using matrix A with two differences: a zero element is never stored, and the number of nonzero elements is a minimum.

This procedure has been successfully applied to the solution of a number of cases. For example with a 50 × 50 matrix containing twenty disperse elements, CPU time is 1.321 s and main memory required is 3 501 words on a Univac 1108. This compares to 1.327 s and 7 060 words of memory for the same example by the method of Kubićek et al. (1976).

APPENDIX: PROOF OF PROPERTY 1

Let X, Y be an element of vector B-T. Consider two arrangements of the vector, where the only difference is a permutation of unit X and unit Y. If the arrangement in which X precedes Y generates n nonzero disperse block elements, then from the counting rule the other arrangement in which Y precedes X must generate $(n + X + Y - 2)$ nonzero disperse block elements, where X and Y also stand for the respective number of stages in units X and Y, respectively. Therefore, the first arrangement will contain less nonzero disperse block elements provided that $(X + Y) > 2$, which will always be the case.

NOTATION

A' = augmented Jacobian matrix
$\underline{B}-T$ = bottom-top vector
$\bar{F}$ = vector of functions
f = transformed function
$F-V$ = functions-variables matrix
J = Jacobian matrix
M = dimension of matrix J
P = off-diagonal, nonzero elements
$\underline{V}$ = stored vector
$\overline{\Delta x}$ = correction vector
$\bar{x}$ = vector of variables
X = coordinate of disperse element
X,Y = reciprocal stream connection between bottom of unit X and top of unit Y
y = coordinate of disperse element
Z = pointer
α,β = nonzero disperse elements

Superscripts

m = iteration index
T = transpose

Subscript

i = stage number
p = number of disperse nonzero elements

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Sulfur Dioxide Transport Through Aqueous Solutions:

Part I. Theory

Expressions are derived for the steady state flux of sulfur dioxide through films of water and neutral and alkaline salt solutions. A local equilibrium approximation yields an analytical expression for the flux through water and neutral salt solutions. To account for deviations from local equilibrium, the conversion from sulfur dioxide (aq) to sulfur containing ions (and vice versa) is assumed frozen near the boundaries of the film ($x = 0, x = 1$). The thickness of the boundary layer near $x = 1$ is pH dependent, indicating an increasing deviation from equilibrium flux in increasingly alkaline solutions. Strong nonequilibrium behavior can be realized under some conditions for a film of concentrated sodium hydroxide operating as a liquid membrane and in conventional scrubbers.

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SCOPE

Transport of sulfur dioxide in aqueous solutions is receiving attention in connection with environmental problems. In the absorption of sulfur dioxide in flue gas desulfurization (FGD) scrubbers and by bodies of water, rain, vegetation and lung mucus, the liquid phase can play an important role (Corbett et al., 1977; Aul et al., 1977; Husar, 1978).

Hetherington (1968), Onda et al. (1971) and Hikita et al. (1977) have derived expressions for the absorption of sulfur dioxide into solutions of sodium hydroxide, sodium bisulfite and sodium sulfite. These expressions are based on penetration theory with the assumption that sulfur dioxide reacts instantaneously and irreversibly with OH^- or $SO_3^=$. Besides assuming

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instantaneous reactions, these studies have not considered the role of ion-pair species (for example, $NaSO_3^-$ in sulfur dioxide/sodium hydroxide solutions). These species are known to be important in lime/limestone scrubbers (Rowland and Abdulsattar, 1978) and in concentrated sulfur dioxide/sodium hydroxide solutions (Roberts, 1979).

Hikita et al. (1978) have assumed instantaneous chemical reactions in developing an expression for the absorption of sulfur dioxide by water. In this study and those mentioned above, the gas phases were pure sulfur dioxide, and enhancement factors no larger than 4 were observed. Under conditions of practical interest ($P_{SO_2} \leq 100$ Pa), enhancement factors up to 10^4 are predicted if instantaneous reactions are assumed. At these lower partial pressures, the chemical reactions are more important, and the assumption that they are instantaneous is more uncertain. An eight order of magnitude discrepancy in reported rate coefficients for the reaction of sulfur dioxide (aq) with water (Eigen et al., 1961; Wang and Himmelblau, 1964) increases the uncertainty of the instantaneous approximation.

In the present study, a theory is developed that avoids the approximation of instantaneous reactions and accounts for all chemical species known to be present. For comparison, an equilibrium theory corresponding to infinitely fast reactions is also derived. Since the theory is developed for a one-dimensional aqueous film, the review of facilitated transport by Schultz et al. (1974) is helpful. Included in the present theory, however, is the (diffusion induced) potential gradient. Meldon et al. (1979) have accounted for the potential gradient in alkaline carbon dioxide solutions.

Previous analyses that account for nonequilibrium reactions have linearized the reaction kinetics near each boundary of the film (Schultz et al., 1974). These regions are therefore called nonequilibrium boundary layers. The nonequilibrium boundary layer analysis (NEBLA) in the present study treats the layers as regions where the interconversion between sulfur dioxide (aq) and sulfur containing ions is frozen. This approach gives more emphasis to the boundary layers and can predict larger deviations from the equilibrium state.

The theory can be applied to liquid membranes similar to those described by Ward (1972) and Matson et al. (1977) and to traditional absorption processes. Calculations using the NEBLA are given for a film of concentrated sodium hydroxide operating as a liquid membrane and for a flue gas scrubber employing a concentrated sodium hydroxide absorbing solution.

CONCLUSIONS AND SIGNIFICANCE

An expression has been derived for the flux of sulfur dioxide through an aqueous film that contains any concentration of neutral and/or alkaline salts. When the (diffusion induced) potential gradient is viewed as imparting an effective diffusivity to the HSO_3^- ion, the flux expression becomes a linear combination of concentration differences. The equilibrium approximation and the NEBLA provide two methods for computing these concentration differences. Both methods reduce the applicable differential equations to algebraic ones. In making computations, each method requires values for the diffusion coefficients of all sulfur containing species and for the equilibrium coefficients of all chemical reactions. The NEBLA further requires a value for the rate coefficient of the reaction of sulfur dioxide (aq) with water.

The equilibrium approximation yields an analytical expression for the flux through water and neutral salt solutions because, in these solutions, sulfur dioxide (aq) and HSO_3^- are the only important sulfur containing species. For alkaline solutions, other sulfur containing species are important. Algebraic equilibrium equations must be solved numerically to compute the flux.

In water and neutral salts, the potential gradient is predicted to increase the effective diffusivity of HSO_3^- by 73%. Because HSO_3^- dominates the flux under partial pressures of practical interest ($P_{SO_2} \leq 100$ Pa), the potential gradient is responsible for approximately 42% of the net flux.

In the NEBLA, the film is divided into three regions: two nonequilibrium boundary layers and an equilibrium core. Since the interconversion between sulfur dioxide (aq) and sulfur containing ions is frozen in the boundary layers, the flux through these layers is solely Fickian diffusion of sulfur dioxide (aq). The expressions for the flux in these layers are correspondingly simple. In the equilibrium core, the expression for the flux is similar to that derived in the equilibrium approximation. The NEBLA requires a simultaneous solution to the flux expressions in the three regions.

Based on dimensional arguments, the thicknesses of the boundary layers are equal to the square root of a diffusion coefficient times a characteristic reaction time (τ_R). Although there are many chemical reactions in the system, the hydrolysis of sulfur dioxide (aq)

$$SO_2(aq) + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_3O^+ + HSO_3^-$$

is assumed to determine τ_R which refers to the forward reaction near $x = 0$ and the reverse reaction near $x = 1$. Because the reverse reaction time is pH dependent, the boundary layer near $x = 1$ gets thicker as the solution becomes more alkaline. Hence, nonequilibrium effects are expected to increase in increasingly alkaline films.

Calculations with the NEBLA for films of concentrated sodium hydroxide show that no facilitation is expected when $L \leq 0.3$ μm. Strong deviation from equilibrium theory is shown for all thicknesses of interest (10^{-2} $\mu m \leq L \leq 10^3$ μm). For 3.0M sodium hydroxide, the flux is almost independent of L when 0.2 $\mu m \leq L \leq 2$ μm. Hence, there is little incentive to produce films thinner than 2 μm unless they can be made significantly thinner than 0.2 μm.

