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Numerical Calculation of Simultaneous Absorption of H₂S and CO₂ in Aqueous Hydroxide Solutions

Simultaneous absorption of H₂S and CO₂ in aqueous hydroxide solutions is studied numerically, considering reversibility effects of all reactions involved. A finite-difference scheme based on film theory is developed, which exhibits excellent convergence characteristics. The effect of finite CO₂ reaction rate is examined, and the role of the second dissociation of CO₂ in enhancing the kinetic selectivity toward H₂S absorption is demonstrated. Under certain conditions, forced desorption of CO₂ is predicted. The effect of temperature on the selectivity of the system at hand is investigated. It is shown that, as the temperature increases, the effect of the accelerated CO₂ reaction is gradually reversed by the increased CO₂ back-pressure and by forced desorption effects. In fact, the results suggest that the selectivity at temperatures around 200 °C may be significantly greater than that attained at room temperature.

Introduction

The problem of simultaneous absorption of two gases accompanied by chemical reaction was first considered by Roper, Hatch, and Pigford (1962). The special case studied involved irreversible, instantaneous reactions and was analyzed based on the concept of the "reaction plane". Ramachandran (1971) considered the case when both reactions are reversible and instantaneous while a number of authors provided approximate solutions for the case of irreversible reactions, one which occurs instantaneously and the other which proceeds at a finite rate (Onda et al., 1970b; Goettler and Pigford, 1971; Ramachandran and Sharma, 1971; Cornelisse et al., 1977).

Relatively recently it was numerically shown by Cornelisse et al. (1980) that the inclusion of reversibility could lead to one component being desorbed under a driving force positive for absorption. This phenomenon of forced desorption was systematically analyzed by Astarita and Savage (1982) for the case of instantaneous reactions, by considering the "shift reaction" between the two gases.

The simultaneous absorption of H₂S and CO₂ in alkaline solutions is a typical industrial operation where the above analyses are applicable. The reaction of H₂S is instantaneous under all conditions, whereas CO₂ reacts at a finite rate. Selective H₂S absorption is often highly desirable, as in the case of H₂S removal to produce an environmentally acceptable off-stream. The application motivating

this study is the selective removal of H₂S, contained together with CO₂ in high-enthalpy geothermal steam, by scrubbing input or output streams with an aqueous hydroxide solution. Process simplicity and operational restrictions (e.g., high temperatures in the case of H₂S removal upstream of the turbines) do not favor the use of alkanol amines, which is widespread in the chemical industry.

Absorption of H₂S and CO₂ in aqueous hydroxide solutions was first studied by Astarita and Gioia (1965). Considering the reactions involved as irreversible, they employed the notion of two reaction planes and showed that the selectivity toward H₂S is considerably higher than expected on the basis of the Roper, Hatch, and Pigford theory. The key assumption made by Astarita and Gioia was that the fast (but not instantaneous) reaction of CO₂ does not take place at all, unless there exists a substantial concentration of OH⁻ ions, in which case it is assumed to proceed to completion instantaneously.

An analysis of the H₂S-CO₂-NaOH system, taking into account reversibility effects of all reactions, has not been presented yet, to the best of our knowledge. It is indicative of the state of the art in absorption tower design that even comprehensive computer simulations such as those of De Leye and Froment (1986) treat the CO₂ absorption as irreversible. This can be attributed in part to the fact that the system at hand is further complicated by the second

dissociation reactions of CO_2 and H_2S , which cannot be neglected at the pH range of practical interest.

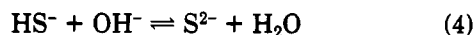
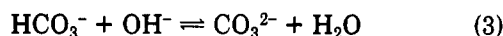
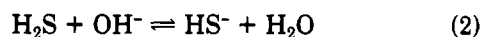
The complete set of reactions is considered in the present work, and an efficient computational scheme is developed for its solution in the framework of film theory. The exact solution derived accounts for a variety of effects, such as reversibility and finite reaction rate. Therefore, at the expense of a modest amount of computational time, it can be used with more confidence than the approximate approach of Astarita and Gioia (1965). The numerical solution of the mass-transfer equations will be incorporated, in future work, in a computer code for the design of gas scrubbers. The use of film theory is, therefore, preferred because of the shorter computation time involved as compared with unsteady-state theories.

