reactions was further employed to interpret the experimental data

of SO_2 - acetic acid and SO_2 - adipic acid systems. The absorption rate of sulfur dioxide from a gas mixture of SO_2 and N_2 was measured at 25°C in the stirred vessel as used before.

The model of gas/liquid mass transfer with simultaneous equilibrium reactions was modified to include the practical SO_2 scrubbing conditions at 55°C and 0.1 M $CaCl_2$. The modified model was applied to the absorption of SO_2 from waste gases into lime or limestone slurries with the following objectives:

(1) to describe the SO_2 absorption mechanism in scrubbers.

(2) to model novel processes such as forced oxidation and buffer additives.

(3) to evaluate the effectiveness of eleven organic acid buffer additives.

Conclusions

1) Mass transfer with instantaneous reversible reactions as complicated as $A + B \rightleftharpoons C + D$ can be modeled by surface renewal theory solved by numerical integration using Kutta's - Simpson's rule.

2) Film theory and surface renewal theory give identical enhancement factors with diffusivity ratios of one. However, deviations between the theories can be as much 100% with a diffusivity ratio of 10.

3) Surface renewal theory can be approximated within 10% with diffusivity ratios of 0.3 to 10.0 by using the film theory

solution with diffusivity ratios replaced by their square roots. This method does not require numerical integration and should be especially useful for complicated reaction systems where surface renewal theory could be difficult to solve.

4) At large values of the equilibrium constants, the solutions for bimolecular equilibrium reactions asymptotically approach the solutions for instantaneous, irreversible reactions.

5) The multiple equilibrium reaction systems can be divided into two categories, non-interacting and interacting systems. The former one requires that there are no common components except the one penetrating through the phase boundary. The characteristics of the constituting single reactions can be directly applied to the multiple reaction system. The effects of multiple reactions on mass transfer rate are the sum of the effects of the constituting single reactions.

   The interacting systems have more than one common component and all the properties of the components can affect the concentration profiles and mass transfer rates. Therefore, each interacting system results in a unique form of mass transfer enhancement factor.

6) The film theory of mass transfer with multiple equilibrium reactions can be solved for most cases. Numerical techniques may be required for complicated reaction systems because they involve high order algebraic equations.

   Only the simplest reaction system can be solved by surface

renewal theory. However, the film theory solutions can be employed to estimate the surface renewal theory mass transfer enhancement factor with approximation method.

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

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

9) For the sulfur dioxide-sodium chloride system, the absorption can be described by surface renewal theory accompanied by an equilibrium reaction of type $A \rightleftharpoons B + C$. The presence of the relatively high concentration of sodium chloride releases the hydrogen ion from the force of electrical potential gradient in the system. 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.

10) The experimental data on the absorption of dilute sulfur dioxide into NaOH solutions agree well with the approximate

solutions of surface renewal theory with instantaneous reversible reactions.

11) The chemical absorption model shows that the reversible SO_2 hydrolysis reaction is significant and H^+ plays an important role in the absorption mechanism when SO_2 partial pressure is much lower than 0.05 atm. When SO_2 partial pressure is higher than 0.05 atm, the hydrolysis of dissolved SO_2 is negligible and the present model gives the same prediction of mass transfer enhancement factor as the irreversible two-reaction plane model.

12) The absorption rate of SO_2 into aqueous acetic and adipic acid solutions can be modeled by approximate surface renewal theory with multiple equilibrium reactions.

13) The SO_2 removal efficiency of scrubber loop forced oxidation is better than that of simple slurry process, because the bisulfite ion which depresses the SO_2 hydrolysis is oxidized into sulfate species. As a result, the liquid phase mass transfer rate is more enhanced by SO_2 hydrolysis in forced oxidation than in simple slurry process.

14) Adipic, sulfopropionic, sulfosuccinic and β-hydroxypropionic acids are the most promising buffer additives for lime/limestone slurry scrubbing of SO_2 from flue gas. Formic and acetic acids are the least expensive buffer additives. However, losses by volatilization in the scrubber may be economically and environmentally significant.

15) 10 - 20 mM adipic acid should be adequate to provide most of the benefit from buffer additives on mass transfer enhancement for a typical SO_2 scrubber.

Recommendations for further work

1) Test the dissolution rate of limestone under SO_2 scrubbing with and without buffer additives.
2) Test SO_2 scrubbing with a variety of organic acids and evaluate the least expensive buffer additives such as formic acid and acetic acid.
3) Test the effect of mass transfer enhancement of HCO_3^-/CO_2 buffer couple.
4) Construct an integrated SO_2 scrubber model which incorporates $CaCO_3$ dissolution rate, $HSO_3^-/SO_3^=$ and/or HCO_3^-/CO_2 buffer couples and organic acid buffer additives.

APPENDIX A. ESTIMATION OF EXCESS SALT NEEDED TO LIBERATE THE DIFFUSING IONS.

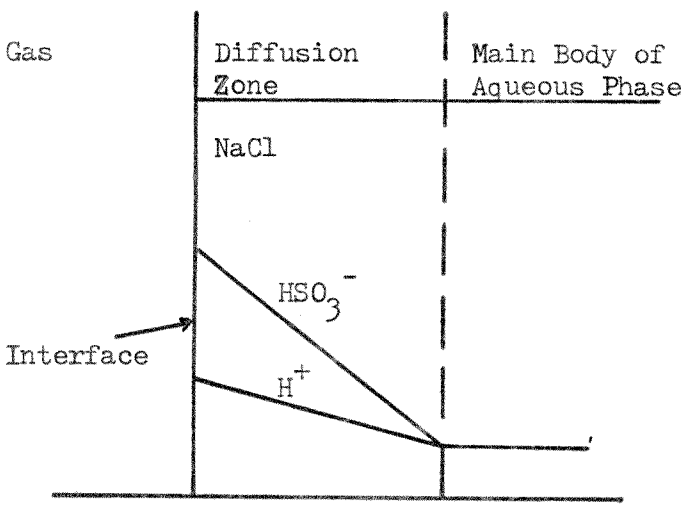
In a system of mixed electrolytes, the unidirectional diffusion flux of each ion species results from a combination of electrical and concentration gradients was given as (Vinograd and McBain, 1941)

$$D_{\pm}G_{\pm} = \frac{RT\lambda_{\pm}}{(Fa)^2 n_{\pm}}\left[G_{\pm} \mp n_{\pm}C_{\pm}\frac{\Sigma\lambda_{+}G_{+}/n_{+} - \Sigma\lambda_{-}G_{-}/n_{-}}{\Sigma\lambda_{+}C_{+} + \Sigma\lambda_{-}C_{-}}\right] \quad (A\text{-}1)$$

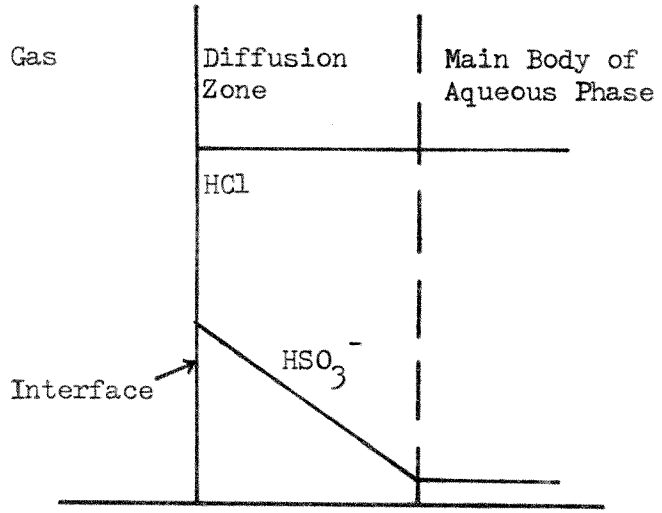
The first term on the right hand side of Equation A-1 outside the paranthesis represents the true diffusivity of the ion at infinite dilution. All the terms within the paranthesis can be considered the correction factors due to the presence of the other ion species. The $D_{\pm}$ of Equation A-1 represents the effective diffusivity of the specified ion.

A simplified concentration distribution diagram of SO_2-NaCl absorption system is shown in Figure A-(1). The assumptions employed by Vinograd and McBain (1941) regarding linear concentration gradients and arithmatic mean concentrations are adopted and the ionic conductance values 350, 50, 76 and 50 $^{-1}cm^2$/mole for H^+, HSO_3^-, Cl^- and Na^+ ions respectively at 25°C will be used for analysis.

The first estimation was made by assuming that the H^+ and HSO_3^- ions have equal concentration gradients. It was found that the effective diffusivity of hydrogen ion deviates from its true value by only about 2% if the minimum concentration ratio of sodium chloride to hydrogen bisulfite is 50. However, in real cases, the slow moving HSO_3^- ion will present a much steeper concentration gradient than



(1)



(2)

Fig. A. Concentration distribution in diffusion zone during absorption of sulfur dioxide by (1) aqueous sodium chloride and (2) aqueous hydrogen chloride.

that of H^+ ion. The minimum concentration ratio between NaCl and HSO_3^- ion will also be much lower than that between NaCl and H^+ ion. All those changes tend to decrease the diffusivity deviation to much less than 2%.

The simplified concentration distribution of SO_2-HCl system is illustrated in Figure A-(2). In this case, the excess hydrogen ion which possesses very high ionic conductance can greatly lower the electrical gradient effect on the diffusion characteristics of moving ions. It was found that the difference between the effective diffusivity and the true diffusivity of HSO_3^- ion is only 1% when concentration ratio of H^+ to HSO_3^- ion is 10.

APPENDIX B

SUMMARIZED DATA

Table B-1. Absorption of SO_2 into NaOH solutions.

Run	T (^{o}C)	L (cm^3/sec)	P_{SO_2} (ppm)	$[SO_3^{=}]_o$ (M)	$[NaOH]_o$ (M)	$k_g a$ (mole/atm)	RPM
1	26	2.42	1540	9.0×10^{-3}	1.0	0.0141	300
2	22	3.27	1260	5.5×10^{-3}	1.0	0.01426	700
3	26	1.92	755	5.5×10^{-3}	1.0	0.01316	300
4	23	4.17	870	2.9×10^{-3}	1.0	0.01389	300
5	23	2.75	410	2.1×10^{-3}	1.0	0.014	300
6	26	1.67	1750	1.2×10^{-3}	1.0	0.01123	220
7	22.5	4.17	1060	2.9×10^{-3}	1.0	0.0112	300
8	22.5	3.33	900	3.0×10^{-3}	1.0	0.01108	205
9	22.5	4.00	670	1.9×10^{-3}	1.0	0.0112	305
10	23	3.00	580	2.2×10^{-3}	1.0	0.01127	325

(continue)

Table B-1. Absorption of SO_2 into NaOH solutions.

