Absorption of Hydrogen Sulfide in Ammoniacal Solution of Zinc Chloride

Harish Chander
P. K. Ghosh
National Physical Laboratory
New Delhi 110012, India

V. A. Juvekar
Department of Chemical Engineering
I.I.T. Bombay 400 076, India

K. K. Baveja
S. C. Dhingra
Department of Chemical Engineering
I.I.T. New Delhi 110016, India

Hydrogen sulfide reacts with ammoniacal solution of zinc chloride yielding high-purity zinc sulfide which is an important starting material for many phosphors. The absorption of hydrogen sulfide in aqueous hydroxide, carbonate-bicarbonate buffer, sodium acetate, sodium chloride, monoethanolamine solutions has been studied by Astarita and Gioia (1967) in detail. However, no information is available in the literature on absorption in complex systems like ammoniacal zinc chloride. In the present investigation the absorption of hydrogen sulfide in the above solution has been carried out in a stirred cell. A model based on the film theory has been proposed to predict the absorption rate of hydrogen sulfide. The experimental results are compared with the model predictions.

Description of System

The absorption of hydrogen sulfide in the zinc-ammonia solution prepared by adding an excess of ammonia to zinc chloride solution can be described by the following reactions:

$$NH_4OH + H_2S \rightleftharpoons NH_4HS + H_2O \qquad (1)$$

$$Zn(NH_3)_4Cl_2 + NH_4HS + 3H_2O \rightarrow ZnS + 3NH_4OH + 2NH_4Cl \qquad (2)$$

$$Zn(NH_3)_4Cl_2 + H_2S + 2H_2O \rightarrow ZnS + 2NH_4OH + 2NH_4Cl \qquad (3)$$

Dissolved hydrogen sulfide may react with ammonium hydroxide and/or ammoniacal solution of zinc chloride. Due to the high affinity of an acid with base in reaction 1 and the presence of a fast precipitation reaction (Eq. 2) (Kolthoff and Elving, 1959), it is unlikely that reaction 1 would be reversible. Thus, it appears that the formation of zinc sulfide is mainly via two instantaneous reactions (Eqs. 1 and 2). There is no significant contribution to zinc sulfide formation by reaction 3.

Model

The sequence of events occurring during the absorption of H_2S in the complex solution is illustrated in Figure 1. Hydrogen sulfide diffuses through the gas film to the liquid surface $x = 0$. It then diffuses in the liquid to a reaction plane 1 at $x = \lambda_1$, where it reacts with ammonium hydroxide which diffuses in the opposite direction from the bulk of liquid at $x = \delta$. Thus, at the plane $x = \lambda_1$, the concentration of H_2S and NH_4OH fall to zero, and NH_4HS is formed. NH_4HS diffuses to another reaction plane 2 at $x = \lambda_2$, where it reacts with the ammoniacal complex of zinc chloride diffusing from the opposite direction to form zinc sulfide and ammonium hydroxide. The formation of ammonium hydroxide at $x = \lambda_2$ will affect the concentration gradient, as indicated in the Figure 1.

The differential equations describing the variation of concentration of various species in the liquid film are as follows:

$$D_{H_2S} \frac{d^2[H_2S]}{dx^2} = 0 \quad \text{For } 0 \leq x \leq \lambda_1 \qquad (1)$$

Correspondence concerning this paper should be addressed to S. C. Dhingra.

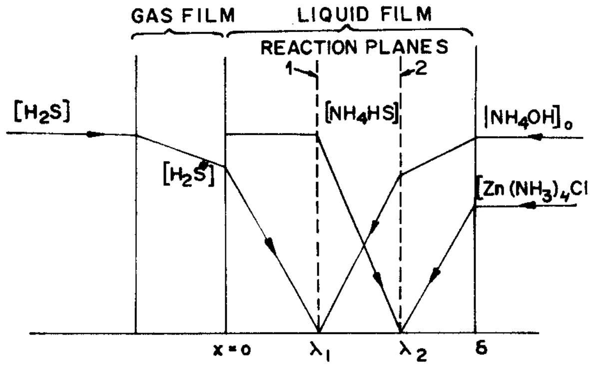

Figure 1. Concentration profiles of H_2S, NH_4OH, NH_4HS, and $Zn(NH_3)_4Cl_2$.

$$D_{NH_4OH}\frac{d^2[NH_4OH]}{dx^2}=0 \quad \text{For } \lambda_1 \le x \le \lambda_2 \tag{2}$$

$$D_{NH_4HS}\frac{d^2[NH_4HS]}{dx^2}=0 \quad \text{For } \lambda_1 \le x \le \lambda_2 \tag{3}$$

$$D_{NH_4OH}\frac{d^2[NH_4OH]}{dx^2}=0 \quad \text{For } \lambda_2 \le x \le \delta. \tag{4}$$

$$D_{Zn(NH_3)_4Cl_2}\frac{d^2[Zn(NH_3)_4Cl_2]}{dx^2}=0 \quad \text{For } \lambda_2 \le x \le \delta \tag{5}$$