The occurrence of a shift reaction in the present chemical system leads to the manifestation of forced desorption phenomena, which have been repeatedly documented in the case of aqueous amine solutions (Cornelisse et al., 1980; Astarita and Savage, 1982; Al-Ghawas and Sandall, 1988). One original feature of the present contribution, however, is the consideration of the more complex situation where two gases are simultaneously absorbed, each by consecutive reactions coupled at every level. Indeed, the second dissociation of CO_2 appears to significantly affect the kinetic selectivity toward H_2S for a wide range of conditions.

Finally, the effect of temperature on the selectivity of the system at hand is investigated. Limited attention has been paid in the literature to this aspect, although it is evident that results concerning single-gas absorption cannot be safely extended to the more complex case of multiple-gas absorption presently considered.

Chemistry

When H_2S and CO_2 are being absorbed in a hydroxide solution, the following reversible reactions should be considered (Astarita and Gioia, 1965):



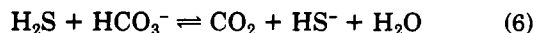
Equilibrium constants are denoted by K_1 , K_2 , K_3 , and K_4 , respectively. Reactions 2, 3, and 4 may be considered instantaneous when compared to the rate of diffusional processes. The rate of reaction 1 is given (Astarita et al., 1983) by the relation

$$R_1 = k([\text{CO}_2][\text{OH}^-] - (1/K_1)[\text{HCO}_3^-]) \quad (5a)$$

with the rate constant k depending on the temperature T and the ionic strength I in the following way:

$$\log k = 13.635 - 2895/T + 0.08I \quad (5b)$$

The occurrence of the shift reaction



is automatically accounted for by considering reactions 1 and 2 as reversible.

As for the physicochemical data needed for the model, Henry's law is assumed to hold, with the dependence of the constants on temperature taken from Astarita et al. (1983). The equilibrium constants as functions of the temperature are given by the above authors and are also tabulated in Barbero et al. (1982).

Mass-Transfer Model

The gas-phase resistance to mass transfer is considered negligible and only the liquid-side mass transfer is modeled. In order to focus attention on the fundamental issues, the simplifying assumption of equal diffusivities is made. This assumption permits an analysis based on the film theory model, which leads to ordinary instead of partial differential equations.

A straightforward extension of the proposed computational scheme includes use of the correct diffusivities and application of the semiempirical correction of Chang and Rochelle (1982), to provide results similar to those of surface renewal theory. Indeed, Glasscock and Rochelle (1989) show that the differences from unsteady-state models are negligible compared to the uncertainty in the actual mass-transfer mechanism. Since, however, no quantitative comparison with data is attempted in the present work, this alternative is not pursued here.

The steady-state mass balances across the liquid film result in the following equations:

carbon dioxide reaction balance

$$D \frac{d^2[\text{CO}_2]}{dx^2} - \left\{ k[\text{CO}_2][\text{OH}^-] - \frac{k}{K_1}[\text{HCO}_3^-] \right\} = 0 \quad (7)$$

total carbon balance

$$D \left\{ \frac{d^2[\text{CO}_2]}{dx^2} + \frac{d^2[\text{HCO}_3^-]}{dx^2} + \frac{d^2[\text{CO}_3^{2-}]}{dx^2} \right\} = 0 \quad (8)$$

total sulfur balance

$$D \left\{ \frac{d^2[\text{H}_2\text{S}]}{dx^2} + \frac{d^2[\text{HS}^-]}{dx^2} + \frac{d^2[\text{S}^{2-}]}{dx^2} \right\} = 0 \quad (9)$$

total hydroxide balance

$$D \frac{d^2[\text{OH}^-]}{dx^2} = R_1 + R_2 + R_3 + R_4 \\ = d \left\{ \frac{d^2[\text{CO}_2]}{dx^2} + \frac{d^2[\text{H}_2\text{S}]}{dx^2} - \frac{d^2[\text{CO}_3^{2-}]}{dx^2} - \frac{d^2[\text{S}^{2-}]}{dx^2} \right\} \quad (10)$$

