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MODELING THE SIMULTANEOUS TRANSPORT OF TWO ACID GASES IN TERTIARY AMINES WITH REVERSIBLE REACTIONS

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ABSTRACT

The objective of this work is to develop a model for the simultaneous mass transfer of two acid gases in tertiary amines accompanied by reversible chemical reactions. The model has been applied to the industrially important system of simultaneous absorption or desorption of CO_2 and H_2S in aqueous methyldiethanolamine (MDEA). In most applications the treated gas must be virtually free of H_2S; however, it is often not necessary or economical to remove substantial amounts of CO_2. Hence, selective removal of H_2S from gas streams such as natural or synthetic gases which contain CO_2 is desirable.

In this research a film theory model describing the simultaneous diffusion and reversible reaction of two gases into a reactive liquid has been used to predict the mass transfer enhancement factors of CO_2 and H_2S in aqueous MDEA solutions. The resulting unstable two point boundary value problem has been solved numerically for a range of the dimensionless parameters that characterize an important application for this system.

In studying the simultaneous transport of CO_2 and H_2S, it is found that the reversibility of the reactions, under certain conditions, causes desorption to take place although absorption would be expected on the basis of overall driving forces. This showed that not only enhancement factors larger but also smaller than unity and even negative values are possible.

INTRODUCTION

The problem of simultaneous absorption of two acid gases into a reactive liquid with which one gas reacts instantaneously and the other reacts at a slow but finite rate has important industrial applications. The absorption of CO_2 and H_2S in tertiary alkanolamine solutions is such an application. Ap-

proximate analytical solutions to the nonlinear differential equations which describe this problem are available. The film theory equations were solved approximately by many investigators (Goettler and Pigford (1), Ouwerkerk (2), Onda *et al.*(3), Ramachandran and Sharma (4), Cornelisse *et al.*(5), Hikita *et al.*(6)). These studies differ in the selection of linearized forms for the nonlinear concentration profiles obtained by using different boundary conditions. It should be noted that these approximations lead to different values for the location of the reaction plane and hence enhancement factors. These solutions also tend to be implicit in the enhancement factors and require iterative numerical methods for implementation. Cornelisse *et al.*(7) showed that under certain conditions, due to the reversibility of reactions, enhancement factors both larger and smaller than one as well as negative values are possible.

In this study the film theory equations for the simultaneous absorption of CO_2 and H_2S into aqueous solutions of a tertiary amine, methyldiethanolamine (MDEA), under reversible reaction kinetics are derived and solved numerically. This problem has industrial significance because of the increasing usage of MDEA as a selective absorbent. The model developed here is capable of dealing with any tertiary amine, however, in this work the numerical results are specific for the simultaneous transport of H_2S and CO_2 in aqueous MDEA. The numerical procedure developed can describe the behavior of the system over a wide range of operating conditions.

The reaction of H_2S with tertiary amines involves a proton transfer and under most conditions it is infinitely fast (second-order rate constant $> 10^9$ ml/gmole sec, Haimour *et al.*(8)):

$$R_3N + H_2S \rightleftharpoons R_3NH^+ + HS^- \tag{1}$$

The subsequent reaction:

$$R_3N + HS^- \rightleftharpoons R_3NH^+ + S^= \tag{2}$$

is negligible under the pH conditions considered ($pH < 11$). Since equilibrium corresponding to reaction (1) is established instantaneously, the net rate of H_2S reaction is not defined. Instead a reaction equilibrium relationship is considered which is defined as

$$K_B = \frac{[R_3NH^+][HS^-]}{[R_3N][H_2S]} = \frac{K_{1,B}K_W}{K_{Am}} \tag{3}$$

where $K_{1,B}$ is the first dissociation constant for H_2S, K_{Am} is the amine association constant, and K_W is the water ionization constant. It is assumed that equilibrium is established always and everywhere in the liquid film, including the gas-liquid interface.

The overall stoichiometry for the reaction of CO_2 in aqueous solutions of a tertiary amine is as follows:

$$R_3N + H_2O + CO_2 \rightleftharpoons R_3NH^+ + HCO_3^- \tag{4}$$

The subsequent reaction:

$$R_3N + HCO_3^- \rightleftharpoons R_3NH^+ + CO_3^= \tag{5}$$

is negligible under the pH conditions considered ($pH < 11$). The equilibrium relationship for (4) is defined as follows:

$$K_A = \frac{[R_3NH^+][HCO_3^-]}{[R_3N][CO_2]} = \frac{K_{1,A}}{K_{Am}} \tag{6}$$

where $K_{1,A}$ is the first dissociation constant for H_2CO_3. The equilibrium relationship for CO_2 is satisfied in the bulk of the liquid phase. The equilibrium constants $K_{1,A}, K_{1,B}, K_{Am}$ and K_W are given in Table 1.