When applied to the film model used in scrubber design, the NEBLA has only one boundary layer (at $x = 0$) because there is only one gas/liquid interface. The thickness of the layer at $x = 0$ is independent of pH. The magnitude of nonequilibrium effects depends on the thickness of the stagnant film at the gas/liquid interface. As k_l^0 increases, the stagnant film gets thinner, and the flux deviates from the equilibrium limit. Thus, operating adjustments designed to increase mass transfer rates by increasing k_l^0 are increasingly less effective.

More calculations and comparisons with experimental data are given in Part II.

SULFUR DIOXIDE TRANSPORT THROUGH AN AQUEOUS FILM

Figure 1 is a schematic diagram of an aqueous film, exposed to a gas phase at each boundary, that contains water or a neutral or alkaline salt (for example, sodium chloride, sodium hydroxide, sodium bisulfite). Each gas phase has a total pressure of 1 atm and is a mixture of nitrogen and sulfur dioxide humidified to prevent evaporation of the film. Some of the species present in the film are shown. Ion pairs (for example, $NaSO_3^-$) will be present in sufficiently concentrated solutions and are included in the theory for completeness.

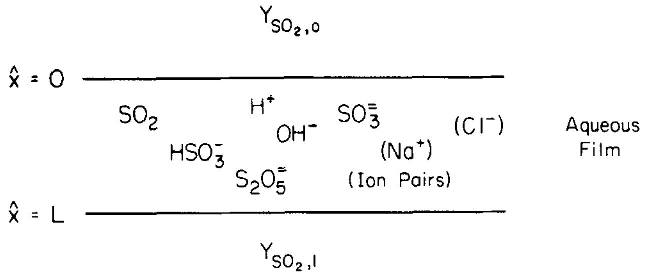

Figure 1. Physical system. Aqueous film, exposed to sulfur dioxide, with or without a neutral or alkaline salt. The goal of theory is to predict flux of sulfur dioxide through film.

When $y_{SO_2,0} > y_{SO_2,1}$, sulfur dioxide passes through the film from $\hat{x} = 0$ to $\hat{x} = L$. The goal of the theory is to predict the flux of sulfur dioxide through the film under steady conditions given any $y_{SO_2,0}$, $y_{SO_2,1}$ and the concentrations of any salts in the aqueous film.

Although the theory can be derived for any salt solution, neutral and alkaline sodium salts are used as examples in the following discussions because data in Part II are taken with solutions of sodium chloride, sodium hydroxide, sodium bisulfite and sodium sulfite. The quantity Na_{tot}, therefore, is used as the acid neutralizing capacity (for example, a solution of 0.25M sodium sulfite with 0.1M sodium chloride has Na_{tot} = 0.5M, not 0.6M). References to sodium are to be recognized as the cation of interest when the theory is applied to other systems with one or more cations.

Fundamental Equations

The following equations determine the behavior of this system:

Conservation of mass (each species)

$$\frac{dN_i}{dx} = r_i \qquad (1)$$

boundary conditions

$$N_{NV} = 0 \qquad x = 0,\ 1 \qquad (2)$$

$$C_{SO_2}(0) = \frac{y_{SO_2,0} P_{tot}}{\gamma_{SO_2} H_{SO_2}} \qquad C_{SO_2}(1) = \frac{y_{SO_2,1} P_{tot}}{\gamma_{SO_2} H_{SO_2}} \qquad (3a,\ b)$$

Electroneutrality

$$\sum_i z_i C_i = 0 \qquad (4)$$

Flux expression

$$N_i = -D_i \frac{dC_i}{dx} - z_i D_i C_i \frac{F}{RT} \frac{d\Phi}{dx} \qquad (5)$$

Reaction mechanisms

$$r_i = r_i(T,P,C_n) \qquad (6)$$

Equation (2) states that nonvolatile species (ions, ion pairs) have zero flux at the boundaries. In Equation (6), the reaction rates are unspecified functions of the temperature, pressure and species concentrations.

Parameters and variables in Equations (1) to (6) have been nondimensionalized as follows:

$$N_i = \frac{L\hat{N}_i}{D^0_{SO_2}\bar{C}} \qquad (7)$$

$$C_i = \frac{\hat{C}_i}{\bar{C}} \qquad (8)$$

$$x = \frac{\hat{x}}{L} \qquad (9)$$

$$r_i = \frac{L^2\hat{r}_i}{D^0_{SO_2}\bar{C}} \qquad (10)$$

$$D_i = \frac{\hat{D}_i}{D^0_{SO_2}} \qquad (11a)$$

$$H_{SO_2} = \frac{\hat{H}_{SO_2}\bar{C}}{P_0} \qquad (11b)$$

$$P_{tot} = \frac{\hat{P}_{tot}}{P_0} \qquad (11c)$$

The hatted symbols have dimensions.

When a sodium salt is added to the film in a concentration $\hat{C}_0$, conservation of sodium yields the following integral constraint:

$$\int_0^1 \left(\sum_k n_k C_k \right) dx = C_0 \qquad (12)$$

$$k = \text{sodium containing species}$$

Similar constraints apply to any nonvolatile substances added to the film.

If there are N species in solution other than water, Equations (1) to (6) define $N + 1$ equations for $N + 1$ unknowns (N concentrations plus the potential gradient, $d\Phi/dx$). The system is not overspecified when Equation (12) applies, since not all of the equations for the sodium containing species are independent (see Goddard et al., 1970).

Although analytical solutions for these equations have not been found, significant progress can be made in determining the flux. At any point in the film, conservation of sulfur requires

$$\sum_j n_j r_j = 0 \qquad (13)$$

(subscript j refers only to sulfur containing species). Substituting r_j from Equation (1) and integrating, we get

$$\sum_j n_j N_j = \text{constant} \equiv A_{SO_2} \qquad (14)$$

where A_{SO_2} is some (unknown) constant. Since at $x = 0$, $N_j = 0$ for $j \neq SO_2$, and since $n_{SO_2} = 1$, the constant A_{SO_2} must be N_{SO_2}.

Substituting Equation (5) into Equation (14) and integrating, we get

$$N_{SO_2} = \frac{1}{x_1 - x_0} \sum_j n_j D_j \left[C_j(x_0) - C_j(x_1) \right] - \frac{1}{x_1 - x_0} \frac{F}{RT} \int_{x_0}^{x_1} \frac{d\Phi}{dx} \left(\sum_j z_j n_j D_j C_j \right) dx \qquad (15)$$

where the D_j are assumed constant, and x_1 and x_0 are arbitrary values of the independent variable x.

The absence of an electric current in the film implies

$$\sum_i z_i N_i = 0 \qquad (16)$$

Substituting Equation (5) into Equation (16), we get

$$-\frac{F}{RT} \frac{d\Phi}{dx} = \frac{\frac{d}{dx}\left(\sum_i z_i D_i C_i \right)}{\sum_i z_i^2 D_i C_i} \qquad (17)$$

Therefore, Equation (15) becomes

$$N_{SO_2} = \frac{1}{x_1 - x_0} \sum_j n_j D_j \left[C_j(x_0) - C_j(x_1) \right] + \frac{1}{x_1 - x_0} \int_{x_0}^{x_1} \frac{\sum_j z_j n_j D_j C_j}{\sum_i z_i^2 D_i C_i} \frac{d}{dx} \left(\sum_i z_i D_i C_i \right) dx \qquad (18)$$

Although Equation (18) has been derived for an aqueous sulfur dioxide solution, a similar equation would apply for any number of volatile species (carbon dioxide, ammonia, hydrogen sulfide, etc.) undergoing transport simultaneously. The subscript j would refer to a given species just as it refers in Equation

(18) to sulfur in oxidation state +4. Equation (18) is similar to Equation (I.3.47) of Schultz et al. (1974) except that Equation (18) includes the contribution of the potential gradient.

