Simultaneous absorption of hydrogen sulphide and carbon dioxide in aqueous sodium hydroxide solutions was studied, and theoretical equations for the rate of absorption were derived. Experimental results were in good agreement with theory. Selectivity for hydrogen sulphide is also discussed.

Introduction

A number of experimental and theoretical studies of gas absorption with chemical reactions have treated cases in which only one gas species dissolves in liquid phase, and then reacts with liquid phase components. However, the gas absorptions which are important in industrial practice are in general processes of greater complexity; for example, the simultaneous absorption of hydrogen sulphide and carbon dioxide into an alkaline solution in the gas purification process. Roper, et al. have given a theoretical treatment of simultaneous absorption of two gases which react with a liquid phase component. In their treatment, it has been assumed that the two reactions take place instantaneously at a single reaction plane. On the other hand, Astarita and Gioia have given a theoretical solution based on a film model assuming that all the diffusivities of the reacting species are equal, and that two reaction planes exist in the liquid phase. However, in their work no comparison of experimental results and theoretical solutions was made, and experimental data obtained by a wetted-wall column were not discussed quantitatively.

In the present paper, absorption rates of H₂S and CO₂ into aqueous sodium hydroxide solutions have been measured in a wetted-wall column. The experimental results are compared with the theoretical solutions given by the previous workers and this study, which takes into the account ionic effects. Furthermore, selectivity for hydrogen sulphide is discussed.

Theoretical

The process of simultaneous absorption of H₂S and CO₂ in an aqueous hydroxide solution may be accompanied by one or more of the following instantaneous and irreversible reactions as suggested by Astarita and Gioia:

\[
\begin{align*}
\text{CO}_2 + 2\text{OH}^- & \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \\
\text{H}_2\text{S} + \text{OH}^- & \rightarrow \text{HS}^- + \text{H}_2\text{O} \\
\text{H}_2\text{S} + \text{CO}_3^{2-} & \rightarrow \text{HS}^- + \text{HCO}_3^- \\
\text{HCO}_3^- + \text{OH}^- & \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}
\end{align*}
\]

As they have discussed, it is assumed that there exist two planes in the liquid phase, i.e., one reaction plane (which is called "secondary" below) where CO₂ reacts, according to Reaction (1), with OH⁻ ion instantaneously and another reaction plane (which is called "primary") where H₂S reacts with CO₃²⁻ ion instantaneously by Reaction (3). The liquid phase is divided by the two reaction planes into three regions, denoted by I, II and III. Thus a plausible sketch of the concentration profiles in the liquid is shown in Fig. 1.

If all of the species are non-electrically charged molecules and gas-phase resistance is neglected, material balance equation for each species based on the penetration model over a slice of liquid of thickness \(dx\) within the diffusion path would yield

\[
\frac{\partial A}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} \\
\frac{\partial B}{\partial t} = D_B \frac{\partial^2 B}{\partial x^2} \\
\frac{\partial C}{\partial t} = D_C \frac{\partial^2 C}{\partial x^2} \\
\frac{\partial E}{\partial t} = D_E \frac{\partial^2 E}{\partial x^2} \\
\frac{\partial F}{\partial t} = D_F \frac{\partial^2 F}{\partial x^2}
\]

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Fig. 1 Concentration profile of each species in simultaneous absorption

\[ \frac{\partial G}{\partial x} = D_G \frac{\partial^2 G}{\partial x^2} \]  
with the boundary conditions

- For \( x > 0, t > 0 \): \( A = A_F, B = B_F, F = F, G = G \)
- For \( x = 0, t > 0 \): \( A = A_0, B = B_0, F = F_0, G = G_0 \)
- For \( x = x_c, t > 0 \): \( B = B_0, F = F_0 \)
- For \( x = x_a, t > 0 \): \( A = A_0, B = B_0, F = F_0 \)
- For \( x = x_o, t > 0 \): \( A = A_0, B = B_0, F = F_0 \)

The analytical solutions are obtained by a method similar to that given by Sherwood and Pigford\(^\text{15}\).