(continue)

Run	T (^oC)	L (cm^3/sec)	P_{SO_2} (ppm)	$[SO_3^=]_o$ (M)	$[NaOH]_o$ (M)	$k_g a$ (mole/atm)	RPM
11	23	4.17	1420	5.1×10^{-3}	1.0	0.01496	250
12	22.5	2.33	1050	6.8×10^{-3}	1.0	0.0151	350
13	22.5	1.43	760	8.0×10^{-3}	1.0	0.015	350
14	23	4.27	805	2.9×10^{-3}	1.0	0.015	350
15	24	1.50	348	3.3×10^{-3}	1.0	0.015	350

Table B-2. Absorption of SO_2 into HCl solutions.

Run	T (^oC)	L (cm^3/sec)	P_{SO_2} (ppm)	$[HSO_3^-]_o + [SO_2]_o$ (M)	$[HCl]_o$ (M)	ϕ_e -
1	24	2.50	1620	2.1×10^{-4}	1.0	-
2	23	3.83	1580	1.3×10^{-4}	1.0	-
3	23	3.22	1100	1.2×10^{-4}	0.05	1.345
4	23.5	3.00	907	1.1×10^{-4}	0.05	1.315
5	23.5	3.00	590	6.8×10^{-5}	0.05	1.308
6	24	2.17	307	4.9×10^{-5}	0.05	1.295
7	23.5	3.20	880	1.3×10^{-4}	0.02	1.80
8	24	2.55	565	1.1×10^{-4}	0.02	1.75
9	23.5	1.75	330	8.6×10^{-5}	0.02	1.75
10	23.5	2.42	415	1.2×10^{-5}	0.01	2.47
11	23.5	2.25	270	7.6×10^{-5}	0.01	2.42

Table B-3. Absorption of SO_2 into pure water.

Run	T (°C)	L (cm^3/sec)	P_{SO_2} (ppm)	$[SO_2]_o + [HSO_3^-]_o$ (ppm)	ϕ_e -	ϕ_T -
1	25	6.33	4300	5.7×10^{-4}	2.95	2.80
2	25	6.33	2175	3.6×10^{-4}	3.75	3.57
3	25	6.33	1500	2.6×10^{-4}	4.02	4.16
4	25	6.33	1040	2.3×10^{-4}	5.17	4.78
5	25.5	3.91	585	2.7×10^{-4}	6.57	6.01
6	25.5	6.50	301	1.0×10^{-4}	8.47	8.29
7	25	6.50	272	9.0×10^{-5}	8.47	8.65
8	25.5	6.42	200	8.3×10^{-5}	10.92	10.08
9	25	6.25	124	6.2×10^{-5}	13.36	12.8

Table B-4. Absorption of SO_2 into NaCl solutions.

Run	T ($^{\circ}C$)	$[NaCl]_o$ (M)	L (cm^3/sec)	P_{SO_2} (ppm)	$[SO_2]_o + [HSO_3^-]_o$ (M)	N_{exp} (g-mole/sec)
1	24	0.05	5.00	1250	3.3×10^{-4}	1.677×10^{-6}
2	24	0.1	4.83	1250	3.7×10^{-4}	1.77×10^{-6}
3	24	0.2	4.75	1250	3.9×10^{-4}	1.83×10^{-6}
4	24	0.4	5.00	1250	3.9×10^{-4}	1.95×10^{-6}
5	24	0.7	4.83	1250	4.0×10^{-4}	1.93×10^{-6}
6	24	1.0	4.91	1250	3.9×10^{-4}	1.91×10^{-6}

Table B-5. Absorption of SO_2 into NaCl solutions.

Run	T (^oC)	L (cm^3/sec)	P_{SO_2} (ppm)	$[HSO_3^-]_o + [SO_2]_o$ (M)	$[NaCl]_o$ (M)	ϕ_e -
1	25	5.00	2900	6.7×10^{-4}	0.5	4.25
2	24.5	5.33	1810	4.7×10^{-4}	0.4	5.38
3	24.5	5.00	1250	3.9×10^{-4}	0.4	5.98
4	24.5	7.50	470	1.5×10^{-4}	0.3	9.85
5	25.0	6.00	285	1.45×10^{-4}	0.2	12.70
6	25.0	9.00	230	8.85×10^{-5}	0.2	15.1
7	24.5	10.42	200	6.5×10^{-5}	0.2	14.78

Table B-6. Absorption of SO_2 into dilute NaOH solutions.

Run	T (°C)	L (cm^3/sec)	$[NaOH]_o$ (M)	P_{SO_2} (ppm)	$[SO_3^=]_o$ (M)	ϕ_e -
1	25.5	5.83	0.01	1035	1.08×10^{-3}	27.2
2	25.5	5.83	0.01	1325	1.16×10^{-3}	20.6
3	25.5	5.42	0.01	1735	1.4×10^{-3}	16.05
4	25.0	5.83	0.005	785	6.8×10^{-4}	20
5	25.0	5.83	0.005	1175	8.2×10^{-4}	14.5
6	25.5	6.25	0.005	1630	8.6×10^{-4}	11.9
7	25.0	5.00	0.001	735	5.2×10^{-4}	11.9
8	25.5	5.00	0.001	1050	6.2×10^{-4}	9.44
9	25.5	5.25	0.001	1370	7.2×10^{-4}	8.7

$$k_l a = 3.3 \times 10^{-4} \text{ l/sec}$$

Table B-7. Absorption of SO_2 into acetic acid solutions.

Run	T (^oC)	$[HAC]_o + [AC^-]_o$ (M)	pH_{out}	$[AC^-]_o$ (M)	L (cm^3/sec)	$HSO_3^-{}_o$ (M)	P_{SO_2} (ppm)	ϕ_e
1	25.5	5.0×10^{-3}	5.40	4.3×10^{-3}	5.00	8.0×10^{-4}	1950	6.0
2	25.5	5.0×10^{-3}	5.21	3.98×10^{-3}	4.75	4.8×10^{-4}	580	13.8
3	25.5	5.0×10^{-3}	5.23	4.0×10^{-3}	4.83	4.5×10^{-4}	580	12.9
4	26	5.0×10^{-3}	5.13	3.8×10^{-3}	3.33	4.4×10^{-4}	270	22.4
5	25.5	1.0×10^{-2}	5.21	8.0×10^{-3}	4.50	4.9×10^{-4}	330	33.4
6	25.5	1.0×10^{-2}	5.25	8.2×10^{-3}	4.50	5.1×10^{-4}	335	33.8
7	25	1.0×10^{-2}	5.19	8.0×10^{-3}	4.67	6.0×10^{-4}	615	17.0
8	25	1.0×10^{-2}	5.23	8.0×10^{-3}	5.83	6.0×10^{-4}	1080	10.6
9	25	1.0×10^{-2}	5.21	8.0×10^{-3}	5.30	8.5×10^{-4}	1990	6.8
10	25.5	1.0×10^{-2}	5.59	9.0×10^{-3}	5.83	6.0×10^{-4}	2030	7.6
11	25.5	2.0×10^{-2}	4.81	1.25×10^{-3}	5.42	9.1×10^{-4}	1180	15.0
12	25.5	2.0×10^{-2}	4.83	1.25×10^{-3}	5.42	7.3×10^{-4}	700	23.9

(continue)

Table B-7. Absorption of SO_2 into acetic acid solutions.

(continue)

Run	T (°C)	$[HAC]_o + [AC^-]_o$ (M)	pH_{out}	$[AC^-]_o$ (M)	L (cm^3/sec)	$[HSO_3^-]_o$ (M)	P_{SO_2} (ppm)	ϕ_e -
13	25	2.0×10^{-2}	5.22	1.6×10^{-3}	5.50	9.6×10^{-4}	2040	8.0
14	25.5	2.0×10^{-2}	5.31	1.65×10^{-3}	5.67	8.2×10^{-4}	750	28.0
15	25.5	2.0×10^{-2}	5.41	1.75×10^{-4}	5.50	9.6×10^{-4}	1220	16.2

Table B-8. Absorption of SO_2 into adipic acid solutions.

Run	T (^oC)	$[H_2Ad]_o + [HAd^-]_o + [Ad^=]_o$ (M)	pH_{out} -	$2[Ad^=]_o + [HAd^-]_o$ (M)	L (cm^3/sec)	$[HSO_3^-]_o$ (M)	P_{SO_2} (ppm)	ϕ_e -
1	25.5	$1.0x10^{-2}$	5.02	$1.3x10^{-2}$	5.00	$1.05x10^{-3}$	2040	8
2	25.5	$1.0x10^{-2}$	5.01	$1.3x10^{-2}$	5.42	$7.3x10^{-4}$	1140	11.6
3	25.5	$1.0x10^{-2}$	5.05	$1.3x10^{-2}$	5.42	$6.1x10^{-4}$	650	20.1
4	25.5	$1.0x10^{-2}$	5.33	$1.5x10^{-2}$	5.33	$4.8x10^{-4}$	350	38.7
5	25.5	$1.0x10^{-2}$	5.61	$1.7x10^{-2}$	5.00	$9.2x10^{-4}$	1160	14.0
6	25.0	$1.0x10^{-2}$	4.63	$9.1x10^{-3}$	5.00	$7.6x10^{-4}$	1100	11.6
7	25.0	$1.0x10^{-2}$	4.61	$9.1x10^{-3}$	4.75	$3.8x10^{-4}$	295	26.8
8	25.0	$2.0x10^{-2}$	4.70	$2.0x10^{-2}$	5.33	$1.3x10^{-3}$	2140	10.1
9	25.5	$2.0x10^{-2}$	4.68	$1.9x10^{-2}$	5.00	$9.4x10^{-4}$	750	28.6
10	25.5	$2.0x10^{-2}$	5.01	$2.6x10^{-2}$	5.75	$1.2x10^{-3}$	2160	10.5
11	25.0	$2.0x10^{-2}$	5.03	$2.6x10^{-2}$	5.42	$1.1x10^{-3}$	1260	18.0
12	25.0	$2.0x10^{-2}$	5.01	$2.6x10^{-2}$	5.00	$1.0x10^{-3}$	790	31.9