MASS TRANSFER MODEL

For convenience symbols will be given to the concentrations of the various species present: $[CO_2], A; [H_2S], B; [R_3N], F; [HCO_3^-], P; [HS^-], S; [R_3NH^+], R$. The model developed in this work satisfies the following set of assumptions and constraints: the interfacial concentrations of dissolved but unreacted A and B are constant and equal to the solubility as determined by Henry's law; the diffusivities are constant; and the concentration gradients of F, R, P, and S are zero at the interface since these components are non-volatile. The steady-state mass balances across the liquid film result in the following dimensionless diffusion-reaction equations:

- Free CO_2 diffusion-reaction balance

$$\frac{d^2a}{dz^2} = M_A(af - a^\circ rp) \tag{7}$$

- Total Amine balance

$$\alpha_0 \frac{d^2r}{dz^2} + \frac{d^2f}{dz^2} = 0 \tag{8}$$

- Total CO_2 balance

$$\alpha_1 \frac{d^2a}{dz^2} + \frac{d^2p}{dz^2} = 0 \tag{9}$$

- Total H_2S balance

$$\alpha_2 \frac{d^2b}{dz^2} + \frac{d^2s}{dz^2} = 0 \tag{10}$$

- Electroneutrality balance

$$\alpha_3 \frac{d^2a}{dz^2} + \alpha_4 \frac{d^2b}{dz^2} + \frac{d^2r}{dz^2} = 0 \tag{11}$$

- H_2S-Amine reaction equilibrium

$$bf = b^\circ sr \tag{12}$$

TABLE 1

Thermodynamic Parameters

Parameter	Correlation	Equilibrium (°C)	Temp.	Reference
K_W	$\log K_W = 8909.483 - 142613.6T^{-1} - 4229.195 \log T + 9.7384T - 0.0129638T^2 + 1.15068 \times 10^{-5}T^3 - 4.602 \times 10^{-9}T^4$	$H_2O = H^+ + OH^-$	0-300	Olofsson and Hepler (14)
K_{Am}	$\log K_{Am} = 14.01 + 0.018T$	$AmH^+ = H^+ + Am$	25-60	Barth, *et al.* (15)
$K_{1,A}$	$\log K_{1,A} = 179.648 + 0.019244T - 67.341 \log T - 7495.441\ T^{-1}$	$CO_2 + H_2O = H^+ + HCO_3^-$	0-250	Read (16)
$K_{1,B}$	$\log K_{1,B} = 19.84 + 930.8T^{-1} - 1.21581 \log T$	$H_2S + OH^- = H_2O + HS^-$	0-300	Barbero, *et al.* (17)
k_{2A}	$k_{2A} = 8.741 \times 10^{12} \exp(-8625/T)$	---------	15-35	Haimour *et al.* (18)

where the dimensionless concentrations are defined as:

$$a = \frac{A}{A_i}, b = \frac{B}{B_i}, f = \frac{F}{F^\circ}, p = \frac{P}{P^\circ}, r = \frac{R}{R^\circ}, s = \frac{S}{S^\circ}$$

and

$$\alpha_0 = \frac{D_R R^\circ}{D_F F^\circ}, \alpha_1 = \frac{D_A A_i}{D_P P^\circ}, \alpha_2 = \frac{D_B B_i}{D_S S^\circ}, \alpha_3 = \frac{D_A A_i}{D_R R^\circ}, \alpha_4 = \frac{D_B B_i}{D_R R^\circ}$$

The boundary conditions are:

at the gas-liquid interface,

$$z = 0, a = 1; b = 1; \frac{df}{dz} = \frac{dr}{dz} = \frac{dp}{dz} = \frac{ds}{dz} = 0 \tag{13}$$

and at the edge of the liquid film,

$$z = 1, a = a^\circ; b = b^\circ; f = r = p = s = 1 \tag{14}$$

The system of Equations (7)-(14) describes the simultaneous absorption of two acid gases into a tertiary Amine solution with reversible chemical reactions. Equations (8)-(11) are linear, homogeneous, second-order ordinary differential equations which can be integrated directly using the boundary conditions (13) and (14). The results of these integrations are:

$$f = 1 + \alpha_0(1 - r) \tag{15}$$

$$p = 1 - \alpha_1(a - a^\circ) - \alpha_1 a'(0)(1 - z) \tag{16}$$

$$s = 1 - \alpha_2(b - b^\circ) - \alpha_2 b'(0)(1 - z) \tag{17}$$

$$r = 1 - \alpha_3(a - a^\circ) - \alpha_4(b - b^\circ) - (\alpha_3 a'(0) + \alpha_4 b'(0))(1 - z) \tag{18}$$

where $a'(0)$ and $b'(0)$ are the concentration gradients of a and b at $z = 0$. Equations (15) and (18) are combined to give:

$$f = 1 + \alpha_0[\alpha_3(a - a^\circ) + \alpha_4(b - b^\circ) + (\alpha_3 a'(0) + \alpha_4 b'(0))(1 - z)] \tag{19}$$