The solubilities of carbon dioxide and hydrogen sulphide at the gas-liquid interface may be estimated by the results given by Onda et al\(^\text{2}\).

Although the analytical solutions are based on the assumption that all of the species are uncharged molecules, this reaction system involves four ionic species. Furthermore, it has long been known\(^\text{7}\) that ions, since they are electrically charged, obey a different law of diffusion from that for molecular species. Therefore, to use the solutions above derived for predicting gas absorption rates, the effective ionic diffusivities of four ionic species have to be evaluated. In the present model, the ratio of the effective ionic diffusivity for each ion to the diffusivity of hydrogen sulphide can be obtained based on the film theory by a method similar to that given by Sherwood and Wei\(^\text{16}\).

\[ r = \frac{D_G}{D_c} \left( \frac{2(c_0 + 2e_0)}{m_2 + c_0 + 2e_0} \right) \]  
\[ r = \frac{D_G}{D_c} \left( \frac{3m_2}{m_2 + m_3} \right) \]  
\[ r = \frac{D_G}{D_c} \left( \frac{2(c_0 + e_0)(c_0 + 2e_0 - m_3) + 1}{m_2 + m_3} \right) \]  
\[ r = \frac{D_G}{D_c} \left( \frac{2m_2}{m_2 + m_3} \right) \]  
where

\[ m_1 = f_i + g_i \]  
\[ m_2 = \frac{1}{3} \left( 1 + 2D'_c f_i \right) \]
Fig. 2 Schematic diagram of experimental apparatus

The abosroption rates were determined by soap-film technique for CO₂-H₂O, H₂S-Na₂CO₃ and H₂S-NaOH systems and by chemical analysis of the exit liquid for H₂S-NaOH and H₂S-CO₂-NaOH systems. In chemical analysis, the total amount of gas absorbed was determined by the Warder method and the amount of H₂S absorbed was decided by iodometric titration. The absorption rate of CO₂ was determined by subtracting the latter from the former.

Results and Discussion

Physical absorption of carbon dioxide into water

To check the reliability of the experimental apparatus, physical absorption of carbon dioxide into water was carried out at 25°C. On the basis of the penetration theory, square of the average absorption rate of carbon dioxide in the wetted-wall column would be given as follows

\[
(N_A)_t^2 = \frac{d \Delta P}{d \theta} (A_w^s)^2 D_{aw} L h
\]

where the effective wetted-wall length \( h \) is evaluated from the difference between the wetted-wall length \( h \), and the end effect \( h_c \). The values of \( D_{aw} \) and \( A_w^s \) used in the present paper are \( 1.94 \times 10^{-4} \text{ cm}^2/\text{s} \).
Experimental results are shown in Fig. 3, together with the theoretical lines calculated from Eq.(48). The good agreement between the experimental data and the theoretical values indicates the reliability of the experimental apparatus and the applicability of the penetration model to the experimental results. Also, this suggests no effect of the surfactant on the absorption rate.

Absorption of hydrogen sulphide into an aqueous sodium carbonate solution

In this system, Reaction (3) may take place and this reaction is presumed to be instantaneous. Thus, reaction factor for hydrogen sulphide may be evaluated from the theoretical equation given by Sherwood and Pigford15. Diffusivity of hydrogen sulphide was evaluated by the following expression given by Onda et al.10

\[ D_{W} = 1 + 0.669x_{2} + 0.412x_{2}^{2} \] (49)

where

\[ \mu = 1 + x_{1} \phi + x_{2} \phi^{2} \] (50)

The effective diffusivity of carbonate ion and solubility of H$_{2}$S in the solution were evaluated by the methods given by Sherwood and Wei16 and Onda et al.9, respectively. The values of $D_{W}$ and $B_{W}$ used in the present work are $2.21 \times 10^{-4}$ cm$^{2}$/sec and $9.99 \times 10^{-1}$ g-mol/cm$^{3}$, respectively.