APPENDIX C

COMPUTER PROGRAMS FOR RIGOROUS SURFACE RENEWAL THEORY WITH SINGLE EQUILIBRIUM REACTIONS

```
C    ****************************************************************
C    FOR MASS TRANSFER WITH REACTION A=2E
C    ****************************************************************
       DIMENSION VV(110),ZZ(110),UU(110)
 2. 1    FORMAT(5(5X,E16.7)//)
C    ****************************************************************
C    DATA
C    ****************************************************************
C    TEMPERATURE; T. EQUILIBRIUM CONSTANT; EK.
C    INTERFACE CONCENTRATION; AI,EI.
C    BULK CONCENTRATION; A0,E0.
C    DIFFUSIVITIES; DUA,DUE.
C    ****************************************************************
 3.       T=298.
 4.       EK=1.0
 5.       AI=0.001
 6.       DUA=1.76E-5
 7.       DUE=10.0*DUA
 8. 600   A0=0.8*AI
 9.       EI=SQRT(AI*EK)
10.       E0=SQRT(A0*EK)
11.       L=1
C    ****************************************************************
C    CALCULATE APPROXIMATE SOLUTION AS STARTING VALUE
C    ****************************************************************
12.       C1=DUE/DUA
13.       C2=2.*EI/EK
14.       C3=2.*(EI-E0)/EK
15.       E=1.0
16.       N=1
17.       VV(1)=0.
18.       ZZ(1)=0.
19.       FII=1.+SQRT(EK*DUE/DUA)/(SQRT(AI)+SQRT(A0))
20.       FIH=FII
21.       FII=DUA*FII*(AI-A0)/SQRT(3.1416)
22.       FII=FII/((EI-E0)*(2.*DUA*EI/EK+DUE))
```

```
23.         UU(1)=FII
      C     ************************************************************
      C     NUMERICAL INTERATION
      C     ************************************************************
24.         DVV=0.01
25.   100   VF=VV(N)
26.         ZF=ZZ(N)
27.         UF=UU(N)
28.         FX=UU(N)*(2./(1.-VV(N))-VV(N)*(1.+C2-C3*ZZ(N))
           1/(2.*(1.-VV(N))**3*(C1+C2-C3*ZZ(N)))+C3*UU(N)/(C1+C2-C3
           1*ZZ(N)))
29.         GX=UU(N)
30.         D1=GX*DVV
31.         DL1=FX*DVV
32.         VV(N)=VF+DVV/2.
33.         ZZ(N)=ZF+D1/2.
34.         UU(N)=UF+DL1/2.
35.         FX=UU(N)*(2./(1.-VV(N))-VV(N)*(1.+C2-C3*ZZ(N))
           1/(2.*(1.-VV(N))**3*(C1+C2-C3*ZZ(N)))+C3*UU(N)/(C1+C2-C3
           1*ZZ(N)))
36.         GX=UU(N)
37.         D2=GX*DVV
38.         DL2=FX*DVV
39.         VV(N)=VF+DVV/2.
40.         ZZ(N)=ZF+D2/2.
41.         UU(N)=UF+DL2/2.
42.         FX=UU(N)*(2./(1.-VV(N))-VV(N)*(1.+C2-C3*ZZ(N))
           1/(2.*(1.-VV(N))**3*(C1+C2-C3*ZZ(N)))+C3*UU(N)/(C1+C2-C3
           1*ZZ(N)))
43.         GX=UU(N)
44.         D3=GX*DVV
45.         DL3=FX*DVV
46.         VV(N)=VF+DVV
47.         ZZ(N)=ZF+D3
48.         UU(N)=UF+DL3
49.         FX=UU(N)*(2./(1.-VV(N))-VV(N)*(1.+C2-C3*ZZ(N))
```

```
     1/(2.*(1.-VV(N))**3*(C1+C2-C3*ZZ(N)))+C3*UU(N)/(C1+C2-C3
     1*ZZ(N)))
50.   GX=UU(N)
51.   D4=GX*DVV
52.   DL4=FX*DVV
53.   DZZ=(1./6.)*(D1+2.*D2+2.*D3+D4)
54.   DUU=(1./6.)*(DL1+2.*DL2+2.*DL3+DL4)
55.   VV(N)=VF
56.   ZZ(N)=ZF
57.   UU(N)=UF
58.   N=N+1
59.   VV(N)=VF+DVV
60.   ZZ(N)=ZF+DZZ
61.   UU(N)=UF+DUU
62.   IF(L.EQ.2) GO TO 20
63.   IF(L.EQ.3) GO TO 30
64.   IF(N.LT.101) GO TO 100
65.   DO 5 K=1,100
66.   IF(ZZ(K).GE.1.0) GO TO 200
67.   I=K+1
68.   IF(ZZ(I).LT.ZZ(K)) GO TO 400
69. 5 CONTINUE
C    ************************************************************
C    ITERATION
C    ************************************************************
70. 400 L=3
71.   FII=FII*1.01
72.   UU(1)=FII
73.   VV(1)=0.
74.   ZZ(1)=0.
75.   N=1
76.   GO TO 100
77. 200 L=2
78.   FII=FII*0.99
79.   UU(1)=FII
```

```
      VV(1)=0.
      ZZ(1)=0.
      N=1
      T=T+1.
      GO TO 100
20    IF(ZZ(N).GE.1.) GO TO 200
      IF(N.LT.101) GO TO 100
      GO TO 300
30    J=N-1
      IF(ZZ(N).LT.ZZ(J)) GO TO 400
      IF(ZZ(N).GT.1.) GO TO 300
      IF(N.GT.101) GO TO 400
      GO TO 100
300   DO 2 M=1,101
2     CONTINUE
      FFI=UU(1)*(EI-ED)
      FFI=FFI*(2.*DUA*EI/EK+DUE)
      FFI=FFI*SQRT(3.1416)/(DUA*(AI-AO))
      AIK=AI/EK
      AOI=AO/AI
      DEA=DUE/DUA
      PRINT 1,DEA,AIK,AOI,FFI,FIH
      IF(AI.GE.400.0) GO TO 500
      AI=AI*10.0
      GO TO 600
500   STOP
      END
```

```
C     ************************************************************
C     MASS TRANSFER WITH REACTION A+B=C
C     ************************************************************
        DIMENSION VV(110),AA(110),BB(110),DAA(110),DBB(110)
2.      DIMENSION ERR(110),AFF(110),BFF(110),AFD(110),BFD(110)
3.  1     FORMAT(6(5X,E16.7))
C     ************************************************************
C     DATA
C     ************************************************************
C     EQUILIBRIUM CONSTANT;  EK
C     INTERFACE CONCENTRATIONS;  AI,BI,CI.
C     BULK CONCENTRATIONS; AL,BL,CL
C     DIFFUSIVITIES;  DA, DB, DC.
C     ************************************************************
4.        AL=0.
5.        EL=0.
6.        DA=1.0
7.        DB=10.0
8.        DE=DB
9.        AI=1.0
10.       EK=0.01
11.       BL=10.0
C     ************************************************************
C     CALCULATE APPROXIMATE SOLUTION AS STARTING VALUE
C     ************************************************************
12. 600   BI=BL*((DB/DE/EK+AL)/(DB/DE/EK+AI))
13.       L=1
14.       N=1
15.       J=1
16.       M=1
17.       BI1=BI
18.       FFI=1.-(DB/DA)*(BI1-BL)/(AI-AL)
19.       BI=BL*((SQRT(DB/DE)/EK+AL)/(SQRT(DB/DE)/EK+AI))
20.       FII=1.-SQRT(DB/DA)*(BI-BL)/(AI-AL)
21.       FIK=FII
22.       FII=FII/SQRT(3.1416)*(AI-AL)*DA
```

```
      FII=FII/(DA+(DB*DE*BI*EK/(DB+DE*AI*EK)))*(-1.)
      FFF=FII
      FIJ=FII*(-1.0)*(DE*BI*EK/(DB+DE*AI*EK))
      VV(1)=0.
      AA(1)=AI
      BB(1)=BI
      DAA(1)=FII
      DBB(1)=FIJ
C     ************************************************************
C     NUMERICAL INTERATION
C     ************************************************************
      DVV=0.01
100   VF=VV(N)
      AF=AA(N)
      BF=BB(N)
      DAF=DAA(N)
      DBF=DBB(N)
      BD=BI-BL
      AD=AI-AL
      C1=DB+DE*AA(N)*EK+DB*DE*BB(N)*EK/DA
      C2=-VV(N)/(2.0*C1*(1.0-VV(N))**3)
      DUA=DAA(N)
      DUAA=C2*DAA(N)*(DE*AA(N)*EK+DB+DB*BB(N)*EK)-C2
     1*DBB(N)*(DE*AA(N)*EK-DB*AA(N)*EK)-2.0*DE*DB*EK/DA
     1*DAA(N)*DBB(N)/C1+2.0*DAA(N)/(1.0-VV(N))
      DUB=DBB(N)
      DUBB=C2*DAA(N)*(DA*BB(N)*EK-DE*BB(N)*EK)+C2*DBB(N)
     1*(DA+DA*AA(N)*EK+DE*BB(N)*EK)-2.0*DE*EK*DAA(N)
     1*DBB(N)/C1+2.0*DBB(N)/(1.0-VV(N))
      DA1=DUA*DVV
      DLA1=DUAA*DVV
      DB1=DUB*DVV
      DLB1=DUBB*DVV
      VV(N)=VF+DVV/2.
      AA(N)=AF+DA1/2.
```

```
51.          BB(N)=BF+DB1/2.
52.          DAA(N)=DAF+DLA1/2.
53.          DBB(N)=DBF+DLB1/2.