where R_1 , R_2 , R_3 , and R_4 represent the rates of reactions 1–4. The equilibrium of the instantaneous reactions provides the following equations:

$$[\text{HS}^-] = K_2[\text{H}_2\text{S}][\text{OH}^-] \quad (11)$$

$$[\text{CO}_3^{2-}] = K_3[\text{HCO}_3^-][\text{OH}^-] \quad (12)$$

$$[\text{S}^{2-}] = K_4[\text{HS}^-][\text{OH}^-] \quad (13)$$

The bulk of the liquid is assumed to be in equilibrium for a given loading of total carbon and sulfur (C = total carbon concentration, S = total sulfur concentration, and M = total metallic ion concentration are given). These constraints, together with an equation representing the electrical charge balance (negative charge concentration = M), uniquely determine the liquid composition in the bulk. The boundary conditions at the edge of the liquid film, $x = 0$, equate the concentration of each component to its bulk value.

$$\begin{aligned} [\text{H}_2\text{S}] &= [\text{H}_2\text{S}]_b, \quad [\text{HS}^-] = [\text{HS}^-]_b, \\ [\text{S}^{2-}] &= [\text{S}^{2-}]_b, \quad [\text{OH}^-] = [\text{OH}^-]_b, \quad [\text{CO}_2] = [\text{CO}_2]_b, \\ [\text{HCO}_3^-] &= [\text{HCO}_3^-]_b, \quad [\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_b \\ &\text{on } x = 0 \quad (14) \end{aligned}$$

At the gas-liquid interface, $x = \delta$, the following equations hold:

$$N_{\text{CO}_2} = -D \left(\frac{d[\text{CO}_2]}{dx} \right)_i \quad (15)$$

$$N_{\text{H}_2\text{S}} = D \left\{ -\frac{d[\text{H}_2\text{S}]}{dx} - \frac{d[\text{HS}^-]}{dx} - \frac{d[\text{S}^{2-}]}{dx} \right\}_i \quad (16)$$

$$D \left(\frac{d[\text{HCO}_3^-]}{dx} \right)_i + D \left(\frac{d[\text{CO}_3^{2-}]}{dx} \right)_i = 0 \quad (17)$$

$$D \left(\frac{d[\text{OH}^-]}{dx} \right)_i = N_{\text{H}_2\text{S}} + D \left\{ \frac{d[\text{H}_2\text{S}]}{dx} + \frac{d[\text{HCO}_3^-]}{dx} - \frac{d[\text{S}^{2-}]}{dx} \right\}_i \quad (18)$$

Relations 15 and 16 equate the transfer rates at the gas and liquid sides for CO_2 and H_2S , respectively. Equation 17 states that no carbon-containing ions pass the interface, nor can they be converted infinitely fast into CO_2 . Equation 18 is a budget of $[\text{OH}^-]$ ions at the interface and is the outcome of the following arguments: Since no $[\text{OH}^-]$ ions cross the interface, the diffusion-induced flux and the surface rate of consumption at the interface sum up to zero.

$$R_{i1} + R_{i2} + R_{i3} + R_{i4} - D \left(\frac{d[\text{OH}^-]}{dx} \right)_i = 0 \quad (19)$$

where R_{i1} , R_{i2} , R_{i3} , and R_{i4} are the surface rates of reactions 1, 2, 3, and 4 respectively, right on the interface. It is noted that the surface rate of consumption can be nonzero only for instantaneous reactions; therefore $R_{i1} = 0$. The other surface rates are calculated by writing down appropriate budgets at the interface for each instantaneous reaction separately, as follows:

$$N_{\text{H}_2\text{S}} = R_{i2} - D \left(\frac{d[\text{H}_2\text{S}]}{dx} \right)_i \quad (20)$$

$$N_{\text{HCO}_3^-} = 0 = R_{i3} - R_{i1} - D \left(\frac{d[\text{HCO}_3^-]}{dx} \right)_i \quad (21)$$

$$N_{\text{S}^{2-}} = 0 = -R_{i4} - D \left(\frac{d[\text{S}^{2-}]}{dx} \right)_i \quad (22)$$

By substituting (20), (21), and (22) in (19), (18) is derived.