Role of the Potential Gradient

The potential gradient poses a difficulty in the analysis because it gives rise to the term

$$\bar{B} = \int_{x_0}^{x_1} \frac{\sum_j z_j n_j D_j C_j}{\sum_i z_i^2 D_i C_i} \frac{d}{dx}\left(\sum_i z_i D_i C_i\right) dx \qquad (19)$$

in Equation (18). Because the concentration profiles are unknown, $\bar{B}$ cannot be computed without numerical solution of the differential equations.

In certain limiting cases, however, $\bar{B}$ can be evaluated analytically. In sufficiently concentrated solutions exposed to sulfur dioxide ($Na_{tot} > 3 \cdot 10^{-2}M$), the pH is typically 7 to 8. Thus, the concentrations of H_3O^+ and OH^- are negligible, and the diffusivities of the remaining species are approximately equal (see Table 2). Thus

$$\sum_i z_i D_i C_i \simeq D \sum_i z_i C_i = 0 \text{ (electroneutrality)} \qquad (20)$$

Hence, $\bar{B} \simeq 0$.

Solutions with sufficiently low alkalinity ($Na_{tot} \le 10^{-3}M$) can be treated as binary electrolytes consisting of H_3O^+ and HSO_3^-. For these solutions, Equation (18) becomes

$$N_{SO_2} = \frac{1}{x_1 - x_0} \sum_j n_j D_j^* \left[C_j(x_0) - C_j(x_1)\right] \qquad (21)$$

$$j = SO_2(aq),\ HSO_3^-$$

with

$$D_{SO_2}^* = D_{SO_2} \qquad (22)$$

and

$$D_{HSO_3^-}^* = \frac{2\, D_{H_3O^+} D_{HSO_3^-}}{D_{H_3O^+} + D_{HSO_3^-}} \qquad (23)$$

Equation (23) is similar to the binary salt diffusivity derived by Nernst (1888). Using the values of $D_{H_3O^+}$ and $D_{HSO_3^-}$ given in Table 2, we get

$$D_{HSO_3^-}^* = 1.727 \cdot D_{HSO_3^-} \quad (25°C) \qquad (24)$$

Thus, the potential gradient enhances the diffusivity of HSO_3^- by a factor of 1.727 in solutions with $Na_{tot} \le 10^{-3}M$.

The enhancement of $D_{HSO_3^-}$ by the potential gradient in the dilute limit should decrease continuously as Na_{tot} is increased. A linear interpolation for $D_{HSO_3^-}$ is proposed for the transition. Thus, Equation (18) can be simplified to

$$N_{SO_2} = \frac{1}{x_1 - x_0} \sum_j n_j D_j' \left[C_j(x_0) - C_j(x_1)\right] \qquad (25)$$

with

$$D_j' = D_j \quad \text{for} \quad j \neq HSO_3^- \qquad (26)$$

and

$$D'_{HSO_3^-} = \begin{cases} D_{HSO_3^-}^* & Na_{tot} \le 10^{-3}M \\ \dfrac{\left(D_{HSO_3^-} - D_{HSO_3^-}^*\right)}{0.029 \text{ mole/l}} \cdot \left[Na_{tot} - 10^{-3}M\right] & \\ \quad + D_{HSO_3^-}^* & 10^{-3}M < Na_{tot} < 3 \cdot 10^{-2}M \\ D_{HSO_3^-} & Na_{tot} \ge 3 \cdot 10^{-2}M \end{cases} \qquad (27)$$

where $D_{HSO_3^-}^*$ is given by Equation (23).

The potential gradient in neutral salt solutions can be treated approximately, and Equations (25) to (27) can be shown to hold. Since $Na_{tot} \equiv 0$ in neutral salt solutions, Equation (27) summarizes completely the role of the potential gradient. Equations (25) to (27), therefore, are the basic equations for the flux of sulfur dioxide through an aqueous film. Approximations discussed in the following sections allow these equations to be used to compute the flux.

EQUILIBRIUM THEORY

With $x_0 = 0$ and $x_1 = 1$, Equation (25) expresses the flux in terms of the boundary concentrations of the sulfur containing species. If all chemical reactions are assumed to be instantaneous, then equilibrium expressions relate $C_j(0)$ to $C_{SO_2}(0)$ and $C_j(1)$ to $C_{SO_2}(1)$. Since $C_{SO_2}(0)$ and $C_{SO_2}(1)$ are known [Equations (3a, b)], $C_j(0)$ and $C_j(1)$ can be computed. These computations are similar to standard calculations in equilibrium solution chemistry. The calculations and computer program for sodium based salts are described by Roberts (1979, Appendix A).

When alkaline sodium is present in solution, the equilibrium calculations assume that the total sodium concentration is equal at the boundaries to the initial concentration added to the film [see Equation (12)]. This approximation will be valid to the extent that the important sodium containing species (Na^+, $NaHSO_3$, $NaSO_3^-$, Na_2SO_3) have equal diffusivities. Table 2 shows that this approximation is good.

Equilibrium theory applied to water. When $y_{SO_2} > 10^{-9}$, the important species in sulfur dioxide/water solutions are sulfur dioxide (aq), $H_3O^+$and HSO_3^- (Roberts, 1979). In most applications, therefore, the only equilibrium to consider is

$$SO_2\text{ (aq)} + 2H_2O \rightleftarrows H_3O^+ + HSO_3^- \qquad (28)$$

Electroneutrality requires $C_{H_3O^+} = C_{HSO_3^-}$ so that

$$C_{HSO_3^-} = \left[\frac{K_1\, \gamma_{SO_2}\, C_{SO_2}}{\gamma_{H_3O^+}\, \gamma_{HSO_3^-}}\right]^{\frac{1}{2}} \qquad (29)$$

Since sulfur dioxide (aq) and HSO_3^- are the only important sulfur containing species, Equation (25) is a two-term sum. With $x_0 = 0$ and $x_1 = 1$, and using Equations (29) and (3a), (b) Equation (25) yields

$$\begin{aligned} N_{eq} = {} & \frac{D_{SO_2} P_{tot}}{\gamma_{SO_2} H_{SO_2}} \left[y_{SO_2,0} - y_{SO_2,1}\right] \\ & + D_{HSO_3^-}^* \left[\frac{K_1 P_{tot}}{\gamma_{H_3O^+} \gamma_{HSO_3^-} H_{SO_2}}\right]^{\frac{1}{2}} \left[y_{SO_2,0}^{\frac{1}{2}} - y_{SO_2,1}^{\frac{1}{2}}\right] \end{aligned} \qquad (30)$$

Thus, the facilitation factor is

$$\begin{aligned} F_{eq} = {} & \frac{D_{HSO_3^-}^*}{D_{SO_2}} \left(\frac{K_1 H_{SO_2}}{P_{tot}}\right)^{\frac{1}{2}} \\ & \frac{\gamma_{SO_2}}{(\gamma_{H_3O^+} \gamma_{HSO_3^-})^{\frac{1}{2}}} \left[\frac{y_{SO_2,0}^{\frac{1}{2}} - y_{SO_2,1}^{\frac{1}{2}}}{y_{SO_2,0} - y_{SO_2,1}}\right] \end{aligned} \qquad (31)$$

Equilibrium Theory Applied to Neutral Salt Solutions

A neutral salt $M_{\nu+}A_{\nu-}$ in an aqueous film contributes two inert, nonvolatile species: the cation M^{z+} and the anion A^{z-}. Equations (1) and (2) show that the flux of any inert, nonvolatile species is zero everywhere in the film. Thus, Equation (16) can be written as

$$\sum_{i \neq IN} z_i N_i = 0 \qquad (32)$$

where $i \neq$ IN indicates that the sum excludes inert, nonvolatile species. Therefore, Equation (15) can be written as

$$\begin{aligned} N_{SO_2} = {} & \frac{1}{x_1 - x_0} \sum_j n_j D_j \left[C_j(x_0) - C_j(x_1)\right] \\ & + \frac{1}{x_1 - x_0} \int_{x_0}^{x_1} \frac{\sum_j z_j n_j D_j C_j}{\sum_{i \neq IN} z_i^2 D_i C_i} \frac{d}{dx} \\ & \left(\sum_{i \neq IN} z_i D_i C_i\right) dx \end{aligned} \qquad (33)$$

Because the only important ions other than M^{z+} and A^{z-} are H_3O^+ and HSO_3^-, the expressions for the flux through a sulfur dioxide/water solution and a sulfur dioxide/neutral salt solution are identical [compare Equations (18) and (33)]. Therefore, if

$$C_{H_3O^+} = C_{HSO_3^-} \tag{34}$$

in a neutral salt solution, then Equations (25) to (27) apply, and Equations (30) and (31) apply under the equilibrium approximation.