54.          C1=DB+DE*AA(N)*EK+DB*DE*BB(N)*EK/DA
55.          C2=-VV(N)/(2.0*C1*(1.0-VV(N))**3)
56.          DUA=DAA(N)
57.          DUAA=C2*DAA(N)*(DE*AA(N)*EK+DB+DB*BB(N)*EK)-C2
            1*DBB(N)*(DE*AA(N)*EK-DB*AA(N)*EK)-2.0*DE*DB*EK/DA
            1*DAA(N)*DBB(N)/C1+2.0*DAA(N)/(1.0-VV(N))
58.          DUB=DBB(N)
59.          DUBB=C2*DAA(N)*(DA*BB(N)*EK-DE*BB(N)*EK)+C2*DBB(N)
            1*(DA+DA*AA(N)*EK+DE*BB(N)*EK)-2.0*DE*EK*DAA(N)
            1*DBB(N)/C1+2.0*DBB(N)/(1.0-VV(N))
60.          DA2=DUA*DVV
61.          DLA2=DUAA*DVV
62.          DB2=DUB*DVV
63.          DLB2=DUBB*DVV
64.          VV(N)=VF+DVV/2.
65.          AA(N)=AF+DA2/2.
66.          BB(N)=BF+DB2/2.
67.          DAA(N)=DAF+DLA2/2.
68.          DBB(N)=DBF+DLB2/2.
69.          C1=DB+DE*AA(N)*EK+DB*DE*BB(N)*EK/DA
70.          C2=-VV(N)/(2.0*C1*(1.0-VV(N))**3)
71.          DUA=DAA(N)
72.          DUAA=C2*DAA(N)*(DE*AA(N)*EK+DB+DB*BB(N)*EK)-C2
            1*DBB(N)*(DE*AA(N)*EK-DB*AA(N)*EK)-2.0*DE*DB*EK/DA
            1*DAA(N)*DBB(N)/C1+2.0*DAA(N)/(1.0-VV(N))
73.          DUB=DBB(N)
74.          DUBB=C2*DAA(N)*(DA*BB(N)*EK-DE*BB(N)*EK)+C2*DBB(N)
            1*(DA+DA*AA(N)*EK+DE*BB(N)*EK)-2.0*DE*EK*DAA(N)
            1*DBB(N)/C1+2.0*DBB(N)/(1.0-VV(N))
75.          DA3=DUA*DVV
76.          DLA3=DUAA*DVV
77.          DB3=DUB*DVV
```

```
      DLB3=DUBB*DVV
      VV(N)=VF+DVV
      AA(N)=AF+DA3
      BB(N)=BF+DB3
      DAA(N)=DAF+DLA3
      DBB(N)=DBF+DLB3
      C1=DB+DE*AA(N)*EK+DB*DE*BB(N)*EK/DA
      C2=-VV(N)/(2.0*C1*(1.0-VV(N))**3)
      DUA=DAA(N)
      DUAA=C2*DAA(N)*(DE*AA(N)*EK+DB+DB*BB(N)*EK)-C2
     1*DBB(N)*(DE*AA(N)*EK-DB*AA(N)*EK)-2.0*DE*DB*EK/DA
     1*DAA(N)*DBB(N)/C1+2.0*DAA(N)/(1.0-VV(N))
      DUB=DBB(N)
      DUBB=C2*DAA(N)*(DA*BB(N)*EK-DE*BB(N)*EK)+C2*DBB(N)
     1*(DA+DA*AA(N)*EK+DE*BB(N)*EK)-2.0*DE*EK*DAA(N)
     1*DBB(N)/C1+2.0*DBB(N)/(1.0-VV(N))
      DA4=DUA*DVV
      DLA4=DUAA*DVV
      DB4=DUB*DVV
      DLB4=DUBB*DVV
      DAX=(DA1+2.*DA2+2.*DA3+DA4)/6.
      DBX=(DB1+2.*DB2+2.*DB3+DB4)/6.
      DAAX=(DLA1+2.*DLA2+2.*DLA3+DLA4)/6.
      DBBX=(DLB1+2.*DLB2+2.*DLB3+DLB4)/6.
      N=N+1
      AFF(N)=(AI-AF)/AD
      BFF(N)=(BI-BF)/BD
      FAC=FII*(-1.)*(DA+(DB*DE*BI*EK/(DB+DE*AI*EK)))
     1*SQRT(3.1416)/DA/(AI-AL)
      VV(N)=VF+DVV
      AA(N)=AF+DAX
      BB(N)=BF+DBX
      DAA(N)=DAF+DAAX
      DBB(N)=DBF+DBBX
      IF(N.LT.60) GO TO 100
      I=N-2
```

```
109.          K=N-1
110.          AFD(N)=AFF(N)-AFF(K)
111.          BFD(N)=BFF(N)-BFF(K)
112.          AFD(K)=AFF(K)-AFF(I)
113.          BFD(K)=BFF(K)-BFF(I)
114.          BFDD=ABS(4.*BFD(K))
115.          IF(J.EQ.4) GO TO 80
116.          IF(BFD(N).GT.0..AND.ABS(BFD(N)).LT.BFDD) GO TO 50
      C     ************************************************************
      C     ITERATION
      C     ************************************************************
117.  80      BB(K)=BB(I)
118.          BB(N)=BB(K)
119.          DBB(K)=DBB(I)
120.          DBB(N)=DBB(K)
121.          J=4
122.  50      IF(L.EQ.2) GO TO 20
123.          IF(L.EQ.3) GO TO 30
124.          IF(AFD(N).LT.0..OR.AFD(N).GT.5.*AFD(K)) GO TO 60
125.          IF(AFF(N).GE.1.0) GO TO 70
126.          IF(N.LT.101) GO TO 100
127.  60      L=3
128.          FII=FII*1.03
129.          GO TO 200
130.  70      L=2
131.          FII=FII*.97
132.          GO TO 200
133.  20      K=N-1
134.          IF(AFF(N).GE.1.1) GO TO 300
135.          IF(AFF(N).GE.1.0) GO TO 70
136.          IF(AFD(N).LE.0.) GO TO 300
137.          IF(N.LT.101) GO TO 100
138.          GO TO 300
139.  30      K=N-1
140.          IF(AFD(N).LE.0.) GO TO 60
```

```
      IF(AFF(N).GE.1.1) GO TO 60
      IF(AFF(N).GE.1.0) GO TO 300
      IF(N.GE.101) GO TO 60
      GO TO 100
300   M=M+1
      K=M-1
      J=N-1
      AFL=AFF(J)
      BFL=BFF(J)
      PRINT 1,VF,AFL,BFL,FAC,FIK,BI
      ERR(M)=ABS(1.0-AFF(J))+ABS(1.0-BFF(J))
      IF(M.GT.2) GO TO 3
      BI=BI*0.97
      FII=FFF
      L=1
      GO TO 200
3     IF(M.GT.3) GO TO 5
      IF(ERR(M).GT.ERR(K)) GO TO 8
      Y=1.
      BI=BI*0.97
      FII=FFF
      L=1
      GO TO 200
8     BI=BI*1.03
      Y=2.
      FII=FFF
      L=1
      GO TO 200
5     IF(ERR(M).GT.ERR(K)) GO TO 7
      IF(Y.EQ.1.) GO TO 6
      BI=BI*1.03
      FII=FFF
      L=1
      GO TO 200
6     BI=BI*0.97
      FII=FFF
```

```
177.          L=1
178.          N=1
179.          J=1
180.          FIJ=FII*(-1.)*(DE*BI*EK/(DB+DE*AI*EK))
181.          VV(1)=0.
182.          AA(1)=AI
183.          BB(1)=BI
184.          DAA(1)=FII
185.          DBB(1)=FIJ
186.          GO TO 100
167.      7   PRINT 1,VF,AFL,BFL,FAC,FIK,BI
188.          DBBA=DB/DA
189.          BLA=BL/AI
190.          RRR=DB/(DE*AI*EK)
191.          PRINT 2,DBBA,BLA,RRR,FFI
192.      2   FORMAT(4(5X,E16.7)//)
193.          EK=EK*10.
194.          IF(EK.LT.400.) GO TO 600
195.          STOP
196.          END
```

```
      C     ************************************************************
      C     MASS TRANSFER WITH REACTION A=B+E
      C     ************************************************************
            DIMENSION VV(110),EE(110),BB(110),DEE(110),DBB(110)
     2.     DIMENSION ERR(100),EFF(110),BFF(110)
     3.     DIMENSION EFD(101),BFD(101)
     4. 1   FORMAT(6(5X,E16.7))
      C     ************************************************************
      C     EQUILIBRIUM CONSTANT; EK
      C     DIFFUSIVITIES;  DA,DB DE.
      C     INTERFACE CONCENTRATIONS;   AI,BI,EI.
      C     BULK CONCENTRATIONS; AL,BL,EL
      C     ************************************************************
     5.     EK=0.001
     6. 600 J=1
     7.     L=1
     8.     M=1
     9.     AL=0.0
    10.     BL=0.0
    11.     EL=0.0
    12.     DA=1.0
    13.     DB=1.0
    14.     DE=2.0
    15.     AI=1.0
      C     ************************************************************
      C     CALCULATE APPROXIMATE SOLUTION AS STARTING VALUE
      C     ************************************************************
    16.     DBE=SQRT(DB/DE)
    17.     DEA=SQRT(DE/DA)
    18.     EI=0.5*(EL-DB/DE*BL+SQRT((EL-DB/DE*BL)**2+4.*DB/DE*AI*EK))
    19.     FFI=1.+DE/DA*(EI-EL)/(AI-AL)
    20.     EI=0.5*(EL-DBE*BL+SQRT((EL-DBE*BL)**2+4.*DBE*AI*EK))
    21.     BI=AI*EK/EI
    22.     FII=1.+DEA*(EI-EL)/(AI-AL)
    23.     FIK=FII
```

```
24.          FK=DA*BI/EK+DA*DE*EI/DB/EK+DE
25.          FII=FII*(-1.)
26.          FII=FII*(AI-AL)/FK/SQRT(3.1416)*DA
27.          FFF=FII
28.          FIJ=FFF*DE/DB
29.          N=1
30.          VV(1)=0.
31.          EE(1)=EI