Equations 8, 9, and 10 can be readily integrated twice, using boundary conditions (14)–(18), to arrive at the following equations valid everywhere in the film:

$$([\text{H}_2\text{S}] - [\text{H}_2\text{S}]_b) + ([\text{HS}^-] - [\text{HS}^-]_b) + ([\text{S}^{2-}] - [\text{S}^{2-}]_b) + (N_{\text{H}_2\text{S}}\delta/D)(x/\delta) = 0 \quad (23)$$

$$([\text{CO}_2] - [\text{CO}_2]_b) + ([\text{HCO}_3^-] - [\text{HCO}_3^-]_b) + ([\text{CO}_3^{2-}] - [\text{CO}_3^{2-}]_b) + (N_{\text{CO}_2}\delta/D)(x/\delta) = 0 \quad (24)$$

$$([\text{OH}^-] - [\text{OH}^-]_b) + ([\text{HCO}_3^-] - [\text{HCO}_3^-]_b) + ([\text{HS}^-] - [\text{HS}^-]_b) + 2([\text{CO}_3^{2-}] - [\text{CO}_3^{2-}]_b) + 2([\text{S}^{2-}] - [\text{S}^{2-}]_b) = 0 \quad (25)$$

The enhancement factors of H_2S and CO_2 , f_1 and f_2 , respectively, are defined as

$$f_1 = \frac{N_{\text{H}_2\text{S}}(\delta/D)}{([\text{H}_2\text{S}]_i - [\text{H}_2\text{S}]_b)}, \quad f_2 = \frac{N_{\text{CO}_2}(\delta/D)}{([\text{CO}_2]_i - [\text{CO}_2]_b)} \quad (26)$$

For given values, $[\text{H}_2\text{S}]_i$ and $[\text{CO}_2]_i$, of the gas concentration on the interface, (7), (11)–(13), and (23)–(25) constitute the system to be solved. The unknowns are the enhancement factors f_1 and f_2 and the concentration of each component across the liquid film.

Numerical Method

The equations are nondimensionalized using the metallic ion concentration, M , as the characteristic concentration and the film thickness δ as the characteristic length. The fundamental dimensionless group appearing is the reaction-diffusion parameter A , given by

$$A = kM\delta^2/D \quad (27)$$

where $t_D = \delta^2/D$ is the characteristic diffusion time. For a reasonably well mixed liquid, t_D varies within a relatively narrow range (Astarita et al., 1983):

$$4 \times 10^{-3} < t_D < 4 \times 10^{-2} \text{ s} \quad (28)$$

The system is solved numerically by discretizing the equations to $N + 2$ points across the liquid film. In this formulation, the unknowns are the concentrations of each of the seven species at the $N + 1$ points (point 1 is at the edge of the liquid film) and the two enhancement factors, a total of $[7(N + 1) + 2]$. Equations 11–13 and 23–25 are applied to each point across the film, giving $6(N + 1)$ equations. Two equations are provided by specifying the H_2S and CO_2 concentrations on the interface and another N by applying (7) to the N interior points of the film. To this end, the derivative in (7) is approximated by central finite differences.

The last equation needed is provided by applying (7) at the point $N + 2$, right on the interface. Boundary condition 15 is discretized at point $N + 2$ by a central finite difference formula, and the hypothetical concentration at point $N + 3$, outside the gas-liquid interface, is used to derive the following expression for the second derivative on the interface:

$$\left(\frac{d^2y}{dx^2} \right)_{N+2} = \frac{2y_{N+1} - 2y_{N+2} - 2(\Delta x)(N_{\text{CO}_2}/D)}{(\Delta x)^2} \quad (29)$$

The above computational scheme produces a system of nonlinear algebraic equations, which is solved by Newton's method. The standard procedure is modified by including in the algorithm a constraint which rejects negative values of the concentration during the iteration, thus leading to the physically significant solution. An additional improvement to the computational scheme involves the unequal distribution of the discretization points across the film in order to achieve finer resolution close to the interface. The numerical method exhibits excellent convergence characteristics and presents no stability problems like the ones reported in the literature concerning solution of similar systems by a shooting technique (Al-Ghawas and Sandall, 1988).

