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## Dissolution of Cadmium Sulphide at pH = 2 in Aqueous Solutions of Sulphuric Acid and Sulphuric Acid Containing Cadmium Sulphate\*

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Dissolution of particulate CdS suspended in aqueous solution of H<sub>2</sub>SO<sub>4</sub> (pH = 2) containing 0.00, 0.05 and 0.10 mol m<sup>-3</sup> CdSO<sub>4</sub> respectively was followed by measuring cadmium concentration in suspension filtrates. It takes about 150 days for cadmium concentration in solution to become constant. An exponential type relation correlating cadmium concentration with system parameters (initial cadmium concentration in solution, mass transfer coefficient, weight and specific surface area of CdS, solution volume) and the time. All systems aligned with a single, experimentally determined (mean) mass transfer coefficient value of  $(8.0 \pm 1.4) \times 10^{-11}$  ms<sup>-1</sup>. Dissolution of CdS was not solute diffusion but probably a surface chemical reaction controlled process.

### INTRODUCTION

Aqueous semiconductor colloids and suspensions show interesting photochemical and catalytic properties. Absorption of light by a small particle creates mobile electrons  $e^-$  and holes  $h^+$  which may migrate to the surface and undergo redox processes with adsorbed chemical species.<sup>1</sup> Splitting water into hydrogen and oxygen is one of the most salient examples of photocatalytic processes to be induced by visible light illumination of suspensions of small particles of n-type semiconductor oxides (like TiO<sub>2</sub>) and sulphides (like CdS).

The origin of this study is in an attempt to obtain information on the kinetics of bi-directional transport (exchange) of cadmium across the solid-liquid interface in non-illuminated systems obtained by equilibration (in dark) of CdS particles at pH = 2 with either dilute H<sub>2</sub>SO<sub>4</sub> or dilute H<sub>2</sub>SO<sub>4</sub> containing 0.05 and 0.10 mol m<sup>-3</sup> CdSO<sub>4</sub> respectively.<sup>2</sup> Preparation of such systems is a very crucial part of the experimentation.

Equilibration of CdS with acid solutions is essentially a dissolution process eventually leading to a constant cadmium concentration in the solution (concentration at saturation, equilibrium concentration or solubility<sup>3</sup>). In or-

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der to be able to estimate the time needed for the attainment of this concentration *ie* the steady state, a relation correlating cadmium concentration in the solution and time is required. The present study was initiated to establish such a relation and to gain some insight into the mechanism of dissolution of CdS in above-mentioned acid solutions.

#### EXPERIMENTAL SECTION

Three different CdS powders were used. One was obtained commercially (Fluka AG, Switzerland). Two others were prepared via reaction of H<sub>2</sub>S with Cd<sup>2+</sup> in aqueous solutions containing Cd(NO<sub>3</sub>)<sub>2</sub> and HCl or CdSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. The details of preparation and the results of characterization of these two powders have been summed-up in Table 1 of a previous paper<sup>4</sup> (precipitates denoted »no 11« and »no 21« respectively). A compilation of some powder properties relevant to the present study is given in Table I.

TABLE I  
Characteristics of CdS powders relevant for this study<sup>4</sup>

Powder type	Fluka	»no 11«	»no 21«
Purity [in % CdS]	99.999		
Impurity [in (mol kg <sup>-1</sup> ) / 10 <sup>-3</sup> ]		234 Cl <sup>-</sup>	50 SO <sub>4</sub> <sup>2-</sup>
Modification [in % α- or β-CdS*]	100 α	100 α	23 α + 77 β
Particle shape	Irregular	Spherical	Spherical
Particle size [in m/10 <sup>-6</sup> ]	1.2 (±0.4) ‡	0.9 (±0.3) ‡	0.6 (±0.2) ‡
Specific surface area [in (m <sup>2</sup> kg <sup>-1</sup> ) / 10 <sup>3</sup> ]	1.2 (±0.01) ‡	4.6 (±0.6) ‡	9.1 (±0.5) ‡

\* The crystal structures of α-CdS and β-CdS are respectively hexagonal and cubic.

‡ Standard deviation

Aqueous solutions of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> + CdSO<sub>4</sub> were prepared from reagent grade chemicals and distilled deionized water. Solutions of the same acidity (pH = 2) but of different cadmium concentrations (0.00, 0.05 and 0.10 mol m<sup>-3</sup>) were applied as CdS solvents.

The dissolution of CdS was followed by measuring cadmium concentration in filtrates of samples obtained from suspensions of CdS. The suspensions consisted of 2 × 10<sup>-3</sup> m<sup>3</sup> acid solution and 1.48 × 10<sup>-3</sup> to 10.20 × 10<sup>-3</sup> kg CdS and were contained in 2 × 10<sup>-3</sup> m<sup>3</sup> screw-stopped polyethylene flasks which were constantly rolled around their axis in order to maintain an adequate state of dispersion. All dissolution experiments were carried out at 25 °C and in dark. At times appropriate to the dissolution rate 1.2 × 10<sup>-6</sup> m<sup>3</sup> samples were withdrawn from the suspension and the solution was separated from the solid by vacuum filtration using cellulose acetate membrane filters (pore size 2.5 × 10<sup>-8</sup> m). In thus obtained filtrates cadmium concentration was measured by means of an atomic absorption spectrometer.