32.          BB(1)=BI
33.          DEE(1)=FII
34.          DBB(1)=FIJ
     C    ************************************************************
     C    NUMERICAL INTERATION
35.          DVV=0.01
36.  100     VF=VV(N)
37.          EF=EE(N)
38.          BF=BB(N)
39.          DEF=DEE(N)
40.          DBF=DBB(N)
41.          ED=EI-EL
42.          BD=BI-BL
43.          C1=(DE*DB+DA*DB*BB(N)/EK+DE*DA*EE(N)/EK)/DA
44.          C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
45.          DUE=DEE(N)
46.          DUEE=DBB(N)*C2*(DB*EE(N)/EK-DA*EE(N)/EK)+DEE(N)*C2
            1*(DB+DB*BB(N)/EK+DA*EE(N)/EK)-DBB(N)*DEE(N)*2.
            1*DB/(EK*C1)+2.*DEE(N)/(1.-VV(N))
47.          DUB=DBB(N)
48.          DUBB=DBB(N)*C2*(DE+DE*EE(N)/EK+DA*BB(N)/EK)+DEE(N)
            1*C2*(DE*BB(N)/EK-DA*BB(N)/EK)-2.*DE*DBB(N)*DEE(N)
            1/(C1*EK)+2.*DBB(N)/(1.-VV(N))
49.          DB1=DUB*DVV
50.          DLB1=DUBB*DVV
51.          DE1=DUE*DVV
52.          DLE1=DUEE*DVV
```

```
      VV(N)=VF+DVV/2.
      EE(N)=EF+DE1/2.
      BB(N)=BF+DB1/2.
      DEE(N)=DEF+DLE1/2.
      DBB(N)=DBF+DLB1/2.
      C1=(DE*DB+DA*DB*BB(N)/EK+DE*DA*EE(N)/EK)/DA
      C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
      DUE=DEE(N)
      DUEE=DBB(N)*C2*(DB*EE(N)/EK-DA*EE(N)/EK)+DEE(N)*C2
     1*(DB+DB*BB(N)/EK+DA*EE(N)/EK)-DBB(N)*DEE(N)*2.
     1*DB/(EK*C1)+2.*DEE(N)/(1.-VV(N))
      DUB=DBB(N)
      DUBB=DBB(N)*C2*(DE+DE*EE(N)/EK+DA*BB(N)/EK)+DEE(N)
     1*C2*(DE*BB(N)/EK-DA*BB(N)/EK)-2.*DE*DBB(N)*DEE(N)
     1/(C1*EK)+2.*DBB(N)/(1.-VV(N))
      DB2=DUB*DVV
      DLB2=DUBB*DVV
      DE2=DUE*DVV
      DLE2=DUEE*DVV
      VV(N)=VF+DVV/2.
      EE(N)=EF+DE2/2.
      BB(N)=BF+DB2/2.
      DEE(N)=DEF+DLE2/2.
      DBB(N)=DBF+DLB2/2.
      C1=(DE*DB+DA*DB*BB(N)/EK+DE*DA*EE(N)/EK)/DA
      C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
      DUE=DEE(N)
      DUEE=DBB(N)*C2*(DB*EE(N)/EK-DA*EE(N)/EK)+DEE(N)*C2
     1*(DB+DB*BB(N)/EK+DA*EE(N)/EK)-DBB(N)*DEE(N)*2.
     1*DB/(EK*C1)+2.*DEE(N)/(1.-VV(N))
      DUB=DBB(N)
      DUBB=DBB(N)*C2*(DE+DE*EE(N)/EK+DA*BB(N)/EK)+DEE(N)
     1*C2*(DE*BB(N)/EK-DA*BB(N)/EK)-2.*DE*DBB(N)*DEE(N)
     1/(C1*EK)+2.*DBB(N)/(1.-VV(N))
```

```
      DB3=DUB*DVV
      DLB3=DUBB*DVV
      DE3=DUE*DVV
      DLE3=DUEE*DVV
      VV(N)=VF+DVV
      EE(N)=EF+DE3
      BB(N)=BF+DB3
      DEE(N)=DEF+DLE3
      DBB(N)=DBF+DLB3
      C1=(DE*DB+DA*DB*BB(N)/EK+DE*DA*EE(N)/EK)/DA
      C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
      DUE=DEE(N)
      DUEE=DBB(N)*C2*(DB*EE(N)/EK-DA*EE(N)/EK)+DEE(N)*C2
     1*(DB+DB*BB(N)/EK+DA*EE(N)/EK)-DBB(N)*DEE(N)*2.
     1*DB/(EK*C1)+2.*DEE(N)/(1.-VV(N))
      DUB=DBB(N)
      DUBB=DBB(N)*C2*(DE+DE*EE(N)/EK+DA*BB(N)/EK)+DEE(N)
     1*C2*(DE*BB(N)/EK-DA*BB(N)/EK)-2.*DE*DBB(N)*DEE(N)
     1/(C1*EK)+2.*DBB(N)/(1.-VV(N))
      DB4=DUB*DVV
      DLB4=DUBB*DVV
      DE4=DUE*DVV
      DLE4=DUEE*DVV
      DEX=(DE1+2.*DE2+2.*DE3+DE4)/6.
      DBX=(DB1+2.*DB2+2.*DB3+DB4)/6.
      DEEX=(DLE1+2.*DLE2+2.*DLE3+DLE4)/6.
      DBBX=(DLB1+2.*DLB2+2.*DLB3+DLB4)/6.
      FAC=FII*(-1.)*FK*SQRT(3.1416)/DA/(AI-AL)
      N=N+1
      EFF(N)=(EI-EF)/ED
      BFF(N)=(BI-BF)/BD
      VV(N)=VF+DVV
      EE(N)=EF+DEX
      BB(N)=BF+DBX
```

```
      DEE(N)=DEF+DEEX
      DBB(N)=DBF+DBBX
      IF(N.LT.60) GO TO 100
      Z=L
      I=N-2
      K=N-1
      EFD(N)=EFF(N)-EFF(K)
      BFD(N)=BFF(N)-BFF(K)
      EFD(K)=EFF(K)-EFF(I)
      BFD(K)=BFF(K)-BFF(I)
      BFDD=ABS(5.*BFD(K))
      IF(J.EQ.4) GO TO 80
      IF(BFD(N).GT.0..AND.ABS(BFD(N)).LT.BFDD) GO TO 50
80    BB(K)=BB(I)
      BB(N)=BB(K)
      DBB(K)=DBB(I)
      DBB(N)=DBB(K)
      J=4
C     ************************************************************
C     ITERATION
C     ************************************************************
50    IF(L.EQ.2) GO TO 20
      IF(L.EQ.3) GO TO 30
      IF(EFD(N).LT.0..OR.EFD(N).GT.5.*EFD(K)) GO TO 60
      IF(EFF(N).GE.1.0) GO TO 70
      IF(N.LT.101) GO TO 100
60    L=3
      FII=FII*1.03
      GO TO 200
70    L=2
      FII=FII*0.97
      GO TO 200
20    K=N-1
      IF(EFF(N).GE.1.1) GO TO 300
```

```
140.          IF(EFF(N).GE.1.0) GO TO 70
141.          IF(EFD(N).LE.0.) GO TO 300
142.          IF(N.LT.101) GO TO 100
143.          GO TO 300
144.  30      K=N-1
145.          IF(EFD(N).LE.0.) GO TO 60
146.          IF(EFF(N).GE.1.1) GO TO 60
147.          IF(EFF(N).GE.1.0) GO TO 300
148.          IF(N.GT.101) GO TO 60
149.          GO TO 100
150.  300     M=M+1
151.          K=M-1
152.          J=N-1
153.          EFL=EFF(J)
154.          BFL=BFF(J)
155.          PRINT 1,VF,EFL,BFL,FAC,FIK,EI
156.          ERR(M)=ABS(1.0-EFF(J))+ABS(1.0-BFF(J))
157.          IF(M.GT.2) GO TO 3
158.          EI=EI*0.95
159.          FII=FFF
160.          L=1
161.          GO TO 200
162.  3       IF(M.GT.3) GO TO 5
163.          IF(ERR(M).GT.ERR(K)) GO TO 8
164.          Y=1.
165.          EI=EI*0.95
166.          FII=FFF
167.          L=1
168.          GO TO 200
169.  8       EI=EI*1.05
170.          Y=2.
171.          FII=FFF
172.          L=1
173.          GO TO 200
174.  5       IF(ERR(M).GT.ERR(K)) GO TO 7
175.          IF(Y.EQ.1.) GO TO 6
```

```
      EI=EI*1.05
      FII=FFF
      L=1
      GO TO 200
  6   EI=EI*0.95
      FII=FFF
      L=1
200   N=1
      J=1
      FIJ=FII*DE/DB
      BI=AI*EK/EI
      VV(1)=0.
      EE(1)=EI
      BB(1)=BI
      DEE(1)=FII
      DBB(1)=FIJ
      GO TO 100
  7   PRINT 1,VF,EFL,BFL,FAC,FIK,EI
      RDBA=DB/DA
      RDEA=DE/DA
      EIA=EK/AI
      ALA=AL/AI
      BLA=BL/AI
      PRINT 2,RDBA,RDEA,EIA,ALA,BLA,FFI
  2   FORMAT(6(5X,E16.7)//)
      EK=EK*10.0
      IF(EK.LT.400.) GO TO 600
      STOP
      END
```

```
      C     ************************************************************
      C     FOR MASS TRANSFER WITH REACTION A+B=C+D
      C     ************************************************************
            DIMENSION VV(110),AA(110),BB(110),CC(110),DD(110)
 2.         DIMENSION DAA(110),DBB(110),DCC(110),DDD(110)
 3.         DIMENSION ERR(110),BFF(110),CFF(110),DFF(110),BFD(110)
 4.         DIMENSION CFD(101),DFD(101),PRR(101)
 5. 1       FORMAT(6(5X,E16.7))
 6. 600     MM=1
      C     ************************************************************
      C     EQUILIBRIUM CONSTANT;  EK.
      C     DIFFUSIVITIES;  DA,DB,DC,DOD.
      C     INTERFACE CONCENTRATIONS;  AI,BI,CI,DI.
      C     BULK CONCENTRATIONS;  AL,BL,CL,DL.
      C     ************************************************************
 7.         EK=0.1
 8.         X=1.