Starting from electroneutrality, we can show that Equation (34) applies when the following condition is met:

$$\frac{z^+ [C_M - \overline{C}_M] + z^- [C_A - \overline{C}_A]}{C_{H_3O^+}} << 1 \tag{35}$$

Here, $\overline{C}_M$ and $\overline{C}_A$ are the average concentrations of cation and anion in the film. From Equation (5) and the zero flux condition on M^{z+} and A^{z-}, one finds

$$\frac{1}{z^+}\frac{d\ln C_M}{dx} = -\frac{F}{RT}\frac{d\Phi}{dx} = \frac{1}{z^-}\frac{d\ln C_A}{dx} \tag{36}$$

Hence, when the potential gradient is nonzero, the pointwise values of C_M and C_A are not equal to the average values.

Since much complexity arises from Equation (36), Equation (35) will be assumed to hold. With this assumption, Equations (34) and (25) to (27) apply to neutral salt solutions. With the equilibrium approximation, Equations (30) and (31) also apply. Equations (30) and (31) agree well with the data (Part II), justifying the simplicity of the approach at least in this case.

NONEQUILIBRIUM BOUNDARY LAYER APPROXIMATION

Schultz et al (1974) review analyses that account for deviation from the equilibrium regime. These analyses use matched asymptotic (singular perturbation) expansions and are valid in the limit of fast reactions. These techniques rely on the postulate that near each boundary of the film, the rate of reaction and the rate of diffusion are comparable. Far from these boundary layers, the reaction rates are treated as much faster than diffusion. As a first approximation, therefore, the reactions are at equilibrium in the core of the film.

The analysis developed by Kreuzer and Hoofd (1972) and generalized by Schultz et al. (1974) has been the most successful technique (K+H method). It has been shown to be valid in the equilibrium limit of instantaneous reactions and, for some systems, has succeeded well into the nonequilibrium regime. This technique linearizes the reaction rates in the boundary layers by expanding the reaction rate terms at the point where the boundary layer and equilibrium core meet. This linearization makes the mathematics tractable. The technique is verified if the results agree with data or a full numerical solution.

Experimental results (Part II) show that the K+H method overpredicts the flux for nearly all sulfur dioxide/alkaline solutions. The data lie far from the equilibrium limit yet far from the limit of zero chemical reaction [Fickian diffusion of sulfur dioxide (aq)]. Consequently, it is necessary to develop a new nonequilibrium boundary layer analysis (NEBLA). Because the K+H method overpredicts the flux, one is led to believe that the linearization overestimates reaction rates in the boundary layer. Therefore, the new technique (NEBLA) reduces the importance of chemical reactions in the boundary layers.

The principles of the NEBLA will be discussed in terms of an arbitrary facilitated transport system with nonvolatile carrier species. The ideas will then be applied to aqueous sulfur dioxide solutions. Algebraic equations result that allow N_{SO_2} to be calculated.

Physical Basis of NEBLA

Consider a gaseous species A diffusing across a film in which it reacts to form carrier species that assist in the transport process. Since A is the only species that can leave the film, the entire flux must be carried by A across the boundaries $x = 0, 1$. Figure 2 illustrates the fraction of the flux that is carried by A at any point in the film. This figure shows that the faster the reactions, the larger the fraction of the flux borne by the carrier species throughout most of the film. The carrier contributions, however, always vanish at the boundaries.

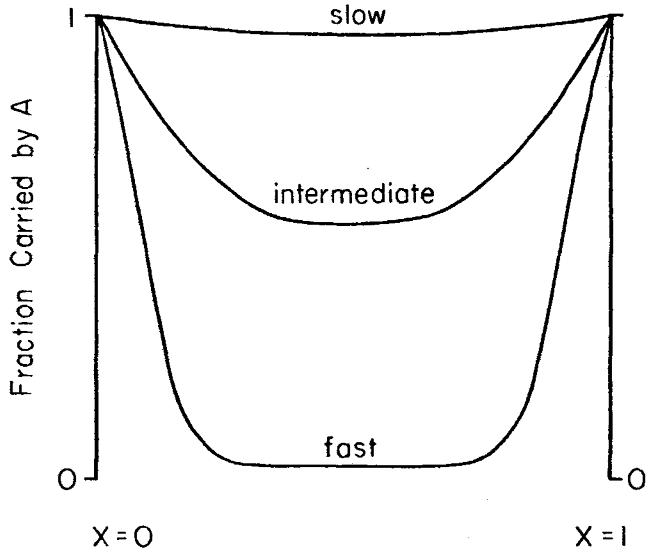

Figure 2. Fraction of flux carried by species A. Only the volatile species A can contribute to the flux at $x = 0, 1$. Carriers assist in the core of the film. The contribution of the carriers increases with the rate of the chemical reactions (slow, intermediate, fast).

When A enters the film at $x = 0$, it diffuses some distance towards $x = 1$ before it reacts in solution. For diffusion limited reactions, this distance is the distance between intermolecular collisions. For slower reactions, A will diffuse much farther before reacting. In the NEBLA it is this distance that A diffuses before it reacts that is the width of the boundary layer near $x = 0$.

The boundary layer near $x = 1$ is defined by similar considerations involving the carrier species. Figure 2 implies that the concentration of A is decreasing more rapidly near $x = 1$ than elsewhere in the film (except near $x = 0$). Near $x = 1$, therefore, as carriers diffuse toward $x = 1$, they will be reacting to produce A. When these reactions are slower than diffusion limited reactions, the carriers can diffuse some distance toward $x = 1$ before further reaction occurs to form A. Thus, there must be a distance close enough to $x = 1$ where the carriers diffuse all the way to the boundary before reacting further. Over this distance, the carrier concentrations are constant because these species have zero concentration gradients at the boundaries. In the NEBLA, the boundary layer at $x = 1$ has a thickness defined qualitatively by the close enough described above and is characterized by constant carrier concentrations. Consequently, only species A contributes to the flux across the boundary layer.

In the NEBLA, then, the boundary layers are defined to be regions where the interconversion between species A and the carrier species does not occur. Reactions that would produce A from carriers (or vice versa) are, therefore, effectively frozen. The foregoing discussion could be generalized to include N gaseous species undergoing transport simultaneously; N boundary layers of different widths would result.

NEBLA Applied to Aqueous Sulfur Dioxide Solutions

Figure 3 shows the concepts of the NEBLA applied to the transport of sulfur dioxide in aqueous solutions. The film is divided into boundary layer and core regions. Sulfur dioxide enters the film, penetrates and forms HSO_3^-. This ion diffuses across the film where it discharges sulfur dioxide. Diffusion of H_3O^+ (concurrent with HSO_3^-) and of OH^- (countercurrent) maintains zero net current flow. These ions and other carrier species are omitted for simplicity.

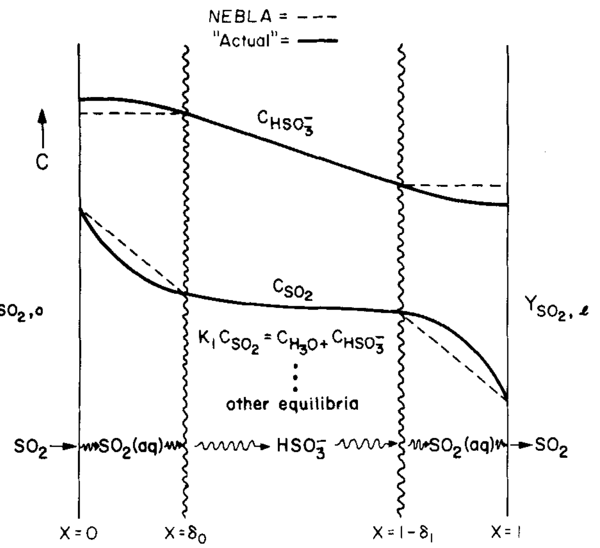

Figure 3. Nonequilibrium boundary layers in aqueous sulfur dioxide solutions. Sulfur dioxide enters film, diffuses a distance δ_0 and reacts to form HSO_3^-. Sulfur containing ions carry most of the flux across the equilibrium core. Since the ions cannot leave the film, they must react near $x = 1$ to form sulfur dioxide (aq) which diffuses across the boundary layer of thickness δ_1.