Substitution of Equations (16), (18) and (19) into Equation (7) gives in general form:

$$\frac{d^2 a}{dz^2} = g_1(z, a, b) \tag{20}$$

And Equations (17), (18) and (19) can be substituted into Equation (12) to give:

$$\begin{aligned} b = &\{b^\circ[1 - \alpha_2(b - b^\circ) - \alpha_2 b'(0)(1 - z)] \\ &\times[1 - \alpha_3(a - a^\circ) - \alpha_4(b - b^\circ) - (\alpha_3 a'(0) + \alpha_4 b'(0))(1 - z)]\} \\ &/\{1 + \alpha_0[\alpha_3(a - a^\circ) + \alpha_4(b - b^\circ) + (\alpha_3 a'(0) + \alpha_4 b'(0))(1 - z)]\} \end{aligned} \tag{21}$$

Differentiation of b with respect to z yields:

$$\frac{db}{dz} = \left[\alpha_2 b'(0) rf + \left(\alpha_3 a'(0) + \alpha_4 b'(0) - \alpha_3 \frac{da}{dz}\right) sf + \alpha_0 \left(\alpha_3 a'(0) + \alpha_4 b'(0) - \alpha_3 \frac{da}{dz}\right) rs\right] / \left[\frac{f^2}{b^\circ} + \alpha_2 rf + \alpha_4 sf + \alpha_0 \alpha_4 rs\right] \tag{22}$$

which can be written in general form as:

$$\frac{db}{dz} = g_2\left(z, a, b, \frac{da}{dz}\right) \tag{23}$$

Equations (20) and (23) can be written as a system of three non-linear first-order ordinary differential equations:

$$\frac{da}{dz} = y \tag{24}$$

$$\frac{dy}{dz} = g_1(z, a, b) \tag{25}$$

$$\frac{db}{dz} = g_2\left(z, a, b, \frac{da}{dz}\right) \tag{26}$$

with the following boundary conditions:

$$\text{at } z = 0, a = 1; b = 1; \frac{da}{dz} = \textit{unspecified} \tag{27}$$

$$\text{and at } z = 1, a = a^\circ; b = b^\circ; \frac{da}{dz} = \textit{unspecified} \tag{28}$$

The enhancement factor is defined as the ratio of the absorption rate with reaction to that of purely physical absorption under the same hydrodynamic conditions. The rates of absorption with chemical reaction are obtained from concentration gradients at the gas-liquid interface. The expression for component A becomes:

$$E_A = \frac{D_A \frac{dA}{dx}|_{x=0}}{k_L^\circ (A_i - A^\circ)} = \frac{a'(0)}{a^\circ - 1} \tag{29}$$

Similarly for component B:

$$E_B = \frac{b'(0)}{b^\circ - 1} \tag{30}$$

NUMERICAL SOLUTION

Equations (24)-(28) cannot be solved analytically. These equations are unstable when integrated in either forward or backward directions. This is because the local Jacobian for the system of equations (24)-(26) must contain at least one positive and one negative eigenvalue over the region of integration. This characteristic makes the integration very sensitive to the assumed initial conditions. Large values of M_A lead to stiff behavior and further increase the sensitivity. The problem then becomes one of making the best choice of integration routine for a system containing a positive eigenvalue. Aiken (9) suggested that a small or zero stability region in the right-half plane is required for the chosen numerical method (as applied to a linear example). This requirement is met by Gear's variable order predictor-corrector package. This routine is used in this work in a simple shooting method to solve the two-point boundary value problem defined above.

Given the solvent loadings for CO_2 and $H_2S(L_A, L_B)$ and the total amine molarity, estimates of the concentrations of all reactive species in the bulk of the liquid phase can be obtained assuming chemical equilibrium, and ignoring the non-ideality of the liquid phase. That is, the activity coefficients of all reactive species are set equal to unity. Six equations are needed to solve for the six unknowns. These are:

- Total amine balance

$$F^\circ + R^\circ = [Am] \tag{31}$$

- Total carbon balance

$$A^\circ + P^\circ = [Am]L_A \tag{32}$$

- Total sulfur balance

$$B^\circ + S^\circ = [Am]L_B \tag{33}$$

- Electroneutrality balance

$$P^\circ + S^\circ = R^\circ \tag{34}$$

- CO_2-amine reaction equilibrium

$$K_A = \frac{R^\circ P^\circ}{F^\circ A^\circ} = \frac{K_{1,A}}{K_{Am}} \tag{35}$$

- H_2S-amine reaction equilibrium

$$K_B = \frac{R^\circ S^\circ}{F^\circ B^\circ} = \frac{K_{1,B}K_W}{K_{Am}} \tag{36}$$

Equations (31)-(36) are solved simultaneously for the six unknowns: $A^\circ, B^\circ, F^\circ, R^\circ, P^\circ$, and S°. These concentrations together with estimates of solubilities and diffusivities (these are given in Table 2 for a 23.4 weight% MDEA solution at 25°C) are used to calculate the coefficients which appear in the equations to be solved.