The boundary conditions are

at $x = 0$

$$[H_2S]=[H_2S^*]; \quad -D_{H_2S}\frac{d[H_2S]}{dx}\bigg|_{x=0}=R_{H_2S} \tag{6}$$

at $x = \lambda_1$

$$[H_2S]=0; \quad [NH_4OH]=0 \tag{7}$$

at $x = \lambda_2$

$$[NH_4HS]=0; \quad [Zn(NH_3)_4Cl_2]=0 \tag{8}$$

at $x = \delta$

$$[NH_4OH]=[NH_4OH]_0; \quad [Zn(NH_3)_4Cl_2]=[Zn(NH_3)_4Cl_2]_0 \tag{9}$$

The rates at which the different species diffuse toward the reaction planes are governed by the stoichiometry of the reactions. The material balance gives

$$-D_{H_2S}\frac{d[H_2S]}{dx}\bigg|_{x=\lambda_{1-}}=D_{NH_4OH}\frac{d[NH_4OH]}{dx}\bigg|_{x=\lambda_{1+}} \tag{10}$$

$$-D_{H_2S}\frac{d}{dx}[H_2S]\bigg|_{x=\lambda_{1-}}=-D_{NH_4HS}\frac{d}{dx}[NH_4HS]\bigg|_{x=\lambda_{1+}} \tag{11}$$

$$-D_{NH_4HS}\frac{d[NH_4HS]}{dx}\bigg|_{x=\lambda_{2-}}=D_{Zn(NH_3)_4Cl_2}\frac{d}{dx}[Zn(NH_3)_4Cl_2]\bigg|_{x=\lambda_{2+}} \tag{12}$$

$$D_{NH_4OH}\frac{d}{dx}[NH_4OH]\bigg|_{x=\lambda_{2+}}+3D_{Zn(NH_3)_4Cl_2}\frac{d}{dx}[Zn(NH_3)_4Cl_2]\bigg|_{x=\lambda_{2+}}=D_{NH_4OH}\frac{d}{dx}[NH_4OH]\bigg|_{x=\lambda_{2-}} \tag{13}$$

Equations 1–5 are solved using boundary conditions and material balances given by Eqs. 6–13. This leads to the following rate expression

$$R_{H_2S}=k_L[H_2S^*]\left\{3\frac{D_{Zn(NH_3)_4Cl_2}}{D_{H_2S}}\frac{[Zn(NH_3)_4Cl_2]_0}{[H_2S^*]}+\frac{D_{NH_4OH}}{D_{H_2S}}\frac{[NH_4OH]_0}{[H_2S^*]}+1\right\} \tag{14}$$

where

$$k_L=\frac{D_{H_2S}}{\delta}$$

Experimental Studies

Absorption experiments were carried out in a 0.083-m-ID-glass stirred cell. The design of the cell is well described in the literature by Jhaveri and Sharma (1967) and others. Batch experiments were conducted by taking 2.5×10^{-4} m^3 of aqueous solution of ammoniacal complex of zinc chloride in the stirred cell. H_2S diluted with N_2 was passed through the cell at a constant rate. The partial pressure of H_2S in the feed gas was varied from 1.5×10^3 to 15×10^3 Pa. Both the gas and the liquid phases were stirred independently. The gas-liquid interface was kept quite smoothly with the use of a cross baffle. The amount of H_2S absorbed was measured by analyzing the filtered sample of liquid for zinc content using EDTA solution with Eriochrome Black T dye as an indicator at the beginning and end of experiment. This was also checked by calculating the amount of H_2S absorbed from inlet and outlet gas analysis. Concentration of free ammonium hydroxide was determined by subtracting the amount of ammonia in complex from total amount determined by analysis.

Estimation of Parameters

The data for the solubility and the diffusivity of H_2S in ammoniacal zinc chloride solution are not available. In the present study, they have been estimated. The solubility of H_2S at an average concentration of the solution during experiment was computed using the following equation (Danckwerts, 1970):

$$\log\left(\frac{He}{He_0}\right)=\Sigma h_i I \tag{15}$$

The diffusivity of H_2S in solution was taken to be same as that in water because of low concentration of the solution used. The

Table 1.