Absorption rates were determined volumetrically by means of a soap-film technique. In Fig. 4, reaction factor for H$_{2}$S, $\beta_{B}$, is plotted against the Na$_{2}$CO$_{3}$ concentration. The solid line represents the theoretical solution for absorption accompanied by the instantaneous and irreversible reaction between hydrogen sulphide and carbonate ion. The agreement between the experimental results and the theoretical line is good enough to justify the hypothesis that Reaction (3) is instantaneous.

Absorption of hydrogen sulphide into an aqueous sodium hydroxide solution

To check the accuracy of chemical analysis for the determination of absorption rate, absorption rate of hydrogen sulphide into an aqueous sodium hydroxide solution was measured by means of chemical analysis and soap-film technique. For chemical analysis two different methods were used; one is based on the difference between the inlet and outlet liquid of NaOH concentration determined by titration with hydrochloric acid to an end point with phenolphthalein and another is based on the determination of the concentration of sodium hydroxide in the exist liquid by back-titration of excess iodide with sodium thiosulphate. The results of measurements are expressed in Fig. 5 as $(N_0)_2$ vs. h.

Absorption in this system may be regarded as an absorption accompanied by an instantaneous and irreversible chemical reaction as that given by previous workers6,11. The solid lines and broken lines in Fig. 5 represent the penetration theory solutions6,11 for absorption accompanied by a one-step instantaneous chemical reaction and for absorption accompanied by a two-step consecutive instantaneous chemical reaction, respectively. In this calculation, the diffusivity of hydrogen sulphide in a solution must be modified, because the effect of the viscosity on the diffusivity is significant. This modification was performed by Eq.(49). The viscosity of aqueous sodium hydroxide solution was measured at 25°C and the values $\omega_1$ and $\omega_2$ were determined to be 0.0977 and 0.0421, respectively. The effective diffusivity of each ion and solubility of hydrogen sulphide in a solution were evaluated by means of the procedure mentioned above.

It may be seen from Fig. 5 that absorption in this system is apparently regarded as an absorption accompanied by a one-step instantaneous chemical reaction between hydrogen sulphide and hydroxyl ion. Furthermore, the reliability of chemical analysis for liquid was confirmed.

Simultaneous absorption of hydrogen sulphide and carbon dioxide in an aqueous sodium hydroxide solution

The experimental results for simultaneous absorption are shown in Fig. 6 for H$_{2}$S and in Fig. 7 for
CO₂, when the H₂S/CO₂ concentration ratio in gas phase is 1.137. If a plot of \( (N_2)^2 \) against \( h \) at constant liquid flow rate gives a straight line, the reaction may be considered to be instantaneous. From Fig. 6 it is found that the absorption of H₂S from the gas mixture into solution is accompanied by instantaneous chemical reaction, though it has already been confirmed as discussed above. Furthermore, as can be seen from Fig. 7, absorption of CO₂ from the gas mixture into the solution may be regarded as an absorption accompanied by an instantaneous chemical reaction. Strictly speaking, the reaction between CO₂ and OH⁻ is not instantaneous, but a second-order chemical reaction. However, all runs in this work may lie in an instantaneous chemical reaction region because the exposure time of liquid to gas is relatively long in this study. Thus the best lines computed by the least square method are drawn through the experimental points in Fig. 7, and from the slopes of these lines the reaction factors for CO₂ are obtained. The scattering of data points for CO₂ was inevitable, because a small amount of CO₂ was absorbed and furthermore it was determined indirectly, as mentioned above.

The experimental results for simultaneous absorption are plotted as reaction factor \( \beta_A \) vs. NaOH concentration in Fig. 8 and as \( \beta_A \) vs. NaOH concentration in Fig. 9. They are compared with the following three theoretical solutions, i.e.,

(a) Theoretical solution based on the assumption that either gas is inert, i.e., each gas is absorbed independently.

(b) Theoretical solution given by Roper et al. based on the assumption that there is only one reaction plane.

(c) Theoretical solution proposed in the present work based on the assumption of two reaction planes.