TABLE 2

Parameters Used in the Film Model With Reversible Reactions

$$\left.\begin{aligned} D_A &= D_P = 1.24 \times 10^{-5} cm^2/s \\ D_B &= D_S = 1.04 \times 10^{-5} cm^2/s \\ D_F &= D_R = 0.60 \times 10^{-5} cm^2/s \end{aligned}\right\} \text{ from Haimour and Sandall (1984)}$$

$$A_i = 2.0 \times 10^{-5} gmole/cm^3$$

$$B_i = 2.0 \times 10^{-5} gmole/cm^3$$

$$[Am] = 2.0 \times 10^{-3} gmole/cm^3$$

$$K_B = 3.1 \times 10^6$$

$$L_A = L_B = 0.01$$

Equations (24)-(28) are solved simultaneously by integration via backward shooting, that is, from $z = 1$ to $z = 0$. Forward shooting proved to be more sensitive to initial guesses and less stable. The values of three unknowns must be provided in order to begin the integration. These are; $\frac{da}{dz}(z = 0)$, $\frac{db}{dz}(z = 0)$ and $\frac{da}{dz}(z = 1)$. These values are adjusted iteratively until convergence is achieved. Convergence is reached when the following set of residuals defined at the boundary $z = 0$ become smaller than a given tolerance:

$$R_1 = 1 - a(calculated) \tag{37}$$

$$R_2 = 1 - b(calculated) \tag{38}$$

$$R_3 = a'(pass) - a'(calculated) \tag{39}$$

where $a, b, a'(calculated)$ refer to the values of a, b, and gradient of a at $z = 0$ obtained by integrating Equations (24)-(26) for any set of guessed unspecified values. $a'(pass)$ is the value initially assumed for the gradient of a at $z = 0$ in the first pass, in order to start the process,and it becomes the value calculated from the Newton-Raphson iteration cycle for subsequent passes. The numerical procedure involves, together with integration by Gear's package, a three-dimensional Newton-Raphson algorithm with maximum pivot strategy technique to solve the resulting system of algebraic equations. The local integration error was chosen to be 10^{-6} and in general less than seven iterations were required for convergence in all runs.

RESULTS AND DISCUSSION

In the previous section the problem of simultaneous mass transfer of two gases into a liquid in which they undergo reversible second-order reactions was modeled and solved numerically for a range of the parameters. It is beyond the scope of this paper to give a complete examination of the influences of all the various parameters on the enhancement factors, E_A and E_B. However it is of interest to demonstrate some of the effects of reactions reversibility on the rates of mass transfer.

The physicochemical properties needed for the model are the gas solubilities and diffusivities in the aqueous solution, the diffusion coefficients of the amine and ionic species in solution, the rate constant for the reaction between CO_2 and MDEA, and the equilibrium constants K_A and K_B. Diffusivities of the ionic species P, S and R were taken equal to those of the reactants A, B and F, respectively. In this study the effects of variation in the parameter M_A and liquid loadings are investigated. Unless otherwise specified the other parameters are evaluated for a 23.4 weight% MDEA solution at 25°C. These parameters are given in Table 2. The diffusivity and solubility of CO_2 in aqueous MDEA have been measured by Haimour and Sandall (10).

Taking $A_i = 0, M_A = 10^{-2}, K_A = 10^{-4}$, and $L_A = 10^{-2}$, the model reduces to mass transfer of one component (H_2S) with an instantaneous reversible reaction. Thus the enhancement factor E_B becomes a function of K_B and L_B only. For infinite values of K_B, as in Table 2, the system becomes that of absorption followed by an instantaneous irreversible reaction. In this case the numerically calculated enhancement factor almost exactly agree with the value calculated using the following approximate analytical result for this regime,

$$E_B = 1 + \frac{D_F F^\circ}{D_B B_i} \tag{40}$$

This equation was derived by Olander (11).

Figures 1 and 2 show E_A and E_B plotted against M_A with K_A as a parameter. It is observed that at low values of M_A, E_A approaches unity, the limit for physical absorption, and E_B approaches the limit predicted by Equation (40). This is expected because at low CO_2 loadings and at low values of M_A the reaction between gas $A(CO_2)$ and liquid is very slow, or the time of contact is very short, so that physical absorption predominates and the reaction has negligible effect. In these circumstances the absorption of gas $B(H_2S)$ is unaffected by the presence of gas A in the liquid and its absorption rate is that for an instantaneous irreversible reaction. The exact numerical solution is very sensitive toward changes in K_A and M_A. At low values of K_A, the numerical solution predicts enhancement factors less than one for E_A and an increase in E_B as M_A increases (Figures 1 and 2). Enhancement factors less than one indicate that equilibrium considerations force the rate of absorption of gas A to be less than that for pure physical absorption. This phenomenon will be explained later. The increase in E_B can be explained by the fact that when the rate of absorption of gas A is decreased, more amine is available to react with gas B, also because the rate of absorption of gas