#### RESULTS AND DISCUSSION

Figure 1. show the results of cadmium concentration measurements during the equilibration of CdS with diluted H<sub>2</sub>SO<sub>4</sub>. The dissolution of CdS appeared to be a very slow process as it takes about 150 days for concentration to become constant. Similar results were obtained for equilibration with diluted H<sub>2</sub>SO<sub>4</sub> containing CdSO<sub>4</sub>.

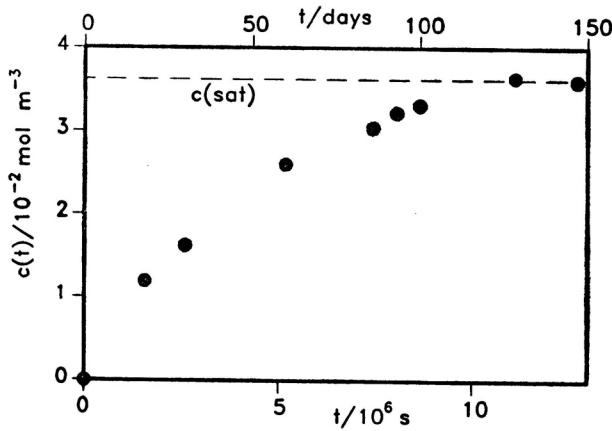


Figure 1. Cadmium concentration versus time plot for a system consisting of  $5.12 \times 10^{-3}$  kg CdS and  $2 \times 10^{-3}$  m<sup>3</sup> pH = 2 H<sub>2</sub>SO<sub>4</sub>.

Based on these experimental results, a tentative equation for time dependence of the cadmium concentration in the solution can be written:

$$c(t) = c(\text{sat}) - [c(\text{sat}) - c(0)]e^{-\kappa t} \quad (1)$$

in which  $c(t)$ ,  $c(\text{sat})$  and  $c(0)$  are the solution cadmium concentrations during, at the end and at the beginning of the equilibration respectively (all in mol m<sup>-3</sup>),  $\kappa$  is the reaction rate constant (in s<sup>-1</sup>) and  $t$  is the time (in s). As shown in Figure 2, the experimental results given in Figure 1, [ $c(0) = 0$ ] plotted as  $\ln\{[c(\text{sat}) - c(t)]/c(\text{sat})\}$  versus equilibration time conform to a straight line which actually proves the validity of equation (1). The experimental results for systems with solution cadmium concentration at the beginning of the equilibration  $c(0) > 0$  plotted as  $\ln\{[c(\text{sat}) - c(t)]/[c(\text{sat}) - c(0)]\}$  versus equilibration time aligned to straight lines as well. Except for the sign the slope of such a line is identical with constant  $\kappa$ .

The equation (1) is essentially the result of integration of the mass balance equation<sup>5</sup>:

$$Vdc(t)/dt = Ak[c(\text{sat}) - c(t)] \quad (2)$$

in which  $V$  is the volume of the solution (in m<sup>3</sup>),  $A$  is the total interfacial area (in m<sup>2</sup>) and  $k$  is the mass transfer coefficient (in m s<sup>-1</sup>). The boundary conditions applying to the forementioned integration define that at the time  $t = 0$  the concentration  $c(t) = c(0)$  and the time  $t = \infty$  the concentration  $c(t) = c(\text{sat})$ .

The mass transfer coefficient is related with the reaction rate constant through the equation:

$$k = \kappa V/A = \kappa V/wS \quad (3)$$

where  $w$  is the total weight of cadmium sulphide (in kg) and  $S$  is its specific surface area (in m<sup>2</sup> kg<sup>-1</sup>).

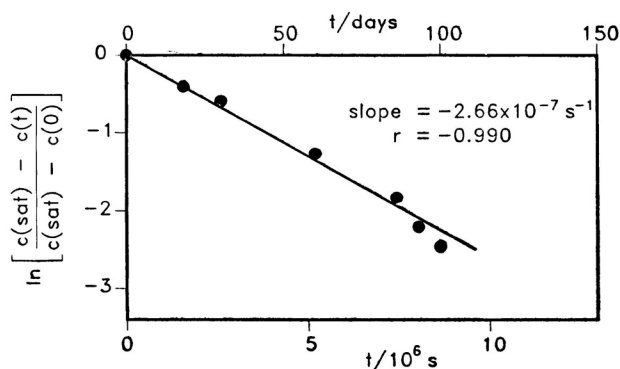


Figure 2.  $\ln\{[c(\text{sat}) - c(t)]/[c(\text{sat}) - c(0)]\}$  versus time plot for the system described in caption to the Figure 1.  $c(\text{sat})$  = mean value of the two last cadmium concentration values in Figure 1.  $c(0) = 0$ . The straight line through the data points was obtained by least squares method. The intercept on the y axis is set to zero.  $r$  = correlation coefficient.