 9.         J=1
10.         L=1
11.         M=1
12.         AI=1.0
13.         BL=10.0*AI
14.         DL=0.
15.         AL=0.3
16.         CL=0.
17.         DA=1.0
18.         DB=2.0
19.         DC=2.0
20.         DOD=2.0
      C     ************************************************************
      C     CALCULATE APPROXIMATE SOLUTION AS STARTING VALUE
      C     ************************************************************
21.         PDC=DOD/DC
22.         PDB=DOD/DB
```

```
      CI=(-(PDC*DL+PDB*EK*AI-CL)+SQRT((PDC*DL+PDB*EK*AI-CL)
     1**2+4.*(PDC*BL*EK*AI+PDB*CL*EK*AI)))/2.
      FFI=1.+(DC/DA)*(CI-CL)/(AI-AL)
      RDC=SQRT(DOD/DC)
      RDB=SQRT(DOD/DB)
      CI=(-(RDC*DL+RDB*EK*AI-CL)+SQRT((RDC*DL+RDB*EK*AI-CL)
     1**2+4.*(RDC*BL*EK*AI+RDB*CL*EK*AI)))/2.
      FII=1.+SQRT(DC/DA)*(CI-CL)/(AI-AL)
      DI=AI*EK*(BL+RDB*DL)/(CI+AI*EK*RDB)
      BI=CI*DI/(AI*EK)
      FIH=FII
      FK=+(DA*DB*CI/(DOD*EK*BI)+DA*DB*DI/(DC*EK*BI)
     1+DA*AI/BI+DB)
      FII=FII*(AI-AL)*DA/FK/SQRT(3.1416)
      FFF=FII
      FIJ=-FII*DB/DC
      FIK=-FII*DB/DOD
C     ***************************************************************
C     NUMERICAL INTERATION
C     ***************************************************************
      DVV=0.01
      N=1
      VV(1)=0.
      BB(1)=BI
      CC(1)=CI
      DD(1)=DI
      AA(1)=AI
      DBB(1)=FII
      DCC(1)=FIJ
      DDD(1)=FIK
      DAA(1)=CC(1)*DDD(1)/(EK*BB(1))+DD(1)*DCC(1)/(EK*BB(1))
     1-AA(1)*DBB(1)/BB(1)
100   VF=VV(N)
      BF=BB(N)
      CF=CC(N)
```

```
51.         DF=DD(N)
52.         AF=CF*DF/(EK*BI)
53.         BDA=BI-BL
54.         CDA=CI-CL
55.         DDA=DI-DL
56.         DBF=DBB(N)
57.         DCF=DCC(N)
58.         DDF=DDD(N)
59.         DAF=CF*DDF/(EK*BF)+DF*DCF/(EK*BF)-AF*DBF/BF
60.         C1=DB*DC*CC(N)/(EK*BB(N))+DB*DOD*DD(N)/(EK*BB(N))
           1+DB*DC*DOD/DA+DC*DOD*AA(N)/BB(N)
61.         C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
62.         C2C=VV(N)/(2.00*(1.-VV(N))**3)*(-1.)
63.         DUB=DBB(N)
64.         DUBB=C2*DBB(N)*(DA*DC*CC(N)/(EK*BB(N))+DA*DOD*DD(N)
           1/(EK*BB(N))+DC*DOD*AA(N)/BB(N)+DC*DOD)+C2*DDD(N)*(DA
           1*DC*CC(N)/(EK*BB(N))-DC*DOD*CC(N)/(EK*BB(N)))+C2*DCC(N)
           1*(DOD*(DA-DC)*DD(N)/(EK*BB(N)))-2.*DOD*DC*DAA(N)*DBB(N)
           1/C1/BB(N)+2.*DC*DOD*DCC(N)*DDD(N)/C1/EK/BB(N)
           1+2.*DBB(N)/(1.-VV(N))
65.         DUC=DCC(N)
66.         DUCC=C2C*DBB(N)*(DA/DC-DA*DB*CC(N)/(C1*EK*BB(N))
           1-DA*DB*DOD*DD(N)/(DC*C1*BB(N)*EK)-DB*DOD*DD(N)/(C1
           1*BB(N))-DB*DOD/C1)+C2C*DCC(N)*(DA/DC-DB*DOD*(DA-DC)
           1*DD(N)/(DC*C1*BB(N)*EK))-C2C*DDD(N)*(DA*DB*CC(N)/(C1
           1*EK*BB(N))-DB*DOD*CC(N)/(C1*EK*BB(N)))+2.*DB*DOD*DAA(N)
           1*DBB(N)/(C1*1.*BB(N))-2.*DB*DOD*DCC(N)*DDD(N)/(
           1C1*EK*BB(N))+2.*DCC(N)/(1.-VV(N))
67.         DUD=DDD(N)
68.         DUDD=C2*DBB(N)*(DA*DC*AA(N)/BB(N)-DB*DC*AA(N)/BB(N))
           1-C2*DCC(N)*(DB*(DA-DC)*DD(N)/(EK*BB(N)))+C2*DDD(N)
           1*(DA*DB*DD(N)/(EK*BB(N))+DB*DC+DA*DC*AA(N)/BB(N)
           1+DC*DB*CC(N)/(EK*BB(N)))+2.*DB*DC*DAA(N)*DBB(N)
           1/(C1*BB(N))-2.*DB*DC*DCC(N)*DDD(N)/(C1
           1*EK*BB(N))+2.*DDD(N)/(1.-VV(N))
```

```
69.         DB1=DUB*DVV
70.         DLB1=DUBB*DVV
71.         DC1=DUC*DVV
72.         DLC1=DUCC*DVV
73.         DD1=DUD*DVV
74.         DLD1=DUDD*DVV
75.         VV(N)=VF+DVV/2.
76.         BB(N)=BF+DB1/2.
77.         CC(N)=CF+DC1/2.
78.         DD(N)=DF+DD1/2.
79.         AA(N)=CC(N)*DD(N)/(EK*BB(N))
80.         DBB(N)=DBF+DLB1/2.
81.         DCC(N)=DCF+DLC1/2.
82.         DDD(N)=DDF+DLD1/2.
83.         DAA(N)=CC(N)*DDD(N)/(EK*BB(N))+DD(N)*DCC(N)/
           1(EK*BB(N))-AA(N)*DBB(N)/BB(N)
84.         C1=DB*DC*CC(N)/(EK*BB(N))+DB*DOD*DD(N)/(EK*BB(N))
           1+DB*DC*DOD/DA+DC*DOD*AA(N)/BB(N)
85.         C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
86.         C2C=VV(N)/(2.00*(1.-VV(N))**3)*(-1.)
87.         DUB=DBB(N)
88.         DUBB=C2*DBB(N)*(DA*DC*CC(N)/(EK*BB(N))+DA*DOD*DD(N)
           1/(EK*BB(N))+DC*DOD*AA(N)/BB(N)+DC*DOD)+C2*DDD(N)*(DA
           1*DC*CC(N)/(EK*BB(N))-DC*DOD*CC(N)/(EK*BB(N)))+C2*DCC(N)
           1*(DOD*(DA-DC)*DD(N)/(EK*BB(N)))-2.*DOD*DC*DAA(N)*DBB(N)
           1/C1/BB(N)+2.*DC*DOD*DCC(N)*DDD(N)/C1/EK/BB(N)
           1+2.*DBB(N)/(1.-VV(N))
89.         DUC=DCC(N)
90.         DUCC=C2C*DBB(N)*(DA/DC-DA*DB*CC(N)/(C1*EK*BB(N))
           1-DA*DB*DOD*DD(N)/(DC*C1*BB(N)*EK)-DB*DOD*DD(N)/(C1
           1*BB(N))-DB*DOD/C1)+C2C*DCC(N)*(DA/DC-DB*DOD*(DA-DC)
           1*DD(N)/(DC*C1*BB(N)*EK))-C2C*DDD(N)*(DA*DB*CC(N)/(C1
           1*EK*BB(N))-DB*DOD*CC(N)/(C1*EK*BB(N)))+2.*DB*DOD*DAA(N)
```

```
     1*DBB(N)/(C1*1.*BB(N))-2.*DB*DOD*DCC(N)*DDD(N)/(
     1C1*EK*BB(N))+2.*DCC(N)/(1.-VV(N))
 91.  DUD=DDD(N)
 92.  DUDD=C2*DBB(N)*(DA*DC*AA(N)/BB(N)-DB*DC*AA(N)/BB(N))
     1-C2*DCC(N)*(DB*(DA-DC)*DD(N)/(EK*BB(N)))+C2*DDD(N)
     1*(DA*DB*DD(N)/(EK*BB(N))+DB*DC+DA*DC*AA(N)/BB(N)
     1+DC*DB*CC(N)/(EK*BB(N)))+2.*DB*DC*DAA(N)*DBB(N)
     1/(C1*BB(N))-2.*DB*DC*DCC(N)*DDD(N)/(C1
     1*EK*BB(N))+2.*DDD(N)/(1.-VV(N))
 93.  DB2=DUB*DVV
 94.  DLB2=DUBB*DVV
 95.  DC2=DUC*DVV
 96.  DLC2=DUCC*DVV
 97.  DD2=DUD*DVV
 98.  DLD2=DUDD*DVV
 99.  VV(N)=VF+DVV/2.
100.  BB(N)=BF+DB2/2.
101.  CC(N)=CF+DC2/2.
102.  DD(N)=DF+DD2/2.
103.  AA(N)=CC(N)*DD(N)/(EK*BB(N))
104.  DBB(N)=DBF+DLB2/2.
105.  DCC(N)=DCF+DLC2/2.
106.  DDD(N)=DDF+DLD2/2.
107.  DAA(N)=CC(N)*DDD(N)/(EK*BB(N))+DD(N)*DCC(N)/
     1(EK*BB(N))-AA(N)*DBB(N)/BB(N)
108.  C1=DB*DC*CC(N)/(EK*BB(N))+DB*DOD*DD(N)/(EK*BB(N))
     1+DB*DC*DOD/DA+DC*DOD*AA(N)/BB(N)
109.  C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
110.  C2C=VV(N)/(2.00*(1.-VV(N))**3)*(-1.)
111.  DUB=DBB(N)
112.  DUBB=C2*DBB(N)*(DA*DC*CC(N)/(EK*BB(N))+DA*DOD*DD(N)
     1/(EK*BB(N))+DC*DOD*AA(N)/BB(N)+DC*DOD)+C2*DDD(N)*(DA
     1*DC*CC(N)/(EK*BB(N))-DC*DOD*CC(N)/(EK*BB(N)))+C2*DCC(N)
     1*(DOD*(DA-DC)*DD(N)/(EK*BB(N)))-2.*DOD*DC*DAA(N)*DBB(N)
     1/C1/BB(N)+2.*DC*DOD*DCC(N)*DDD(N)/C1/EK/BB(N)
```

```
     1+2.*DBB(N)/(1.-VV(N))
113.  DUC=DCC(N)
114.  DUCC=C2C*DBB(N)*(DA/DC-DA*DB*CC(N)/(C1*EK*BB(N))
     1-DA*DB*DOD*DD(N)/(DC*C1*BB(N)*EK)-DB*DOD*DD(N)/(C1
     1*BB(N))-DB*DOD/C1)+C2C*DCC(N)*(DA/DC-DB*DOD*(DA-DC)
     1*DD(N)/(DC*C1*BB(N)*EK))-C2C*DDD(N)*(DA*DB*CC(N)/(C1
     1*EK*BB(N))-DB*DOD*CC(N)/(C1*EK*BB(N)))+2.*DB*DOD*DAA(N)
     1*DBB(N)/(C1*1.*BB(N))-2.*DB*DOD*DCC(N)*DDD(N)/(
     1C1*EK*BB(N))+2.*DCC(N)/(1.-VV(N))
115.  DUD=DDD(N)
116.  DUDD=C2*DBB(N)*(DA*DC*AA(N)/BB(N)-DB*DC*AA(N)/BB(N))