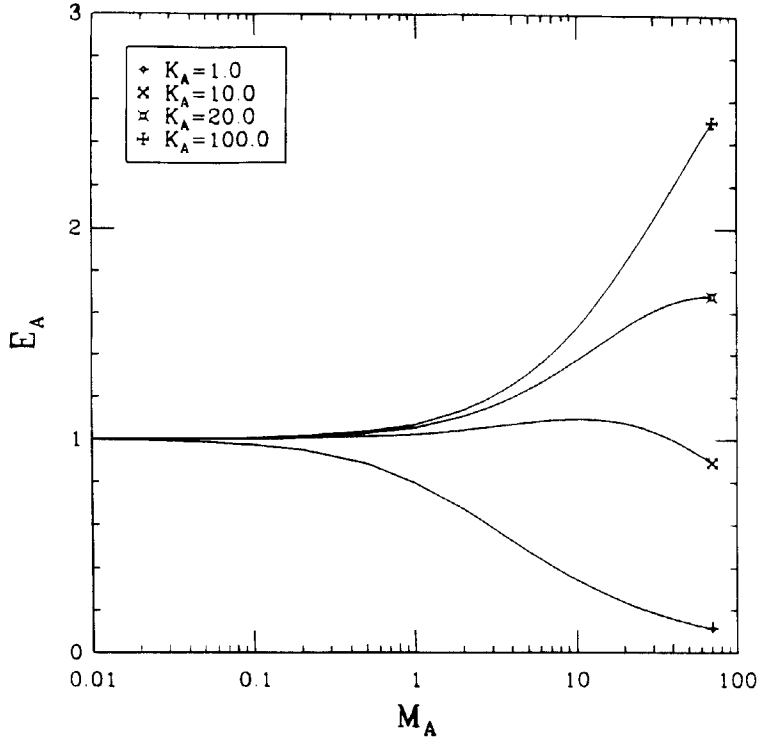

Figure 1 Enhancement factor for gas A as a function of M_A with K_A as a parameter and for system parameters as given in Table 2.

B is a direct function of the free amine concentration. This behavior cannot be predicted by a model which considers only irreversible reactions.

E_A continues to increase with increasing K_A and the opposite is true of E_B. For very large values of M_A and K_A, E_A reaches its limit value for instantaneous irreversible reaction, the region where kinetics of the reverse reaction and equilibrium constraints do not play a role.

When the conditions are as indicated in Table 2 with K_A set equal to $K_B(3.1 \times 10^6)$ and $M_A = 10^3$, the problem becomes close to that of simultaneous absorption of two gases which react irreversibly and instantaneously with a non-volatile liquid reactant. Here again, for these asymptotic conditions, the numerically calculated enhancement factors, E_A and E_B, are in

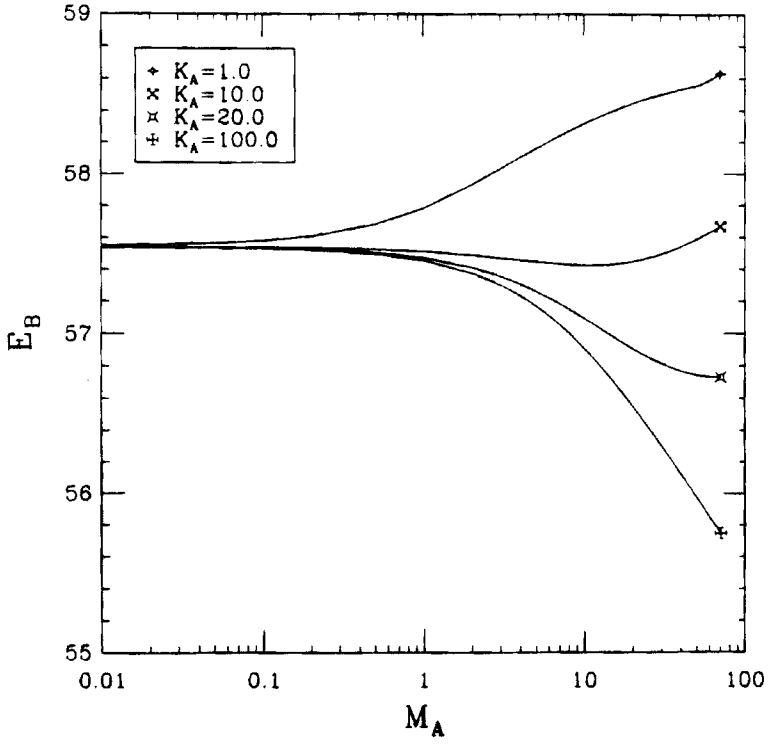

Figure 2 Enhancement factor for gas B as a function of M_A with K_A as a parameter and for system parameters as given in Table 2.

good agreement with the approximate analytical equation derived by Roper, Hatch and Pigford (12),

$$E_A = E_B = 1 + \left(\frac{D_A}{D_F}\right)^{\frac{1}{2}} \left(1 + \frac{D_F F^\circ}{D_A A_i + D_B B_i}\right) \tag{41}$$