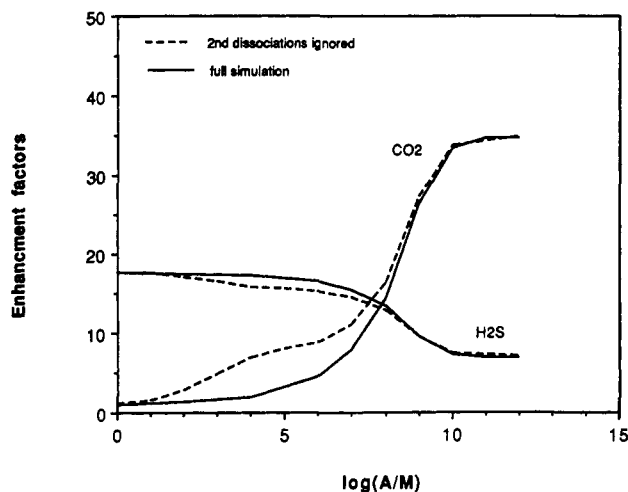
Results

The accuracy of the present numerical scheme was confirmed by successful computation of the analytically tractable cases of absorption of a single component followed either by instantaneous reversible reaction (Onda et al., 1970a) or by irreversible reaction at finite rate (Van Krevelen and Hoftijzer, 1948). The difference of the numerical results from analytic expressions of the above studies was less than 1% and 3%, respectively.

The simultaneous absorption of H_2S and CO_2 was considered next, focusing on the special case where the bulk

Table I. Parameters Used To Study the Effect of Reaction Rate

	25 °C	225 °C
$[H_2S]_i$, kmol/m ³	0.060	0.060
$[CO_2]_i$, kmol/m ³	0.019	0.019
S , kmol/m ³	0.5	0.5
C , kmol/m ³	0.5	0.5
M , kmol/m ³	2.0	2.0
K_1	4.2×10^7	6.2×10^3
K_2	1.0×10^7	2.1×10^4
K_3	4.5×10^3	3.8
K_4	2.1	1.0×10^4

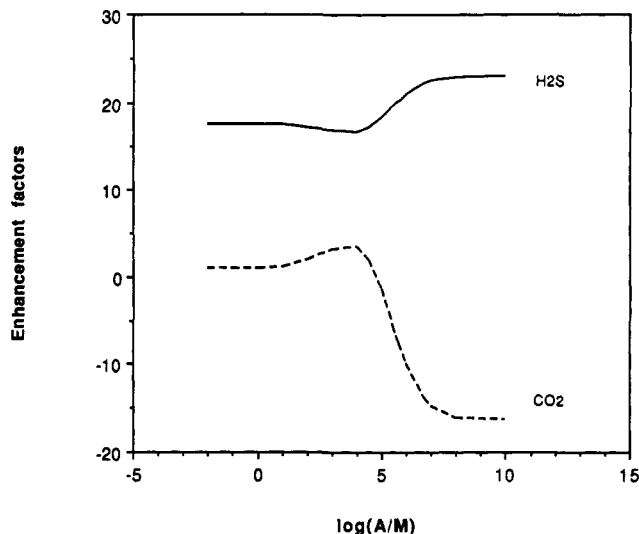
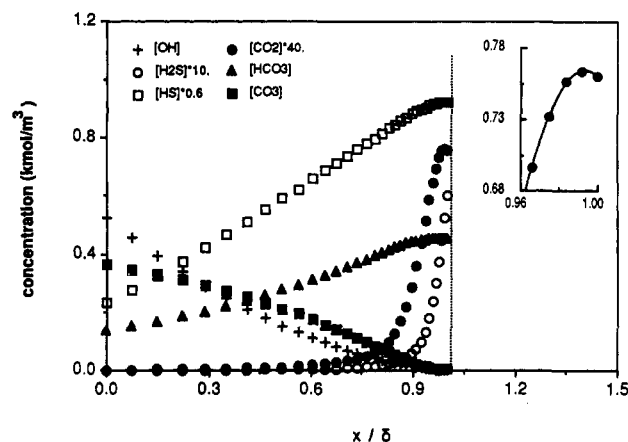
**Figure 1.** H_2S and CO_2 enhancement factors as a function of the reaction-diffusion parameter, using the equilibrium constants at 25 °C and bulk concentrations indicated in Table I.