Sketches of the concentration profiles of sulfur dioxide (aq) and HSO_3^- based on the NEBLA are compared in Figure 3 with the form of the actual concentration profiles. In the boundary layers, profiles of sulfur containing ions are flat, and the profile for sulfur dioxide (aq) is linear because no interconversion between sulfur dioxide (aq) and sulfur containing ions is allowed. Profiles in the equilibrium core are not specified by the NEBLA but can be sketched as shown.

Consider the boundary layer near $x = 0$. Sulfur dioxide molecules entering the film at $x = 0$ can react by

$$SO_2\,(aq) + 2H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_3O^+ + HSO_3^- \tag{37}$$

or diffuse as sulfur dioxide (aq) toward $x = 1$. Qualitatively, it takes one reaction time

$$\tau_R = \frac{1}{k_1} \tag{38}$$

for a sulfur dioxide molecule to react. During this time, the molecule diffuses a distance given qualitatively by $(\hat{D}_{SO_2} \cdot \tau_R)^{\frac{1}{2}}$. Hence, the thickness of the boundary layer near $x = 0$ is taken to be

$$\hat{\delta}_0 = \left[\frac{\hat{D}_{SO_2}}{k_1}\right]^{\frac{1}{2}} \tag{39}$$

In nondimensional terms

$$\delta_0 = \frac{1}{L}\left(\frac{\hat{D}_{SO_2}}{k_1}\right)^{\frac{1}{2}} \tag{40}$$

Because the boundary layer is a region where sulfur dioxide is not converted to sulfur containing species, the flux of sulfur dioxide across the boundary layer must be by Fickian diffusion of sulfur dioxide (aq). Hence

$$N_{SO_2} = \frac{D_{SO_2}}{\delta_0}\,[C_{SO_2}(0) - C_{SO_2}(\delta_0)] \tag{41}$$

where $C_{SO_2}(\delta_0)$ is the unknown concentration of sulfur dioxide (aq) at $x = \delta_0$.

Now consider the boundary layer near $x = 1$. The thickness of this layer is related to the characteristic reaction time of the carrier species. Since HSO_3^- is the main carrier species in aqueous sulfur dioxide solutions, the reaction time should be chosen from a reaction that produces sulfur dioxide (aq) from HSO_3^-.

It is proposed that the reaction time be taken from the reverse of reaction (37). A competing route

$$HSO_3^- \underset{k_R}{\overset{k_F}{\rightleftarrows}} SO_2\,(aq) + {}^-OH \tag{42}$$

is possible but is much slower than reaction (37) (Roberts, 1979). The reaction time of HSO_3^- indicated by Equation (37) is

$$\tau_R = (k_{-1}C^*)^{-1} \tag{43}$$

where C^* is a characteristic value of the H_3O^+ concentration in the boundary layer. Proper choice of C^* is outlined below.

In a time $\hat{\tau}_R$, HSO_3^- can diffuse a distance given qualitatively by $(\hat{D}_{HSO_3^-} \cdot \tau_R)^{\frac{1}{2}}$. Thus, the boundary layer thickness near $x = 1$ is taken to be

$$\hat{\delta}_1 = \left(\frac{\hat{D}_{HSO_3^-}}{k_{-1}C^*}\right)^{\frac{1}{2}} \tag{44}$$

In nondimensional terms

$$\delta_1 = \frac{1}{L}\left(\frac{\hat{D}_{HSO_3^-}}{k_{-1}C^*}\right)^{\frac{1}{2}} \tag{45}$$

The flux across the boundary layer near $x = 1$ is also Fickian diffusion of sulfur dioxide (aq). Therefore

$$N_{SO_2} = \frac{D_{SO_2}}{\delta_1}[C_{SO_2}(1 - \delta_1) - C_{SO_2}(1)] \tag{46}$$

where $C_{SO_2}(1 - \delta_1)$ is the unknown concentration of sulfur dioxide (aq) at $x = 1 - \delta_1$.

The last step in the NEBLA begins by the evaluation of Equation (25) at $x = 1 - \delta_1$ and $x_0 = \delta_0$, yielding

$$N_{SO_2} = \frac{1}{1 - \delta_1 - \delta_0} \sum_j n_j D_j' \,[C_j(\delta_0) - C_j(1 - \delta_1)] \tag{47}$$

The NEBLA is completed by the postulate that at the boundary layer/core interfaces ($x = \delta_0, x = 1 - \delta_1$), all chemical reactions are at (local) equilibrium. This postulate is consistent with the existence of an equilibrium core and with the definition of the boundary layers. It proposes, however, a discontinuity in the reaction rate terms (ionic to molecular sulfur reactions are considered frozen in the boundary layers and instantaneous in the core).

With this postulate, $C_j(\delta_0)$ in Equation (47) are related by equilibrium expressions to $C_{SO_2}(\delta_0)$ in Equation (41). Similarly, $C_j(1 - \delta_1)$ in Equation (47) are related by equilibrium expressions to $C_{SO_2}(1 - \delta_1)$ in Equation (46). These are the same expressions involved in the equilibrium theory (Roberts, 1979, Appendix A).

The freezing of the conversion from ionic to molecular sulfur in the boundary layers implies that the concentrations of all ionic species in the boundary layers are equal to the values at the boundary layer/core interfaces. Hence, C^* must be the H_3O^+ concentration that is in equilibrium with $C_{SO_2}(1 - \delta_1)$. Thus, computation of N_{SO_2} by the NEBLA involves four equations (41), (45), (46), and (47) for the four unknowns δ_1, $C_{SO_2}(\delta_0)$, $C_{SO_2}(1 - \delta_1)$ and N_{SO_2} [δ_0 is known; Equation (40)].

Numerical solution of these equations is necessary because of the complexity of the equilibrium equations that relate $C_j(\delta_0)$ to $C_{SO_2}(\delta_0)$ and $C_j(1 - \delta_1)$ and C^* to $C_{SO_2}(1 - \delta_1)$. A solution algorithm is: guess $C_{SO_2}(1 - \delta_1)$, compute $C_j(1 - \delta_1)$ and C^* by the equilibrium relationships, compute δ_1 by Equation (45), compute N_{SO_2} by Equation (46), use this value of N_{SO_2} to find $C_{SO_2}(\delta_0)$ by Equation (41), find $C_j(\delta_0)$ from $C_{SO_2}(\delta_0)$ by the equilibrium relationships and use $C_j(\delta_0)$, $C_j(1 - \delta_1)$ and δ_1 in Equation (47) to compute N_{SO_2}. If N_{SO_2} computed in the last step agrees with N_{SO_2} computed in the fourth step, the initial guess for $C_{SO_2}(1 - \delta_1)$ was correct, and the equations are solved. If not, a new guess for $C_{SO_2}(1 - \delta_1)$ is needed.