In Figure 3 E_A is plotted as a function of M_A with $L_A = L_B$ as a parameter. The solutions were obtained for conditions listed in Table 2 with $K_A = 10$. What is important to note in this figure is that for a given K_A an increase in $L_A = L_B$ leads to a decrease in E_A especially for $M_A > 1$. Further increase in the solvent loadings (L_A, L_B) produce enhancement factors for gas A both less than one and even negative values as shown in Figure 3. For pure physical absorption the limit is $E_A = 1$. Therefore E_A values less than one mean that the absorption of gas A is lower than what would

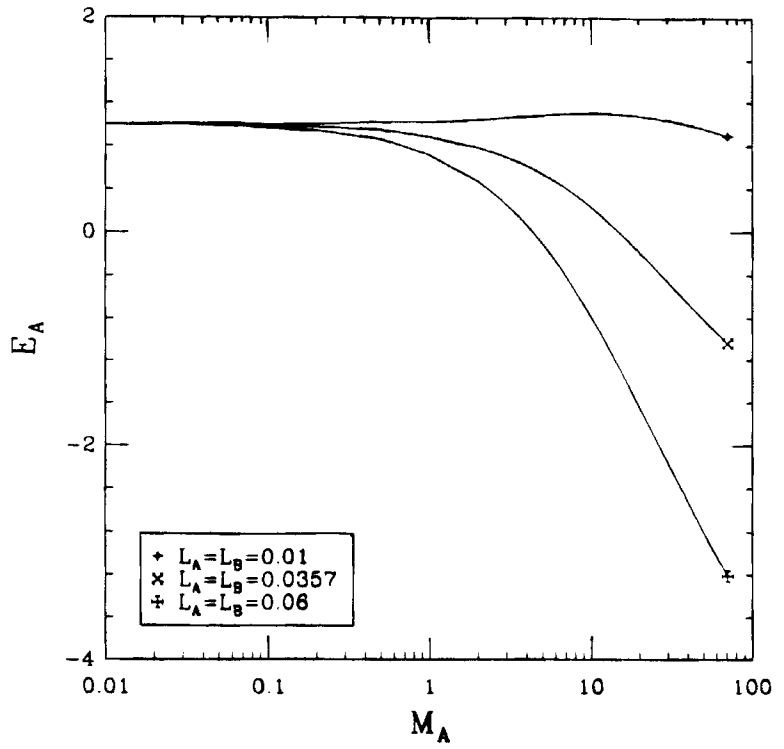

Figure 3 Enhancement factor for gas A as a function of M_A with $L_A = L_B$ as parameters and for system parameters listed in Table 2 with $K_A = 10$.

be expected for physical absorption under the same concentration driving force. Negative values indicate that the concentration gradient of gas A at the interface is positive, and therefore, desorption would occur. Cornelisse *et al.*(7) were first to report negative enhancement factors. They demonstrated this possibility for the simultaneous absorption of CO_2 and H_2S in secondary amine solutions. The Higbie penetration theory model was used and numerical solutions were obtained. Yu and Astarita (13) presented an approximate model for the rate of simultaneous absorption of H_2S and CO_2 into aqueous solutions of a tertiary amine. Their analysis also shows that negative CO_2 mass transfer rates can be predicted even when the interfacial concentration is larger than the value corresponding to equilibrium with the local values of L_A and L_B in the bulk of the liquid.

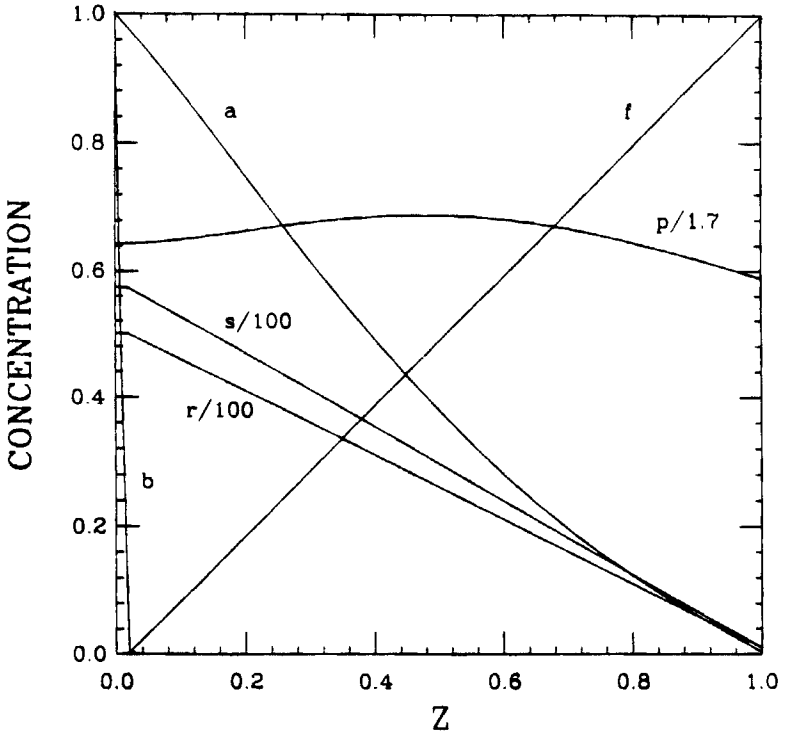

Figure 4 Concentration profiles for simultaneous absorption with reversible reactions of two gases, A and B, in solution containing F for system parameters as given in Table 2 for $K_A = 10, M_A = 15, L_A = L_B = 0.01$