liquid concentration of the reaction products is zero. This permits comparison with the approximate analytical results of Astarita and Gioia (1965). The outcome indicates that the approximate model overestimates the absorption of CO_2 , a discrepancy which diminishes as the CO_2 reaction rate approaches infinity. The most serious drawback of that model, however, is its neglect of reversibility effects. Forced desorption cannot be predicted by the Astarita-Gioia model, and it is under conditions favoring such phenomena that the model is expected to fail.

Following the above comparisons, absorption into a liquid with nonzero concentration of the reaction products is considered and the effect of two parameters, reaction rate and temperature, is studied in detail.

(a) Effect of the Rate of Reaction. To illustrate the effect of the reaction-diffusion parameter, A , the following two cases are considered: The equilibrium constants used are those corresponding to the reactions taking place (case i) at 25 °C and (case ii) at 225 °C. These parameters, as well as the bulk concentrations used, are given in Table I. For the specific system and conditions considered the reaction-diffusion parameter is fully specified. The computations, however, are performed by varying A as a parameter in order to illustrate its effect on the absorption rates. It should be noted that, in the limit of instantaneous reactions ($A \rightarrow \infty$), selective absorption of CO_2 is favored in case i and that of H_2S is favored in case ii.

The results for case i are presented in Figure 1. With decreasing reaction rate, there is a transition from a thermodynamic selectivity favoring the absorption of CO_2 to a kinetically imposed selective absorption of H_2S . It is interesting to note that kinetic selectivity in favor of H_2S is still dominant for values of A/M as high as 10^6 (corresponding to CO_2 reaction rate constant of 10^8 m³/(kmol s)) and thermodynamic selectivity in favor of CO_2 only

**Figure 2.** H_2S and CO_2 enhancement factors as a function of the reaction-diffusion parameter, using the equilibrium constants at 225 °C and bulk concentrations indicated in Table I.**Figure 3.** Concentration profiles across the film for parameter values indicated in Table I (225 °C) and very fast CO_2 reaction. The concentrations are scaled by the factors indicated on the figure to permit presentation on the same plot. A maximum in the CO_2 concentration close to the interface, indicative of forced desorption, is observed.

takes over for values of A/M above 10^8 .

The effect of the second dissociation of CO_2 is illustrated by setting $K_3 = K_4 = 0$ and recalculating the enhancement factors. The results, which appear as dashed lines in Figure 1, indicate that the second dissociation has a favorable effect on the selective absorption of H_2S . For a large range of reaction rates, inclusion of the second dissociation leads to an increase of the H_2S enhancement factor with an even more significant decrease of the CO_2 enhancement factor. This is expected, since in the absence of CO_3^{2-} ions there is a single reaction plane for both gases defined by the depletion of OH^- ions.

It is interesting to contrast this observation with the well-known negative effect of the CO_3^{2-} ions on the *thermodynamic selectivity* of H_2S (Astarita et al., 1983). This is an example of the case where factors influencing the thermodynamic selectivity in one way could have the opposite effect on the kinetic selectivity.

The results for case ii are presented in Figure 2. The CO_2 enhancement factor first increases with reaction rate, reaching a maximum at some intermediate value. The H_2S enhancement factor exhibits a minimum in the same range of reaction rates and then asymptotically reaches a plateau, with CO_2 dipping to large negative values.