The NEBLA can be simplified by comparing the boundary layer thicknesses. Note that

$$\frac{\delta_1}{\delta_0} = \left[\frac{\hat{D}_{HSO_3^-} k_1}{k_{-1}C^*\hat{D}_{SO_2}}\right]^{\frac{1}{2}} \simeq \left(\frac{K_1}{C^*}\right)^{\frac{1}{2}} \tag{48}$$

Since $K_1 = 0.014$ mole/l (Huss and Eckert, 1977, 25°C) and

TABLE 1. SPECIES, EQUILIBRIA AND EQUILIBRIUM COEFFICIENTS (25°C) FOR THE $SO_2/Na^+/H_2O$ SYSTEM

Reaction	Equilibrium coefficient: Symbol	Equilibrium coefficient: Value	Reference
$SO_2 + 2H_2O \rightleftarrows H_3O^+ + HSO_3^-$	K_1	0.014 mole/l	Huss and Eckert (1977)
$HSO_3^- + H_2O \rightleftarrows H_3O^+ + SO_3^=$	K_2	$6.24 \cdot 10^{-8}$ mole/l	Tartar and Garretson (1941)
$2HSO_3^- \rightleftarrows S_2O_5^= + H_2O.$	K_3	0.076 l/mole	Bourne et al. (1974)
$2H_2O \rightleftarrows H_3O^+ + OH^-$	K_4	$1.008 \cdot 10^{-14}$ mole^2/l^2	MacInnes (1932)
$NaHSO_3 \rightleftarrows Na^+ + HSO_3^-$	K_5	3.00 mole/l	Fuoss estimate (see text)
$NaS_2O_5^- \rightleftarrows Na^+ + S_2O_5^=$	K_6	0.19 mole/l	Fuoss estimate (see text)
$Na_2S_2O_5 \rightleftarrows Na^+ + NaS_2O_5^-$	K_7	0.19 mole/l	Fuoss estimate (see text)
$NaSO_3^- \rightleftarrows Na^+ + SO_3^=$	K_8	0.19 mole/l	Fuoss estimate (see text)
$Na_2SO_3 \rightleftarrows Na^+ + NaSO_3^-$	K_9	0.19 mole/l	Fuoss estimate (see text)
$HS_2O_5^- + H_2O \rightleftarrows H_3O^+ + S_2O_5^=$	K_{10}	0.0104 mole/l	Fuoss estimate (see text)
$H_2S_2O_5 + H_2O \rightleftarrows H_3O^+ + HS_2O_5^-$	K_{11}	10 mole/l	Fuoss estimate (see text)
$NaOH \rightleftarrows Na^+ + OH^-$	K_{12}	5.04 mole/l	Moelwyn-Hughes (1972)

Note: Coefficients K_1 to K_4 are chosen as the best available data from several literature sources.

since C^* is characteristic of the high pH side of the film (pH as large as 7 to 8)

$$\frac{K_1}{C^*} \lesssim 10^5 \text{ to } 10^6$$

Hence, $\delta_1 >> \delta_0$ under some conditions.

When $\delta_1 >> \delta_0$, the boundary layer at $x = 0$ may be negligible. In these cases, Equation (47) becomes

$$N_{SO_2} = \frac{1}{1 - \delta_1} \sum_j n_j D'_j \left[C_j(0) - C_j(1 - \delta_1)\right] \tag{49}$$

The $C_j(0)$ are related to $C_{SO_2}(0)$ by equilibrium expressions just as the $C_j(\delta_0)$ were related to $C_{SO_2}(\delta_0)$. Since Equation (3a) gives $C_{SO_2}(0)$, $C_j(0)$ can be computed. (The validity of neglecting the boundary layer at $x = 0$ can be established only when the flux calculated by neglecting it agrees with the flux calculated by including it. If this approximation is invalid, both boundary layers must be retained.)

Equations (45), (46), and (49) are three equations for the unknowns δ_1, N_{SO_2} and $C_{SO_2}(1 - \delta_1)$. These are solved by equating the right-hand sides of Equations (46) and (49) and substituting Equation (45) for δ_1. The result is a single implicit equation for $C_{SO_2}(1 - \delta_1)$ that is solved iteratively. The technique and computer program for sodium based salts are given by Roberts (1979, Appendix A). When $C_{SO_2}(1 - \delta_1)$ is known, Equation (45) yields δ_1, and Equation (46) gives N_{SO_2}.

LIQUID MEMBRANE FOR SULFUR DIOXIDE SEPARATION

Immobilized liquid films have been used in laboratory studies to selectively remove one constituent from a gas mixture (Ward, 1972; Matson et al., 1977). Diffusivities are usually three to four orders of magnitude larger in liquids than in solid (polymeric) materials that have been proposed for membrane separation processes (Ward, 1972; Zavaleta and McCandless, 1976; Kuehne, 1979).

Technical problems remain, including mechanical film support and film evaporation. It is of interest, however, to consider theoretical factors of importance in designing an aqueous film for sulfur dioxide removal. The calculations are made with the NEBLA for films of sodium hydroxide solutions.

Chemical species, equilibria and equilibrium coefficients in sulfur dioxide/Na^+ aqueous solutions are shown in Table 1. Coefficients K_1 to K_4 and K_{12} are taken from the literature, and coefficients K_5 to K_{11} are estimated from the Fuoss equation (Fuoss, 1958). Species omitted in previous sulfur dioxide transport studies are $S_2O_5^=$, sodium bisulfite, $NaS_2O_5^-$, $Na_2S_2O_5$, $NaSO_3^-$, sodium sulfite, $HS_2O_5^-$, $H_2S_2O_5$, and sodium hydroxide. Equilibrium calculations indicate that these species account for two thirds of the total dissolved sulfur when $Na_{tot} = 3M$. In systems with divalent cations, (for example, Ca^{++}, Mg^{++}), such species are important at more dilute concentrations (Rowland and Abdulsattar, 1978).

Diffusion coefficients have been measured for several species (see Roberts, 1979, Table 2.6). Unmeasured coefficients (D_i) can be estimated from measured ones (D_{ref}) by the Stokes-Einstein relation:

$$\frac{D_i}{D_{ref}} = \left(\frac{MW_{ref}}{MW_i}\right)^{1/3} \tag{50}$$

In calculating D_i, it is reasonable to use $D_{ref} = D_{SO_2}$ for i = uncharged species, $D_{ref} = D_{HSO_3^-}$ for i = univalent species and $D_{ref} = D_{SO_3^=}$ for i = divalent species. Diffusion coefficients at infinite dilution, 25°C, calculated in this way are shown with measured coefficients in Table 2.

Roberts (1979, Appendix A) gives details of making the equilibrium and NEBLA calculations based on the speciation in Table 1. Diffusivities in Table 2 are assumed inversely proportional to the solution viscosity. The value of k_1 in Equations (37) and (40) is taken from Eigen et al. (1961).

Since the NEBLA predicts the facilitation factor to depend on the film thickness, the flux will change nonlinearly with L. Although the flux will always increase as L decreases, there will be a trade off between the ability to produce and maintain thin films and the economic value of the flux increase resulting from thinner films. Films of 25 to 75 μm thickness are easily produced in industrial laboratories (Matson et al., 1977). Kuehne has made polymer films for sulfur dioxide separations that are 0.1 μ to 1 μm thick. It is expected, therefore, that somewhere between 1 and 50 μm, the difficulty of film preparation and maintenance on an industrial scale would become significant. In the following calculations, therefore, L is varied from 10^{-2} μm (very difficult to prepare) to 10^3 μm (trivial to prepare).

Conditions chosen for the sample calculations are $P_{SO_2,0} = 100$ Pa, $P_{SO_2,1} = 0.01$ Pa, $T = 298°K$ and $Na_{tot} = 3.0M$ and $0.5M$.

TABLE 2. DIFFUSION COEFFICIENTS, INFINITE DILUTION, 25°C

Species	$10^5 \cdot D_i^0$ cm^{2}s^{-1}	Source
H_3O^+	9.30	Best available data*
OH^-	5.26	Newman (1973)
HSO_3^-	1.47	Best available data*
$S_2O_5^=$	1.00	Calculated
$SO_3^=$	1.10	Best available data*
$SO_2(aq)$	1.60	Best available data*
Na^+	1.33	Newman (1973)
$NaHSO_3$	1.40	Calculated
$NaS_2O_5^-$	0.87	Calculated
$Na_2S_2O_5$	1.10	Calculated
$NaSO_3^-$	1.00	Calculated
Na_2SO_3	1.30	Calculated
$HS_2O_5^-$	0.90	Calculated
$H_2S_2O_5$	1.20	Calculated
NaOH	1.87	Calculated

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* From literature review given by Roberts (1979).