     1-C2*DCC(N)*(DB*(DA-DC)*DD(N)/(EK*BB(N)))+C2*DDD(N)
     1*(DA*DB*DD(N)/(EK*BB(N))+DB*DC+DA*DC*AA(N)/BB(N)
     1+DC*DB*CC(N)/(EK*BB(N)))+2.*DB*DC*DAA(N)*DBB(N)
     1/(C1*BB(N))-2.*DB*DC*DCC(N)*DDD(N)/(C1
     1*EK*BB(N))+2.*DDD(N)/(1.-VV(N))
117.  DB3=DUB*DVV
118.  DLB3=DUBB*DVV
119.  DC3=DUC*DVV
120.  DLC3=DUCC*DVV
121.  DD3=DUD*DVV
122.  DLD3=DUDD*DVV
123.  VV(N)=VF+DVV
124.  BB(N)=BF+DB3
125.  CC(N)=CF+DC3
126.  DD(N)=DF+DD3
127.  AA(N)=CC(N)*DD(N)/(EK*BB(N))
128.  DBB(N)=DBF+DLB3
129.  DCC(N)=DCF+DLC3
130.  DDD(N)=DDF+DLD3
131.  DAA(N)=CC(N)*DDD(N)/(EK*BB(N))+DD(N)*DCC(N)/
     1(EK*BB(N))-AA(N)*DBB(N)/BB(N)
132.  C1=DB*DC*CC(N)/(EK*BB(N))+DB*DOD*DD(N)/(EK*BB(N))
     1+DB*DC*DOD/DA+DC*DOD*AA(N)/BB(N)
133.  C2=VV(N)/(2.*C1*(1.-VV(N))**3)*(-1.)
```

```
134.        C2C=VV(N)/(2.00*(1.-VV(N))**3)*(-1.)
135.        DUB=DBB(N)
136.        DUBB=C2*DBB(N)*(DA*DC*CC(N)/(EK*BB(N))+DA*DOD*DD(N)
           1/(EK*BB(N))+DC*DOD*AA(N)/BB(N)+DC*DOD)+C2*DDD(N)*(DA
           1*DC*CC(N)/(EK*BB(N))-DC*DOD*CC(N)/(EK*BB(N)))+C2*DCC(N)
           1*(DOD*(DA-DC)*DD(N)/(EK*BB(N)))-2.*DOD*DC*DAA(N)*DBB(N)
           1/C1/BB(N)+2.*DC*DOD*DCC(N)*DDD(N)/C1/EK/BB(N)
           1+2.*DBB(N)/(1.-VV(N))
137.        DUC=DCC(N)
138.        DUCC=C2C*DBB(N)*(DA/DC-DA*DB*CC(N)/(C1*EK*BB(N))
           1-DA*DB*DOD*DD(N)/(DC*C1*BB(N)*EK)-DB*DOD*DD(N)/(C1
           1*BB(N))-DB*DOD/C1)+C2C*DCC(N)*(DA/DC-DB*DOD*(DA-DC)
           1*DD(N)/(DC*C1*BB(N)*EK))-C2C*DDD(N)*(DA*DB*CC(N)/(C1
           1*EK*BB(N))-DB*DOD*CC(N)/(C1*EK*BB(N)))+2.*DB*DOD*DAA(N)
           1*DBB(N)/(C1*1.*BB(N))-2.*DB*DOD*DCC(N)*DDD(N)/(
           1C1*EK*BB(N))+2.*DCC(N)/(1.-VV(N))
139.        DUD=DDD(N)
140.        DUDD=C2*DBB(N)*(DA*DC*AA(N)/BB(N)-DB*DC*AA(N)/BB(N))
           1-C2*DCC(N)*(DB*(DA-DC)*DD(N)/(EK*BB(N)))+C2*DDD(N)
           1*(DA*DB*DD(N)/(EK*BB(N))+DB*DC+DA*DC*AA(N)/BB(N)
           1+DC*DB*CC(N)/(EK*BB(N)))+2.*DB*DC*DAA(N)*DBB(N)
           1/(C1*BB(N))-2.*DB*DC*DCC(N)*DDD(N)/(C1
           1*EK*BB(N))+2.*DDD(N)/(1.-VV(N))
141.        DB4=DUB*DVV
142.        DLB4=DUBB*DVV
143.        DC4=DUC*DVV
144.        DLC4=DUCC*DVV
145.        DD4=DUD*DVV
146.        DLD4=DUDD*DVV
147.        DBX=(DB1+2.*DB2+2.*DB3+DB4)/6.
148.        DCX=(DC1+2.*DC2+2.*DC3+DC4)/6.
149.        DDX=(DD1+2.*DD2+2.*DD3+DD4)/6.
150.        DBBX=(DLB1+2.*DLB2+2.*DLB3+DLB4)/6.
151.        DCCX=(DLC1+2.*DLC2+2.*DLC3+DLC4)/6.
152.        DDDX=(DLD1+2.*DLD2+2.*DLD3+DLD4)/6.
```

```
153.          FAC=FII*FK*SQRT(3.1416)/(AI-AL)/DA
154.          N=N+1
155.          BFF(N)=(BI-BF)/BDA
156.          CFF(N)=(CI-CF)/CDA
157.          DFF(N)=(DI-DF)/DDA
158.          VV(N)=VF+DVV
159.          BB(N)=BF+DBX
160.          CC(N)=CF+DCX
161.          DD(N)=DF+DDX
162.          DBB(N)=DBF+DBBX
163.          DCC(N)=DCF+DCCX
164.          DDD(N)=DDF+DDDX
165.          AA(N)=CC(N)*DD(N)/(EK*BB(N))
166.          DAA(N)=CC(N)*DDD(N)/(EK*BB(N))+DD(N)*DCC(N)/
             1(EK*BB(N))-AA(N)*DBB(N)/BB(N)
167.          IF(N.LT.30) GO TO 100
168.          I=N-2
169.          K=N-1
170.          BFD(N)=BFF(N)-BFF(K)
171.          CFD(N)=CFF(N)-CFF(K)
172.          DFD(N)=DFF(N)-DFF(K)
173.          BFD(K)=BFF(K)-BFF(I)
174.          CFD(K)=CFF(K)-CFF(I)
175.          DFD(K)=DFF(K)-DFF(I)
176.          CFDD=ABS(5.*CFD(K))
177.          DFDD=ABS(5.*DFD(K))
178.          IF(J.EQ.4) GO TO 80
179.          IF(CFD(N).GT.0..AND.ABS(CFD(N)).LT.CFDD) GO TO 90
      C     ************************************************************
      C     ITERATION
      C     ************************************************************
180.  80      CC(K)=CC(I)
181.          CC(N)=CC(K)
182.          DCC(K)=DCC(I)
183.          DCC(N)=DCC(K)
184.          J=4
```

```
185. 90     IF(X.EQ.4.) GO TO 91
186.        IF(DFD(N).GT.0..AND.ABS(DFD(N)).LT.DFDD) GO TO 50
187. 91     DD(K)=DD(I)
188.        DD(N)=DD(K)
189.        DDD(K)=DDD(I)
190.        DDD(N)=DDD(K)
191.        X=4.
192. 50     IF(L.EQ.2) GO TO 20
193.        IF(L.EQ.3) GO TO 30
194.        IF(BFD(N).LT.0..OR.BFD(N).GT.5.*BFD(K)) GO TO 60
195.        IF(BFF(N).GE.1.0) GO TO 70
196.        IF(N.LT.101) GO TO 100
197. 60     L=3
198.        FII=FII*1.02
199.        GO TO 200
200. 70     L=2
201.        FII=FII*0.98
202.        GO TO 200
203. 20     K=N-1
204.        IF(BFF(N).GE.1.1) GO TO 300
205.        IF(BFF(N).GE.1.0) GO TO 70
206.        IF(BFD(N).LE.0.) GO TO 300
207.        IF(N.LT.101) GO TO 100
208.        GO TO 300
209. 30     K=N-1
210.        IF(BFD(N).LE.0.) GO TO 60
211.        IF(BFF(N).GE.1.1) GO TO 60
212.        IF(BFF(N).GE.1.0) GO TO 300
213.        IF(N.LT.101) GO TO 100
214. 300    M=M+1
215.        K=M-1
216.        J=N-1
217.        PRINT 1,VF,BFF(J),CFF(J),DFF(J),FAC,FII
```

```
      ERR(M)=ABS(1.-BFF(J))+ABS(1.-CFF(J))+ABS(1.-DFF(J))
      IF(M.GT.2) GO TO 3
      BI=BI*0.98
      FII=FFF
      L=1
      GO TO 200
3     IF(M.GT.3) GO TO 5
      IF(ERR(M).GT.ERR(K)) GO TO 8
      Y=1.
      BI=BI*0.98
      FII=FFF
      L=1
      GO TO 200
8     BI=BI*1.02
      Y=2.
      FII=FFF
      L=1
      GO TO 200
5     IF(ERR(M).GT.ERR(K)) GO TO 7
      IF(Y.EQ.1.) GO TO 6
      BI=BI*1.02
      FII=FFF
      L=1
      GO TO 200
6     BI=BI*0.98
      FII=FFF
      L=1
      GO TO 200
7     MM=MM+1
      KK=MM-1
      J=N-1
      PRINT 2,VF,BFF(J),CFF(J),DFF(J),FAC,FIH
2     FORMAT(6(5X,E16.7),//)
      PRR(MM)=ABS(1.-BFF(J))+ABS(1.-CFF(J))+ABS(1.-DFF(J))
      IF(MM.GT.2) GO TO 31
```

```
      CI=CI*0.98
      FII=FFF
      M=1
      L=1
      GO TO 200
31    IF(MM.GT.3) GO TO 51
      IF(PRR(MM).GT.PRR(KK)) GO TO 81
      KY=1
      CI=CI*0.98
      FII=FFF
      M=1
      L=1
      GO TO 200
81    CI=CI*1.02
      KY=2
      FII=FFF
      M=1
      L=1
      GO TO 200
51    IF(PRR(MM).GT.PRR(KK)) GO TO 71
      IF(KY.EQ.1) GO TO 61
      CI=CI*1.02
      FII=FFF
      M=1
      L=1
      GO TO 200
61    CI=CI*0.98
      FII=FFF
      M=1
      L=1
200   N=1
      X=1.
      J=1
      FIJ=-FII*DB/DC
      FIK=-FII*DB/DOD
```

```
      VV(1)=0.
      BB(1)=BI
      CC(1)=CI
      DD(1)=DI
      AA(1)=AI
      DBB(1)=FII
      DCC(1)=FIJ
      DDD(1)=FIK
      DAA(1)=CC(1)*DDD(1)/(EK*BB(1))+DD(1)*DCC(1)/(EK*BB(1))
     1-AA(1)*DBB(1)/BB(1)
      GO TO 100
71    PRINT 1,VF,BFF(J),CFF(J),DFF(J),FAC,FIH
      RDCA=DC/DA
      RALA=AL/AI
      RDDC=DOD*DL/DC/AI
      RDDK=DOD/DB*EK
      RCLA=CL/AI
      PRINT 12,RDCA,RALA,RDDC,RDDK,RCLA,FFI
12    FORMAT(6(5X,E16.7)//)
      EK=EK*10.0
      IF(EK.LT.4000.) GO TO 600
      STOP
      END
```