Table II. Enhancement Factors for H₂S and CO₂ Absorption as a Function of Temperature

temp, °C	H ₂ S enhancement	CO ₂ enhancement
25	20.3	1.2
75	50.0	2.7
125	68.0	6.4
175	76.5	-23.1
225	80.6	-92.7

The behavior in the limit of large values of the reaction-diffusion parameter is an example of forced desorption, discovered by Cornelisse et al. (1980) and analyzed for irreversible reactions by Astarita and Savage (1982). Indeed, the concentration of CO₂ in the bulk is much smaller than on the interface and an overall driving force for absorption exists. Reversibility effects close to the interface, however, overshoot to CO₂ concentration above the interface value, leading to desorption. A concentration profile for such a case is shown in Figure 3.

(b) Absorption at High Temperatures. Some concern has been expressed in the literature (Hohlfeld, 1980) about the efficiency of selective absorption of H₂S by scrubbing with hydroxide solutions at elevated temperatures, in view of the increased reaction rate of the competitive absorption of CO₂. However, the above results indicate that the process could still prove efficient.

To further investigate the effect of temperature on the selectivity of the system at hand, a series of runs is carried out with bulk concentrations $S = 0.5$, $C = 0.5$, and $M = 2.0$ and temperatures ranging from 25 to 225 °C. The gas phase is assumed to consist of H₂S and CO₂, with partial pressure of 0.5 atm each. The reaction rate constant, as given by (5b), is used and the dependence of Henry's law and equilibrium constants on temperature is also taken into account. The results, which are presented for selected temperatures in Table II, indicate a monotonic increase in the H₂S enhancement factor with temperature. The behavior of CO₂ is more interesting. An increase in the enhancement factor with temperature is observed first, attributable to the increase of the kinetic constant. At high temperatures, however, reversibility effects come into play and finally forced desorption of CO₂ occurs. Actual absorption rates for CO₂ are adversely affected, as noted by Yu and Astarita (1987), even at lower temperatures by the combined effects of the increase in CO₂ back-pressure and Henry's law constant with temperature. On the basis of the results presented, it can be argued that the selectivity in H₂S absorption will initially deteriorate with temperature, possibly reaching a minimum before 100 °C, but will improve dramatically at higher temperatures.

Conclusions

Absorption of H₂S and CO₂ in aqueous hydroxide solutions is studied numerically. A computational scheme is developed for this complex system, which is shown to converge for any possible value of the parameters involved. In particular, varying the reaction rate of the noninstantaneous reaction over more than 15 orders of magnitude causes no convergence problems and the correct asymptotic results (pure diffusion at one end and instantaneous reaction at the other) are recovered. This scheme can easily be adapted to a different set of reactions.

Kinetic selectivity toward H₂S is observed for a wide range of values of the CO₂ reaction rate constant. It is demonstrated that the second dissociation of CO₂ further enhances this phenomenon. Finally, forced desorption of CO₂, possibly leading to very high selectivity, is shown to become important at temperatures well above 100 °C.

In forthcoming work, the numerical scheme presented

here is incorporated in a computer code, which will be used in the interpretation of data from experiments already under way.

Acknowledgment

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Nomenclature

- A = dimensionless reaction-diffusion parameter, $A = kM\delta^2/D$
 C = total carbon concentration, kmol/m³
 D = molecular diffusivity, m²/s
 f_j = enhancement factor of gas j
 I = ionic strength of solution, kion/m³
 k = reaction rate constant, m³/(kmol s)
 K_j = equilibrium constant of reaction j , m³/kmol
 M = total metallic ion concentration in solution, kmol/m³
 N_j = molar flux of species j , kmol/(m² s)
 R_j = volume rate of reaction j , kmol/(m³ s)
 R_{ij} = surface rate at the interface of reaction j , kmol/(m² s)
 S = total sulfur concentration in solution, kmol/m³
 T = absolute temperature, K
 x = distance, measured from the edge of film toward the interface, m
 y_j = CO₂ concentration at location j across the film, kmol/m³

Greek Letters

- δ = film thickness, m

Registry No. H₂S, 7783-06-4; CO₂, 124-38-9; NaOH, 1310-73-2.

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