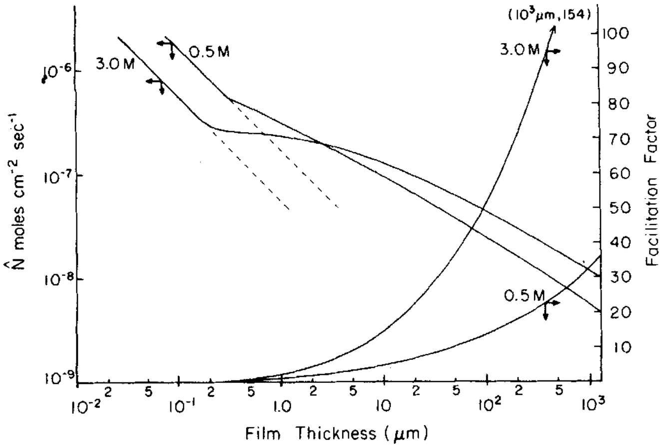

Figure 4. Liquid membrane design. Films of concentrated sodium hydroxide exhibit facilitation and hence nonlinear flux behavior when $L \gtrsim 0.3$ μm. Films that are relatively easy to prepare ($L \gtrsim 25$ μm) have larger transport rates than if the flux were proportional to L^{-1} (dashed lines). If films with $L \lesssim 1$ μm can be produced, less concentrated solutions are more desirable because of the salting out of sulfur dioxide (aq) and the higher viscosity in the more concentrated solutions.

$P_{SO_2,0}$ is typical of flue gas. $P_{SO_2,1}$ may be regarded as low but achievable given advances in liquid film technology. The sodium hydroxide concentrations are chosen since concentrated alkaline solutions are expected to show large facilitation factors under some conditions.

Figure 4 shows the flux and facilitation factor as functions of the film thickness. When $L \lesssim 0.3$ μm, the boundary layers in the NEBLA take up the entire film so that the flux is given by Fick's law for the diffusion of sulfur dioxide (aq) ($F = 0$; $\hat{N} \alpha L^{-1}$). Equilibrium theory predicts facilitation factors of 1 020 and 202 for 3.0M and 0.5M, respectively. The NEBLA, therefore, shows strong deviation from the equilibrium limit for all film thicknesses of interest.

For 3.0M, the flux for $L = 2$ μm is only ~20% lower than for $L = 0.2$ μm. Thus, the facilitation provided by the sodium hydroxide decreases the severity of the demands on thin film technology. There is little advantage for films thinner than 2 μm unless films can be made much thinner than 0.2 μm.

When L increases from 10 to 1 000 μm, N decreases by approximately a factor of 10. This (approximately) inverse square-root dependence of $\hat{N}$ on L means that there is not as severe a penalty for thicker films as for systems with $\hat{N} \alpha L^{-1}$. It is more likely, therefore, that flux requirements could be met with a thick film ($L \sim 1$ mm).

CONVENTIONAL SULFUR DIOXIDE SCRUBBING

Liquid phase resistance is important in a variety of flue gas scrubbing processes, including lime/limestone and several second generation processes (Gleason and Heacock, 1973; McMichael et al., 1976; Aul et al., 1977; Corbett et al., 1977). Hetherington (1968), Onda et al. (1971) and Hikita et al. (1977) have developed expressions for the enhancement factor ϕ. These expressions, however, are specific to sodium hydroxide/sodium bisulfite/sodium sulfite solutions and have been verified under conditions not typical of flue gas scrubbing. Other studies (McMichael et al., 1976; Rochelle and King, 1977) have provided a means of correlating scrubber data but lack a fundamental basis for computing ϕ. It is of interest to apply the theory developed in the present study to the computation of ϕ.

Absorption is often modeled by assuming that a thin, stagnant film exists at the gas/liquid interface through which mass transfer occurs at a steady rate (Sherwood et al., 1975). With this approach, Equations (1) to (11) apply except for the boundary conditions [Equations (2), (3*a*), (*b*)]. The boundary conditions that apply to absorption are

$$N_{NV} = 0 \quad \text{at } x = 0 \tag{51}$$

$$C_{SO_2}(0) = \frac{y_{SO_2,0} P_{tot}}{\gamma_{SO_2} H_{SO_2}} \tag{52}$$

$$C_i(1) = \text{known} = \text{bulk composition} \tag{53}$$

Also, L in Equations (7) and (10) must be replaced by D^0/k_l^0, where k_l^0 is a mass transfer coefficient determined by the absorption of a (chemically unreactive) species that has diffusion coefficient D^0.

Equations (25) to (27) follow directly just as for the aqueous film considered previously. Therefore, equilibrium theory for absorption is

$$N_{SO_2} = \sum_j n_j D'_j [C_j(0) - C_j(1)] \tag{54}$$

where $C_j(0)$ are related to $C_{SO_2}(0)$ by equilibrium expressions, and $C_j(1)$ are known [Equation (53)].

The NEBLA becomes

$$N_{SO_2} = \frac{D_{SO_2}}{\delta_0}[C_{SO_2}(0) - C_{SO_2}(\delta_0)] \tag{55}$$

and

$$N_{SO_2} = \frac{1}{1 - \delta_0} \sum_j n_j D'_j [C_j(\delta_0) - C_j(1)] \tag{56}$$

where the $C_j(\delta_0)$ are in equilibrium with $C_{SO_2}(\delta_0)$. Note that D^0/k_l^0 replaces L in the definition of δ_0 [Equation (40)]. The NEBLA has only one boundary layer in this application because there is only one gas/liquid interface. Equations (55) and (56) can be solved simultaneously for $C_{SO_2}(\delta_0)$ and N_{SO_2}, and the enhancement factor

$$\phi = \frac{N_{SO_2}}{D_{SO_2}[C_{SO_2}(0) - C_{SO_2}(1)]} \tag{57}$$

can then be computed.

When there is gas phase resistance, the following equation applies:

$$N_{SO_2} = k_g (y_{SO_2,b} - y_{SO_2,0}) \tag{58}$$

Equations (52), (54) and (58) or Equations (52), (55), (56) and (58) must be solved simultaneously for the equilbrium or NEBLA theories. In making the equilibrium calculations involved in the equilibrium and NEBLA theories, it is reasonable to assume that the total alkalinity in the bulk liquid is the total alkalinity everywhere in the stagnant film (Roberts, 1979).

Sample calculations for the enhancement factor for a concentrated sodium hydroxide scrubbing solution show some important features. Conditions chosen for these calculations are $y_{SO_2,0}$

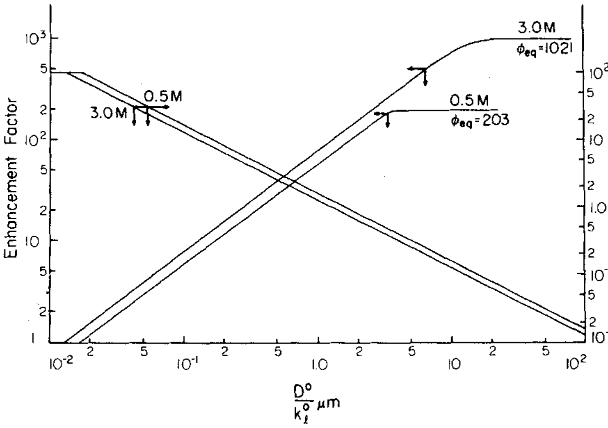

Figure 5. Enhancement factor for sulfur dioxide scrubber. In concentrated sodium hydroxide solutions, the enhancement factor can vary over several orders of magnitude depending on the thickness of the stagnant film at the gas/liquid interface (D^0/k_l^0). For most values of D^0/k_l^0, ϕ is given by $\phi = 1$, $\phi = \phi_{eq}$ or $\phi = 1/\delta_0$. Large deviation from the equilibrium limit is possible when δ_0 is a relatively small fraction of D^0/k_l^0 (for example, $\delta_0 \simeq 10^{-2}$).