1. Henry's Law Constant = 1.166 × 10^6 Pa · m^3/kmol
2. Diffusivity values in solution at 25°C in m^2/s H_2S = 1.60 × 10^{-9}

	Nernst-Haskell Method	Vinograd & McBain Method
NH_4OH	2.85×10^{-9}	2.77×10^{-9}
$Zn(NH_3)_4Cl_2$	1.73×10^{-9}	1.22×10^{-9}

3. Liquid Side Physical Mass Transfer Coefficient, k_L = 1.27 × 10^{-5} m/s
4. Gas Side Mass Transfer Coefficient, k_G = 7.85 × 10^{-9} kmol/m^2 · s · Pa

diffusivity values of $Zn(NH_3)_4Cl_2$ and NH_4OH in the solution were estimated by two different methods:

1. Nernst and Haskell equation
2. Method of Vinogard and McBain (1941).

The liquid-side physical mass transfer coefficient, k_L, was determined by measuring absorption of carbon dioxide gas in deionized water in the same apparatus. In the present study, the absorption of H_2S in the reacting solution is accompanied by the formation of solids. It has been shown by Sada et al. (1977) that k_L is independent of solids concentration up to 20 wt. %. In the experiments conducted in this study, the amount of precipitates formed were within 2 wt. %. The gas-side mass transfer coefficient was calculated by evaporating benzene in flowing nitrogen under similar hydrodynamic conditions. The transfer coefficients so obtained were corrected for the system using diffusivity correlations.

The values of parameters thus obtained and used in present study are listed in Table 1.

Results and Discussion

The specific rate of absorption of hydrogen sulfide is predicted by substituting the values of the transport parameters in Eq. 14. The expressions $R^{(1)}_{H_2S}$ and $R^{(2)}_{H_2S}$ have been obtained using the values of diffusivities of ammonium hydroxide and ammoniacal zinc chloride estimated by Nernst-Haskel equation, and Vinograd and McBain method, respectively.

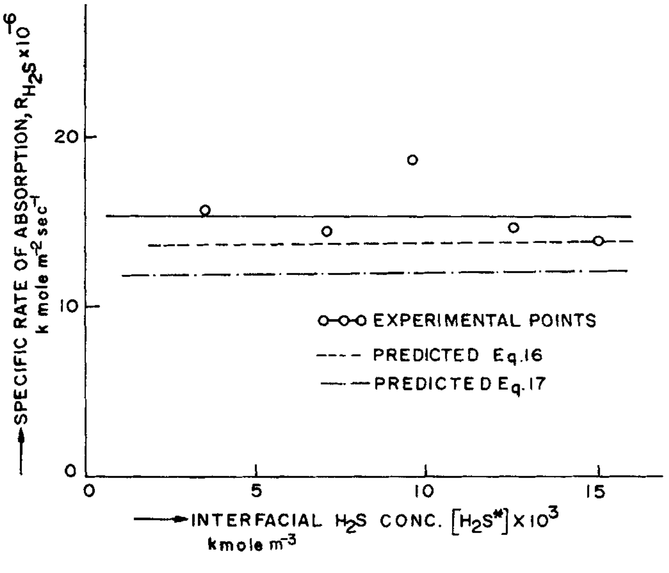

Figure 2. Variation of specific rate of absorption with interfacial H_2S concentration.

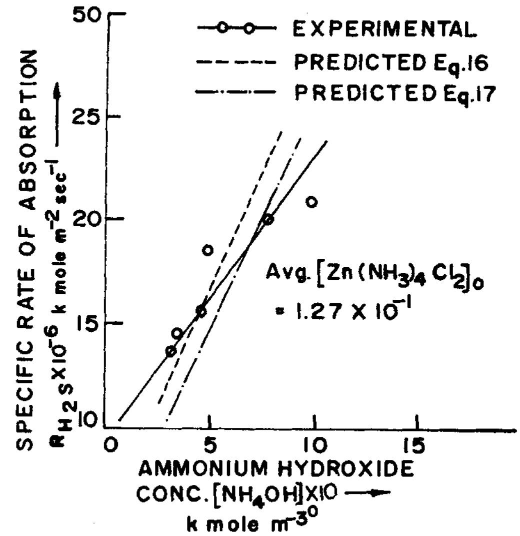

Figure 3. Variation of specific rate of absorption with concentration of ammonium hydroxide in liquid bulk.

$$R^{(1)}_{H_2S} = 2.26 \times 10^{-5}[NH_4OH]_0 + 4.12 \times 10^{-5}[Zn(NH_3)_4Cl_2]_0 + 1.27 \times 10^{-5}[H_2S^*] \quad (16)$$

$$R^{(2)}_{H_2S} = 2.2 \times 10^{-5}[NH_4OH]_0 + 2.9 \times 10^{-5}[Zn(NH_3)_4Cl_2]_0 + 1.27 \times 10^{-5}[H_2S^*] \quad (17)$$