In Fig. 8 it may be seen that the experimental values of reaction factor for H₂S are in good agreement with the theoretical solution (c) derived in this study, which is smaller than solution (a) and larger than solution (b). Similarly, in Fig. 9 it may be seen that the experimental values of reaction factor for CO₂ are in good agreement with theoretical solution (c). Thus, it is clear that the solution (a) and (b) has overestimated the reaction factor for CO₂. In Fig. 10, both \( \beta_A \) and \( \beta_B \) are plotted against NaOH concentration for various gas compositions. The agreement between experimental value and penetration theory solution (c) is quite remarkable. Also the experimental data by Astarita and Gioia agree well with the theoretical solution (c). These indicate that the assumption of two reaction planes is correct. Furthermore, gas-phase resistance may be negligibly small compared to liquid-phase resistance.

In Fig. 11 absorption rate of each gas is plotted against gas composition at constant NaOH concentration \((=0.291 \text{ g-mol/l})\) and \(P=1 \text{ atm}\). Solid lines represent the theoretical solution (c) under the condition that the contact time is 0.176 sec and gas-liquid interfacial area 33.2 cm². This corresponds to \( h=10.0 \text{ cm} \) and \( L=4.0 \text{ cm}^3/\text{sec} \). It may be seen that the absorption rate of H₂S markedly increases with increasing partial pressure of H₂S, while that of CO₂ increases little with partial pressure of CO₂.

Thus, it is interesting to discuss the selectivity for H₂S. The selectivity factor is defined as follows:

\[
\sigma = \frac{\text{rate of absorption of H}_2\text{S}}{\text{partial pressure of H}_2\text{S}} \div \frac{\text{rate of absorption of CO}_2}{\text{partial pressure of CO}_2}
\]

That is, the absorption process is said to be selective for H₂S if the ratio of rates of absorption of H₂S and CO₂ is greater than the ratio of their partial pressures. Such selectivity might be desirable if all the H₂S had to be removed from the gas while the presence of a certain amount of CO₂ were acceptable. In Fig. 11 the selectivity factor \( \sigma \) is also shown as a broken line. It appears that the system considered displays a marked selectivity for hydrogen sulphide.
This work.

Fig. 8 Reaction factor for H₂S vs. sodium hydroxide concentrations in simultaneous absorption

Fig. 9 Reaction factor for CO₂ vs. sodium hydroxide concentrations in simultaneous absorption

Fig. 10 Reaction factors for H₂S and CO₂ in simultaneous absorption

Fig. 11 Effect of partial pressure of H₂S on Nₐ, Nₚ, σ and η in simultaneous absorption

Fig. 12 Effect of the NaOH concentration on Nₐ, Nₚ, σ and η in simultaneous absorption into a mixed solution of NaOH and Na₂CO₃ at total concentration 1.0 [g-mol/l].

particularly in the low partial pressure of H₂S. In the same figure a dotted line represents the value of η which is defined as follows:

\[ \eta = \frac{\text{solubility of H}_2\text{S}}{\text{partial pressure of H}_2\text{S}} \div \frac{\text{solubility of CO}_2}{\text{partial pressure of CO}_2} \]  

The value of η is nearly equal to the ratio of the solubilities of H₂S and CO₂ in water. Thus the selectivity in this system is not only due to the fact that H₂S is more soluble than CO₂, but also due to the chemical reaction effect which is represented by the reaction factor.

Finally, simultaneous absorption into a mixed solution of sodium hydroxide and sodium carbonate is discussed. Absorption rate of each gas can be predicted by the theoretical solutions (c) derived in this work. Fig. 12 shows the absorption rate of each gas against NaOH concentration in a mixed solution whose total concentration is 1.0 g-mol/l. Supposing that CO₃⁻ ion doesn’t react with CO₂, Na₂CO₃ solution contributes nothing to the rate of CO₂ absorption, but to increase the absorption rate
of H₂S. Therefore the rate of absorption of H₂S is much greater than that of CO₂, and this system is highly selective for H₂S, although the absorption rates of the two gases decrease with increasing Na₂CO₃ concentration.