$= 10^{-3}$, $P_{tot} = 100$ kPa, $T = 298°K$ and $Na_{tot} = 0.5M$ and 3.0M. The concentrations in the bulk of the scrubbing liquid [Equation (53)] are assumed to be at chemical equilibrium and have a sulfur dioxide back pressure of 0.01 Pa. These conditions are representative of existing FGD processes. Because ϕ depends on D^0/k_l^0 and k_l^0 depends on the scrubber packing, the gas and liquid flow rates and other design variables particular to a given application, results will be presented with D^0/k_l^0 as an independent variable.

Figure 5 shows the enhancement factor predicted by the NEBLA for a range of values of D^0/k_l^0. The boundary layer thickness δ_0 is also shown; large deviations from the equilibrium limit can occur when δ_0 is as little as 1% of the thickness of the stagnant film (D^0/k_l^0). When δ_0 reaches 100% of D^0/k_l^0, $\phi = 1$, and for sufficiently small δ_0, ϕ agrees with equilibrium theory. Between these limits, ϕ is approximately $1/\delta_0$. This intermediate limit for ϕ can be understood by substituting Equation (55) into Equation (57):

$$\phi = \frac{1}{\delta_0} \frac{[C_{SO_2}(0) - C_{SO_2}(\delta_0)]}{[C_{SO_2}(0) - C_{SO_2}(1)]} \tag{59}$$

Since $C_{SO_2}(1) << C_{SO_2}(0)$

$$\phi \simeq \frac{1}{\delta_0}\left(1 - \frac{C_{SO_2}(\delta_0)}{C_{SO_2}(0)}\right) \tag{60}$$

Figure 5, therefore, shows that for many values of k_l^0, $C_{SO_2}(\delta) << C_{SO_2}(0)$. Qualitatively, this inequality means that the concentrated sodium hydroxide solutions are such an effective sink for sulfur dioxide that the equilibrium region of the stagnant film offers little resistance to the transport. Under this condition, the flux is controlled by the boundary layer at $x = 0$ and is given by Equation (55) with $C_{SO_2}(\delta_0)$ neglected:

$$N_{SO_2} = \frac{D_{SO_2}}{\delta_0} \cdot C_{SO_2}(0) \tag{61}$$

Thus

$$\phi = \frac{1}{\delta_0} = \frac{D^0}{k_l^0}\left(\frac{k_1}{\hat{D}_{SO_2}}\right)^{\frac{1}{2}} \tag{62}$$

One finds, therefore, that in some instances further addition of chemical additives does not affect ϕ even though liquid phase resistance may be controlling the absorption. Note that for $D^0/k_l^0 \lesssim 3$ μm, ϕ would be equal for 3.0M and 0.5M except that the viscosity of a 3.0M solution is greater (that is, lower $\hat{D}_{SO_2}$).

A further implication of Equation (62) is

$$\hat{N}_{SO_2} = [k_1 \hat{D}_{SO_2}]^{\frac{1}{2}} \hat{C}_{SO_2}(0) \tag{63}$$

Thus, the (dimensional) flux is independent of k_l^0 so that energy spent on agitating the liquid increases the absorption only if it increases the amount of gas/liquid contact (interfacial area per unit volume).

It is sometimes difficult to obtain values for k_l^0 as a function of various scrubber operating conditions. If these values cannot be obtained, the exact calculation of ϕ is not possible. The three regimes shown in Figure 5, however, provide qualitative insight in controlling the operation of a particular scrubber. For example, one may find that addition of alkalinity increases the removal efficiency. In this case, the scrubber is operating in a regime that corresponds to $D^0/k_l^0 \gtrsim 5$ μm in Figure 5. One may find the performance independent of increased alkalinity or of efforts to increase k_l^0. In this case, the scrubber would be operating in a regime corresponding to the region $\hat{\delta}_0 < D^0/k_l^0 < 3$ μm. Therefore, through empirical testing and Figure 5, one may be able to understand better the operation of a particular scrubber even in the absence of values for k_l^0.

ACKNOWLEDGMENT

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NOTATION

A^{z-} = anion of neutral salt
B = contribution of potential gradient to the flux
C_i = concentration of species i (mole/l)
C_0 = concentration of nonvolatile species added to film
C^* = characteristic value of H_3O^+ concentration in boundary layer near $x = 1$
$\tilde{C}$ = arbitrary concentration used in nondimensionalizing
D_i = diffusion coefficient of species i
D_i' = diffusion coefficient modified to account for potential gradient, Equations (26) and (27)
D^0 = diffusion coefficient of chemically inert species used for obtaining k_l^0
$D^*_{HSO_3^-}$ = effective (enhanced) diffusivity of HSO_3^-, Equation (23)
F = Faraday's constant, Equation (5)
F = facilitation factor; $(N\text{-}N_0)/N_0$
H_{SO_2} = Henry solubility coefficient
k_1, k_{-1} = forward and reverse rate coefficients for the reaction $SO_2(aq) + 2H_2O \rightleftarrows H_3O^+ + HSO_3^-$
k_l^0 = liquid phase mass transfer coefficient for absorption of chemically inert species
k_g = gas phase mass transfer coefficient
K = equilibrium coefficient, Table 1
L = thickness of aqueous film
M^{z+} = cation of neutral salt
MW_i = molecular weight of species i
n_i = number of sulfur IV atoms in species i
N_i = flux of species i
N_0 = flux of sulfur dioxide in absence of chemical reactions
Na_{tot} = total alkaline sodium concentration (acid neutralizing capacity)
P_0 = arbitrary pressure used in non-dimensionalizing
P_{SO_2} = partial pressure of sulfur dioxide
P_{tot} = total pressure
r_i = rate of production of species i by homogeneous chemical reaction
R = universal gas constant
T = temperature
x = distance variable in aqueous film
x_0, x_1 = arbitrary fixed points in film
y_{SO_2} = mole fraction of sulfur dioxide in gas phase
z_i = algebraic charge on species i
z^- = algebraic charge on anion of neutral salt
z^+ = algebraic charge on cation of neutral salt

Greek Letters

γ_i = activity coefficient of species i
δ_0 = boundary layer thickness near $x = 0$
δ_1 = boundary layer thickness near $x = 1$
ν^- = number of atoms of anion in one molecule of neutral salt
ν^+ = number of atoms of cation in one molecule of neutral salt
τ_R = characteristic reaction time
ϕ = enhancement factor; $F + 1$, Equation (57)
Φ = electric field potential

Subscripts

A = anion
b = bulk of gas phase
eq = equilibrium theory
i = any species
j = sulfur containing species
k = sodium containing species
1 = on $x = 1$ side of film

M = cation
n = any species
NV = nonvolatile species
0 = on $x = 0$ side of film
ref = reference species

Superscripts

0 = infinite dilution
^ = a dimensional variable or parameter

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Part II. Experimental Results and Comparison with Theory

Measurements were made of the steady state flux of sulfur dioxide through films of water and solutions of neutral and alkaline sodium salts (0.1 to 2.0M sodium chloride, 10^{-3} to 3.0M sodium hydroxide, $NaHSO_3$ or sodium sulfite) with sulfur dioxide partial pressures between 10 and 100Pa. In agreement with equilibrium theory (Part I), data from water and sodium chloride solutions show that HSO_3^- is responsible for 83 to 95% of the flux (facilitation factor F between 5 and 19). In alkaline solutions, HSO_3^- and other sulfur containing species cause F to be as large as 1 370. Equilibrium theory, however, overpredicts F by up to a factor of 7. The NEBLA (Part I) accounts for this deviation.

SCOPE

Interest in flue gas desulfurization (FGD) has given rise to a number of fundamental studies on the absorption of sulfur dioxide into water (Hikita et al., 1978) and into sodium hydroxide, $NaHSO_3$, and sodium sulfite solutions (Hikita et al., 1977; Takeuchi et al., 1975; Onda et al., 1971; Hetherington, 1968; Goettler, 1967). With the exception of Takeuchi et al., pure sulfur dioxide was absorbed so that partial pressures of interest in FGD (approximately 10 to 100Pa) were not studied. At the low partial pressures typical of FGD, the sulfur containing ions formed by the reactions of sulfur dioxide in solution are a much

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