APPENDIX D

COMPUTER PROGRAM FOR APPROXIMATE SURFACE RENEWAL THEORY WITH MULTIPLE EQUILIBRIUM REACTIONS

```
C     ****************************************************************
C     FOR SO2-NAOH OR SO2-NA2SO3 SYSTEM
C     ****************************************************************
C       A=H2SO3,  B=H,  C=HSO3,  D=SO3,  E=OH
C     A=B+C
C     C=B+D
C       AK=BC/A,  BK=DB/C,  CK=BE
C     ****************************************************************
C     DATA
C     ****************************************************************
C     EQUILIBRIUM CONSTANTS
C     ****************************************************************
        AK=1.3E-2
2.      BK=6.2E-8
3.      CK=1.0E-14
C     ****************************************************************
C     DIFFUSIVITIES
C     ****************************************************************
4.      DA=SQRT(1.76)
5.      DB=SQRT(9.31)
6.      DC=SQRT(1.33)
7.      DD=SQRT(0.958)
8.      DE=SQRT(5.253)
C     ****************************************************************
C     IONIC STRENGTH
C     ****************************************************************
9.      ZI=0.3
C     ****************************************************************
C     INTERFACE SO2 CONCENTRATION
C     ****************************************************************
10.     AI1=0.1
11.     AI=AI1
C     ****************************************************************
C     BULK OH CONCENTRATION
C     ****************************************************************
```

```
12.          E0=1.0E-5
     C    ***************************************************************
     C    TOTAL SULFITES
     C    ***************************************************************
13.          TSO=5.0*AI
     C    ***************************************************************
     C    ACTIVITY COEFFICIENTS
     C    ***************************************************************
14.          ZII=0.3**0.5
15.          ACA=EXP(2.303*(0.076*ZI))
16.          ACB=EXP(2.303*(0.512)*(-ZII/(1.+0.312*6.0
            U*ZII)+0.4*ZI))
17.          ACC=EXP(2.303*0.512*(-ZII/(1.+0.312*4.5*ZII)))
18.          ACD=EXP(2.303*0.512*4*(-ZII/(1.+0.312*4.5*ZII)))
19.          ACE=EXP(2.303*0.512*(-ZII/(1.+0.312*3.*ZII)+0.3*ZI))
     C    ***************************************************************
     C    EFFECTIVE EQUILIBRIUM CONSTANTS
     C    ***************************************************************
20.          AK=AK*ACA/(ACB*ACC)
21.          BK=BK*ACC/(ACB*ACD)
22.          CK=CK/(ACB*ACE)
     C    ***************************************************************
     C    BULK CONCENTRATIONS
     C    ***************************************************************
23.  20      B0=CK/E0
24.          D0=TSO
25.          C0=D0*B0/BK
26.          A0=B0*C0/AK
27.          PRINT 3,AI,TSO,B0,C0
28.  3       FORMAT(1H ,12X,4(E12.4,3X))
     C    ***************************************************************
     C    TRIAL AND ERROR
     C    ***************************************************************
29.          BI=0.0005*AI
30.  100     FX=DB*(BI-B0)-DC*(AI*AK/BI-C0)-2.*DD*(AI*AK*BK/(BI*BI)-D0)
```

```
        1-DE*(CK/BI-E0)
C     ****************************************************************
C     INTERFACE CONCENTRATIONS
C     ****************************************************************
31.       CI=AI*AK/BI
32.       DI=CI*BK/BI
33.       EI=CK/BI
C     ****************************************************************
C     MASS TRANSFER ENHANCEMENT FACTOR
C     ****************************************************************
34.       EN1=DC*(CI-C0)/DA/(AI-A0)
35.       EN2=DD*(DI-D0)/DA/(AI-A0)
36.       EN3=0.
37.       ENT=1.+EN1+EN2+EN3
38.       IF(FX.GE.0.) GO TO 10
39.       BI=BI*1.01
40.       GO TO 100
41. 10    PRINT 2,FX,AI,BI,CI,DI,EN1,EN2,EN3,ENT
42. 2     FORMAT(1H,9(E12.4,3X)//)
43. 60    STOP
44.       END
```

```
C     ***************************************************************
C     FOR SO2-ADIPIC ACID SYSTEM
C     ***************************************************************
C     A=H2SO3   ,B=H,   C=HSO3   , D=A,   E=HA,   F=H2A,   G=SO3
C     A=B+C
C     C=B+G
C     E=B+D
C     F=B+E
C     AK=BC/A   ,BK=BG/C   ,CK=BD/E,   DK=BE/F
C     ***************************************************************
C     DATA
C     ***************************************************************
C     EQUILIBRIUM CONSTANTS
C     ***************************************************************
        AK=1.3E-2
2.      BK=6.2E-8
3.      CK=3.82E-6
4.      DK=3.87E-5
C     ***************************************************************
C     DIFFUSIVITIES
C     ***************************************************************
5.      DA=SQRT(1.76)
6.      DB=SQRT(9.31)
7.      DC=SQRT(1.33)
8.      DD=SQRT(0.705)
9.      DE=SQRT(0.720)
10.     DF=SQRT(0.736)
11.     DG=SQRT(0.958)
C     ***************************************************************
C     INTERFACE SO2 CONCENTRATION
C     ***************************************************************
12.     AI=0.2E-3
C     ***************************************************************
C     IONIC STRENGTH
C     ***************************************************************
```

```
13.           ZI=0.3
14.           PH=5.0
      C    ***************************************************************
      C    TOTAL ORGANIC ACID ADDED
      C    ***************************************************************
15.           THA=1.0E-6
      C    ***************************************************************
      C    TOTAL SULFITES
      C    ***************************************************************
16.           TSO=1.0E-2
      C    ***************************************************************
      C    ACTIVITY COEFFICIENTS
      C    ***************************************************************
17.           ZII=0.3**0.5
18.           ACA=EXP(2.303*(0.076*ZI))
19.           ACB=EXP(2.303*(0.512)*(-ZII/(1.+0.312*6.0
     U*ZII)+0.4*ZI))
20.           ACC=EXP(2.303*0.512*(-ZII/(1.+0.312*4.5*ZII)))
21.           ACD=EXP(2.303*0.512*(-ZII/(1.+0.312*3.*ZII)+0.3*ZI)*4.)
22.           ACE=EXP(2.303*0.512*(-ZII/(1.+0.312*3.*ZII)+0.3*ZI))
23.           ACF=EXP(2.303*(0.076*ZI))
24.           ACG=EXP(2.303*0.512*4*(-ZII/(1.+0.312*4.5*ZII)))
      C    ***************************************************************
      C    EFFECTIVE EQUILIBRIUM CONSTANTS
      C    ***************************************************************
25.           AK=AK*ACA/(ACB*ACC)
26.           BK=BK*ACC/(ACB*ACG)
27.           CK=CK*ACE/(ACB*ACD)
28.           DK=DK*ACF/(ACB*ACE)
      C    ***************************************************************
      C    BULK CONCENTRATIONS
      C    ***************************************************************
29.  5        B0=1.0/(10.0**PH)/ACB
30.           J=1
```

```
      C0=TSO/(B0/AK+1.0+BK/B0)
      G0=C0*BK/B0
      A0=B0*C0/AK
      D0=C0*BK/B0
      E0=THA/(CK/B0+1.0+B0/DK)
      F0=B0*E0/DK
      D0=CK*E0/B0
      PRINT 3,A0,B0,C0,D0,E0,F0,G0
3     FORMAT(1H ,15X,7(E12.4,3X))
      I=1
C     ***************************************************************
C     TRIAL AND ERROR
C     ***************************************************************
13    BI=0.5*AI
100   EI=(DF*F0+DE*E0+DD*D0)/(DF*BI/DK+DE+DD*CK/BI)
      DI=EI*CK/BI
      FI=BI*EI/DK
      FX=DB*(BI-B0)-DC*(AK*AI/BI-C0)-2.*DG*(BK*AK*AI
     C/(BI*BI)-G0)+DF*(FI-F0)-DD*(DI-D0)
C     ***************************************************************
C     INTERFACE CONCENTRATIONS
C     ***************************************************************
      EI=BI*DI/CK
      CI=AI*AK/BI
      GI=CI*BK/BI
C     ***************************************************************
C     MASS TRANSFER ENHANCEMENT FACTOR
C     ***************************************************************
      EN=1.+(DB*(BI-B0)-DG*(GI-G0)-DD*(DI-D0)
     C+DF*(FI-F0))/DA/(AI-A0)
      IF(FX.GT.0.) GO TO 6
      BI=BI+0.05*AI
      GO TO 100
6     PRINT 2,FX,AI,BI,CI,DI,EI,FI,GI,EN
2     FORMAT(1H ,9(E12.4,3X)//)
      STOP
      END
```

VITA

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