Figure 2 is a plot of specific rate of absorption as a function of the interfacial concentration of hydrogen sulfide in liquid at average bulk concentrations of 3.8 × 10^{-1} and 1.215 × 10^{-1} kmol/m^3 for ammonium hydroxide and zinc ammonium chloride, respectively. The interfacial concentration of hydrogen sul-

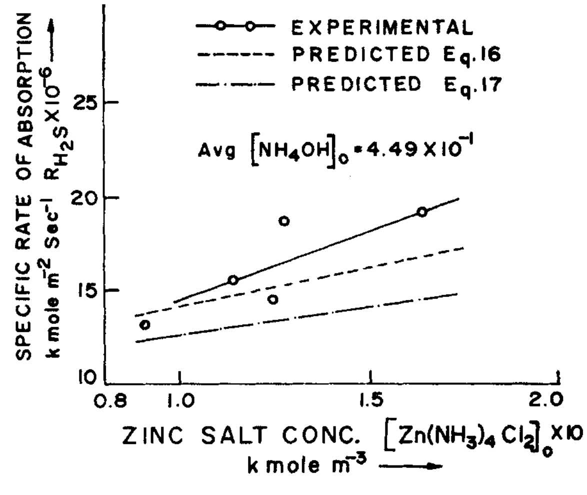

Figure 4. Variation of specific rate of absorption with concentration of zinc ammonium chloride in liquid bulk.

Table 2. Experimental vs. Predicted Specific Rate of Absorption

Sl. No.	Interfacial H_2S Conc. $\times 10^3\ \text{kmol} \cdot \text{m}^{-3}$	Ammonium Hydroxide Conc. $\times 10\ \text{kmol} \cdot \text{m}^{-3}$	Ammoniacal Complex Conc. $\times 10\ \text{kmol} \cdot \text{m}^{-3}$	Specific Rate of Absorption $\times 10^6\ \text{kmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$		
				Exp.	Pred. 1	Pred. 2
1.	7.06	3.03	1.278	14.38	12.12	10.37
2.	15.11	3.17	1.125	13.86	11.80	10.24
3.	12.59	3.54	1.253	14.65	13.17	11.42
4.	6.21	3.99	0.907	13.15	12.76	11.40
5.	3.48	4.63	1.140	15.57	15.17	13.49
6.	9.65	4.84	1.280	18.70	16.20	14.36
7.	9.76	5.36	1.640	19.18	18.88	16.55
8.	8.46	5.52	2.195	16.91	21.53	16.51
9.	6.64	7.74	1.420	20.13	23.36	21.14
10.	4.93	9.78	1.278	21.01	27.39	25.21
11.	3.93	14.08	0.813	27.21	35.20	33.31

fide, $[H_2S^*]$, has been determined taking gas-side resistance into account and using its solubility computed by Eq. 15.

Figures 3 and 4 show variation of specific rate of absorption of H_2S with change of NH_4OH and $Zn(NH_3)_4Cl_2$ concentrations in bulk of liquid phase. Experimental data will be closer to predicted results if these are corrected for average concentration of other species. Table 2 gives concentrations of hydrogen sulfide in liquid at interface, ammonium hydroxide, and zinc ammonium chloride in liquid bulk, and experimental and predicted specific rate of absorption. It is observed that the specific rate of absorption predicted by the proposed model based on instantaneous reactions and formation of ammonium hydrogen sulfide as an intermediate is in reasonable agreement (within 30%) with the experimental data obtained in this study. Experiment, as well as modeling, shows the significant effect of supporting reactant ammonium hydroxide's concentration and marginal influence of interfacial concentration of hydrogen sulfide on specific rate of absorption over the range of variables studied.

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Notation

D = m²/s diffusivity
He = Henry's law constant for the system, Pa · m³/kmol
He_o = Henry's law constant for gas and water, Pa · m³/kmol
h_i = contributions of positive ion, negative ion and gas, m³/kion (mol)
$[H_2S]$ = concentration of hydrogen sulfide in liquid, kmol/m³
$[H_2S^*]$ = concentration of hydrogen sulfide at interface on liquid side, kmol/m³
I = ionic strength of solution, kmol/m³
k_g = gas side physical mass transfer coefficient, kmol/m² · s · Pa
k_L = liquid-side physical mass transfer coefficient, m/s
$[NH_4OH]$ = ammonium hydroxide concentration, kmol/m³
R_{H_2S} = specific rate of absorption of H_2S in the solution, kmol/m² · s
T = temperature, K
x = distance from interface, m
$[Zn(NH_3)_4Cl_2]$ = concentration ammoniacal complex of zinc chloride, kmol/m³
μ = viscosity, kg/m · s
λ_1, λ_2 = positions of reaction planes 1 and 2, m
δ = liquid film thickness, m

Subscripts

o = concentration in bulk

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