Conclusion

Experiments for the simultaneous absorption of hydrogen sulphide and carbon dioxide in aqueous sodium hydroxide solutions were carried out with a wetted-wall column and the absorption rates of each gas were measured by chemical analysis of the liquid. The theoretical solution based on the penetration theory was derived by assuming that two reaction planes exist in the liquid phase. The penetration theory solution was in good agreement with the experimental results. It has also been confirmed that sodium hydroxide solutions show a marked selectivity for hydrogen sulphide in the simultaneous gas absorption.

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Nomenclature

\( A, B, C, E, F, G \) = concentration of CO₂, H₂S, OH⁻, CO₃²⁻, HCO₃⁻, and HS⁻ in the liquid phase, respectively, in the treatment based on the penetration theory [g-mol/cm³]

\( a, b, c, e, f, g, m \) = concentration of CO₂, H₂S, OH⁻, CO₃²⁻, HCO₃⁻, HS⁻, and Na⁺ in the liquid phase, respectively, in the treatment based on the film theory [g-mol/cm³]

\( D \) = effective ionic diffusivity [cm²/sec]

\( D' \) = ionic self-diffusivity [cm²/sec]

\( d \) = outer diameter of wetted-wall column [cm]

\( D_a \) = Faraday constant = 96,500 [coulombs-equiv.]

\( h \) = height of effective liquid film [cm]

\( h_r \) = height of liquid film equivalent to end effect [cm]

\( k_l \) = height of liquid film [cm]

\( k_i, k_s, k_l \) = salting-out parameter [l/g-mol]

\( L \) = liquid flow rate [cm³/sec]

\( N \) = average rate of absorption over contact time \( t \) [g-mol/sec]

\( n \) = ion valency [equiv./g-ion]

\( p \) = partial pressure [atm]

\( P \) = total pressure [atm]

\( Q_i, Q_0, Q_B \) = ratio of \( A_i, C_3 \) and \( E_0 \) to \( B_i \), respectively

\( Q_A, Q_B, Q_C \) = ratio of \( A_0, C_3 \) and \( E_0 \) to \( B_i \), respectively

\( R \) = gas constant = 8.314 [joules/g-ion·K]

\( r_j \) = ratio of effective diffusivity of \( j \)-species to \( D_p \) [-]

\( S \) = gas-liquid interfacial area [cm²]

\( t \) = time of exposure of liquid to gas [sec]

\( x \) = distance from gas-liquid interface [cm]

\( \beta \) = reaction factor in the treatment based on the penetration theory

\( \delta \) = film thickness in the wetted-wall column [cm]

\( \zeta \) = reaction factor in the treatment based on the film theory

\( \gamma \) = defined by Eq.(52)

\( \lambda \) = ionic equivalent conductance [cm²/equiv.ohm]

\( \eta \) = viscosity [g·cm/sec]

\( \sigma \) = selectivity factor

\( \phi, \phi_i \) = dimensionless parameter, defined by Eqs.(29), (30)

\( \phi \) = concentration of electrolyte in aqueous solution [g-mol/l]

\( a_{i0}, a_{i2} \) = coefficients defined by Eq.(50)

\( \alpha_j \) = reaction factor in the treatment based on the film theory

\( \xi \) = defined by Eq.(51)

\( \phi \) = ionic equivalent conductance

\( \eta \) = viscosity

\( \sigma \) = selectivity factor

\( \phi \) = concentration of electrolyte in aqueous solution

\( \alpha_j \) = reaction factor in the treatment based on the film theory

\( \xi \) = defined by Eq.(51)

\( \phi \) = ionic equivalent conductance

\( \eta \) = viscosity

\( \sigma \) = selectivity factor

\( \phi \) = concentration of electrolyte in aqueous solution

\( \alpha_j \) = reaction factor in the treatment based on the film theory

\( \xi \) = defined by Eq.(51)

\( \phi \) = ionic equivalent conductance

\( \eta \) = viscosity

\( \sigma \) = selectivity factor

\( \phi \) = concentration of electrolyte in aqueous solution

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