To explain these results one should consider the equilibrium of the following overall reaction which is obtained by combining Reactions (1) and (4):

$$H_2S + HCO_3^- \rightleftharpoons CO_2 + H_2O + HS^- \tag{42}$$

This overall reaction implies that species appearing on both sides diffuse in the liquid so that equilibrium between the gas and liquid phases, under the influence of concentration driving forces for both CO_2 and H_2S, is reached. As a result the simultaneous absorption of CO_2 and H_2S would experience counteracting effects if both CO_2 and H_2S have the same sign for the driving force, and cooperative effects when the signs are different. If the reaction rate is moderate to slow, the equilibrium of Reaction (42) may not be reached in the liquid film, especially when the concentration driving forces are large and the time of contact is short. In this case the reaction rate is not fast

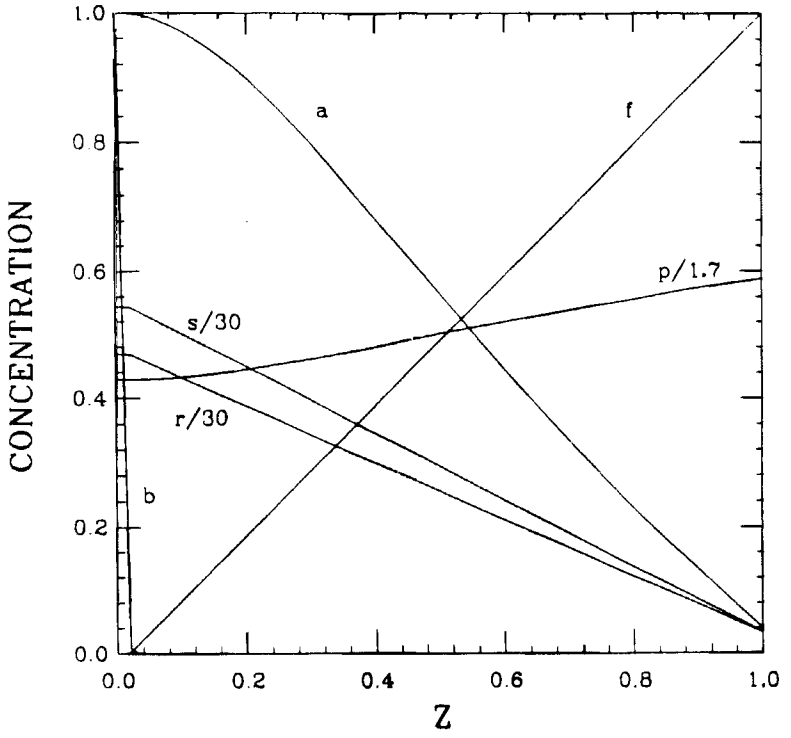

Figure 5 Concentration profiles for simultaneous absorption with reversible reactions of two gases, A and B, in solution containing F for system parameters as given in Table 2 for $K_A = 10, M_A = 15, L_A = L_B = 0.03575$

enough, in converting CO_2 or H_2S to their reaction products, compared to the diffusion transfer rate of the gases. Under these conditions the generation of a significant back pressure in the liquid film, which would result in reducing the overall mass transfer rate, has little or no chance of developing.

If reaction (42) is instantaneous however, equilibrium will be established readily in the liquid phase including the interface. This implies that the absorption of either CO_2 or H_2S would suffer from back pressure limitations or reversibility effects near the interface, and the absorption of the other would be enhanced. Thus, another implication due to this reaction is that it will be impossible to generate a condition which allows both CO_2 and H_2S to react irreversibly in the tertiary amine solution if the rate of the overall reaction (42) is instantaneous. A similar conclusion was reached by Cornelisse *et al.*(7) in the case of simultaneous absorption of CO_2 and H_2S in secondary amine solutions.