TABLE II

*Equilibration systems and the corresponding reaction rate constants  $\kappa$  (in  $\text{s}^{-1}$ ) and mass transfer coefficients  $k$  (in  $\text{m s}^{-1}$ ).  
 $V = 2 \times 10^{-3} \text{ m}^3$  and  $\text{pH} = 2.0$  for all systems.*

Solid CdS Type	Solution				
	Weight	Initial cadmium concentration	Saturation cadmium concentration	Reaction rate constant	Mass transfer coefficient
	$w/10^{-3} \text{ kg}$	$c(0)/10^{-2} \text{ mol m}^{-3}$	$c(\text{sat})/10^{-2} \text{ mol m}^{-3}$	$\kappa/10^{-7} \text{ s}^{-1}$	$k/10^{-11} \text{ m s}^{-1}$
Commercial	5.12	0.00	3.62	2.66	8.96
»Fluka«	5.09	5.00	8.14	2.84	9.62
	10.20	10.00	13.20	4.06	6.86
Precipitate*					
»no. 11«	1.50	0.00	3.20	2.81	8.14
»no. 21«	1.48	0.00	2.50	4.28	6.36
				Mean value: 8.0	Standard deviation: 1.4

\* Obtained by  $\text{H}_2\text{S}$  precipitation.<sup>4</sup>

An overview of the experimental results *ie* the  $\kappa$  and  $k$  values obtained with five different equilibration systems as well as the mean (unique)  $k$  value applicable to all the systems are given in Table II. Combination of equations (1) and (3) results an equation correlating cadmium concentration in the so-

lution with the system parameters (initial cadmium concentration in the solution, mass transfer coefficient, weight and specific surface area of CdS, solution volume) and the time. By substituting in this equation for  $k = 8 \times 10^{-11} \text{ m s}^{-1}$ , that is the mean (experimental) value of the mass transfer coefficient as given in Table II one obtains a practical relation that can be applied to estimate the time needed to reach the (practical) equilibrium concentration [for example  $c(t)/c(\text{sat}) = 0.98$ ].

Diffusion of a dissolved material in the solution away from the dissolving solid surface is one of the possible mechanisms which may govern the dissolution of solid. The mass balance equation describing this situation is identical with equation (2) except that:

$$k = D/l \quad (4)$$

where  $D$  is the diffusion coefficient of the solute (in  $\text{m}^2 \text{ s}^{-2}$ ) and  $l$  is the thickness (in m) of the unstirred liquid layer adjacent to the solid (particle) surface.

Insertion in the equation (4) of the experimentally obtained (mean) mass transfer coefficient  $k$  (see Table II) and an estimated<sup>6</sup> value of diffusion coefficient of  $\text{CdSO}_4$  in  $\text{pH} = 2 \text{ H}_2\text{SO}_4$ ,  $D = 1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-2}$  gives  $l = 17.5 \text{ m}$ ; evidently a non-realistic value for the thickness of the unstirred layer surrounding solid particles immersed in solution. Consequently, the dissolution of CdS in  $\text{pH} = 2 \text{ H}_2\text{SO}_4$  and  $\text{pH} = 2 \text{ H}_2\text{SO}_4$  containing  $\text{CdSO}_4$  is not solute diffusion but probably a surface chemical reaction controlled process.

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#### SAŽETAK

##### Otapanje kadmij-sulfida kod $\text{pH} = 2$ u vodenim otopinama sulfatne kiseline odnosno sulfatne kiseline i kadmij-sulfata

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Otapanje krutih čestica CdS suspendiranih u vodenim otopinama  $\text{H}_2\text{SO}_4$  ( $\text{pH} = 2$ ) bez i sa 0,05 odnosno 0,10 mol  $\text{m}^{-3}$   $\text{CdSO}_4$  je praćeno mjerenjem koncentracije kadmija u filtratima suspenzija. Dobijena je korelacija eksponencijalnoga tipa koja povezuje koncentraciju kadmija u otopini, osobine sistema (početna koncentracija kadmija u otopini, koeficijent prenosa tvari, težina i specifična površina CdS, volumen otopine) i vrijeme. Za sve sisteme vrijedi jedan, eksperimentalno određen (srednji) koeficijent prenosa tvari  $k = (8,0 \pm 1,4) \times 10^{-11} \text{ m s}^{-1}$ . Analiza rezultata pokazuje da otapanje CdS ne upravlja difuzija otopljene tvari (u otopini) nego vjerojatno površinska kemijska reakcija (na CdS česticama).