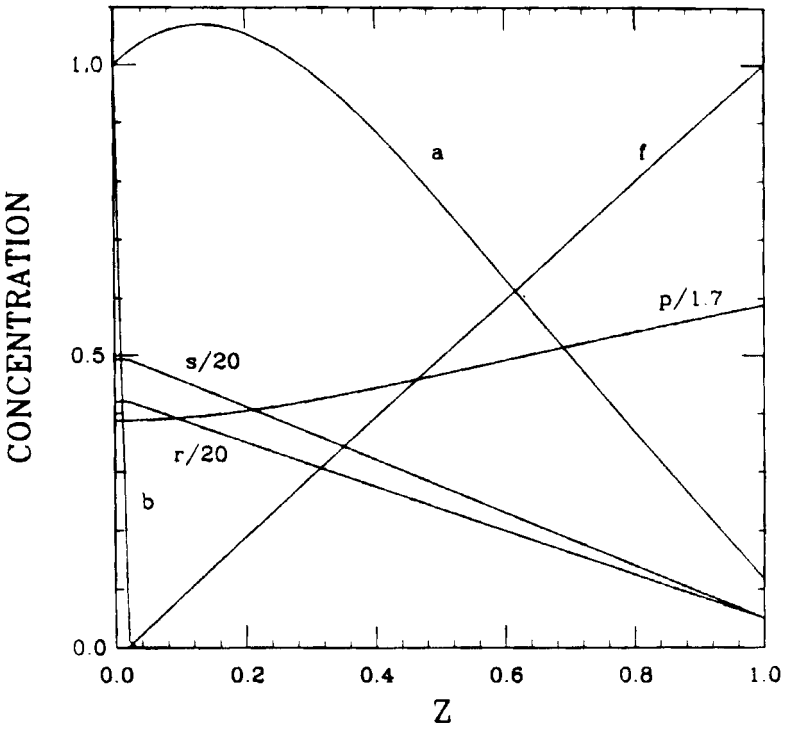

Figure 6 Concentration profiles for simultaneous absorption with reversible reactions of two gases, A and B, in solution containing F for system parameters as given in Table 2 for $K_A = 10, M_A = 15, L_A = L_B = 0.06$

When H_2S absorption is followed by reaction (42) which lies entirely to the right, it is conceivable that the induced CO_2 production generates a back pressure in the liquid film. This induced CO_2 production might be so large and fast that the CO_2 concentration in the film would locally exceed the value which is in equilibrium with the concentration in the gas phase. In this case CO_2 will desorb, even when the overall concentration driving force between the gas and the liquid phases would predict absorption.

Figures 4, 5 and 6 illustrate this phenomenon of forced reversibility on CO_2. These figures show the dimensionless concentrations of all reacting species in the liquid film for $K_A = 10$ and $M_A = 15$, values which may occur in practice, and for the parameters in Table 2. The CO_2 and H_2S loadings, however,though kept equal to each other, were varied as 0.01, 0.03575, and 0.06 in Figures 4, 5 and 6, respectively. It is seen that at low loadings, conditions which may prevail at the top of an absorption column, the transfer

rate of CO_2 is enhanced by a factor of 1.1. At an intermediate point in an absorber, the loadings might rise to a level such that no net mass transfer of CO_2 from the gas phase would occur. In this case, shown in Figure 5, the concentration gradient of CO_2 at the interface is zero, or in other words, the enhancement factor is zero. At the bottom of an absorber the acid gas loadings might become so large that reaction (42) could generate enough back pressure for CO_2 which would force it to desorb. Such a case is shown in Figure 6, for which CO_2 desorption is enhanced by a factor of 1.3.

NOMENCLATURE

a	dimensionless concentration of gas $A, = A/A_i$
A	concentration of gas $A, gmole/ml$
$[Am]$	total molar amine concentration, $gmole/ml$
b	dimensionless concentration of gas $B, = B/B_i$
B	concentration of gas $B, gmole/ml$
D_j	diffusion coefficient of species A, B, F, R, P or $S, cm^2/s$
E_j	enhancement factor for gases A or B
f	dimensionless concentration of liquid reactant $F, = F/F^\circ$
F	concentration of liquid reactant, $gmole/ml$
k_{2A}	second-order reaction rate constant for gas $A, \ell/gmole\ s$
k_L°	physical absorption mass transfer coefficient, cm/s
K_{Am}	$= \frac{[R_3N][H^+]}{[R_3NH+]}, gmole/ml$
$K_{1,A}$	$= \frac{[HCO_3^-][H^+]}{[CO_2]}, gmole/ml$
$K_{1,B}$	$= \frac{[HS^-]}{[H_2S][OH^-]}, ml/gmole$
K_W	$= [H^+][OH^-], gmole^2/ml^2$
L_j	amine loading, = moles of gas absorbed in liquid/moles of amine
M_A	dimensionless diffusion-reaction parameter for $A, = k_{2A}F^\circ D_A/k_L^{\circ 2}$
p	dimensionless concentration of $P, = P/P^\circ$
P	concentration of $P, gmole/ml$
r	dimensionless concentration of $R, = R/R^\circ$
R	concentration of $R, gmole/ml$
s	dimensionless concentration of $S, = S/S^\circ$
S	concentration of $S, gmole/ml$
T	temperature, $^\circ K$
x	distance from gas-liquid interface, cm
x_L	thickness of diffusion film, cm
z	dimensionless distance from gas-liquid interface, $= x/x_L$

Greek Symbols

$\alpha_0 = D_R R^\circ / D_F F^\circ$

$\alpha_1 = D_A A_i / D_P P^\circ$

$\alpha_2 = D_B B_i / D_S S^\circ$

$\alpha_3 = D_A A_i / D_R R^\circ$

$\alpha_4 = D_B B_i / D_R R^\circ$

Subscripts

i property at the gas-liquid interface

Superscripts

$^\circ$ property in the bulk of the liquid phase

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