

HYDROTHERMAL SOLUBILITY AND GROWTH OF SPHALERITE

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ABSTRACT

The solubility of cubic ZnS was studied under hydrothermal conditions in basic media and in NH₄Cl between 300 and 450° C. between 550 and 1380 bars. The temperature dependence followed the Van't Hoff relation with a heat of solution of 7.2 ± 0.5 kcal/mol which was independent of base concentration in KOH between 6.47 and 11.9 molal and had the same value within experimental error in 6.24 and 38.4 m NaOH and 8 m CsOH. The slope of the Van't Hoff plot in NH₄Cl was larger. The solubility was independent of pressure in KOH. The dependence of solubility upon (OH)⁻ in KOH was linear and suggested (ZnSOH)⁻ as the predominant species. The solubilities in (OH)⁻ and NH₄Cl ranged from a few tenths to about 6 wt. per cent while the solubilities in several other mineralizers were found to be less than 1%.

Solubility data were used to choose conditions for ZnS growth. Suitable conditions were found to be crystallization temperature—350°, temperature difference between dissolving and growth zone—10°, mineralizer—10.8 m KOH and per cent fill—80%. The effect of temperature, temperature difference, and pressure upon rate are discussed. Good quality ZnS could be grown in (110) at rates varying from 4–16 mil/da.

INTRODUCTION

Cubic zinc sulfide (sphalerite) crystals have been grown hydrothermally from basic solutions by Laudise and Ballman (1960). Flawing, slow rates and spontaneous nucleation have been problems in ZnS growth, and it was hoped that systematic solubility determinations could suggest more advantageous growth conditions. Large, sound, optically homogeneous sphalerite crystals could be particularly useful as modulators in optical communications. Sphalerite has a substantial electro-optic effect (Schramm, 1936; Namba, 1961) and is cubic so that certain modulator configurations which require an isotropic medium would be possible.

Hydrothermal solubility studies of quartz (Laudise and Ballman, 1961), α -corundum (Barnes *et al.*, 1963), and zincite (Laudise and Kolb, 1963) in several mineralizers have already been reported and it would be useful to compare the results obtained in these systems with the solubility of a sulfide under similar conditions.

EXPERIMENTAL

The apparatus and procedures used for the solubility and phase equilibrium studies were the same as those employed in the corundum and zincite studies and the precision in temperature and pressure control were the same as reported previously (Barnes *et al.*, 1963; Laudise and

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Kolb, 1963). Solubilities were determined by the loss in weight of single crystals of natural sphalerite. Phase equilibria studies were made using finely powdered natural sphalerite. The natural sphalerite was obtained from the areas of Picos de Europa, Santander Province, Spain.² The basic mineralizer solutions were made up and standardized as described previously. Equilibrium time was established at 300° C. (where the solubility was low and the equilibrium time would be expected to be greatest) by measuring apparent solubility as a function of time. There was no change in apparent solubility after six hours. All runs were at least 24 hrs in duration.

Eight replicate determinations were made in 6.47 molal KOH at 360° and 550 bars and the standard deviation of the mean, σ , was $\pm 0.07\%$ and the mean of the solubility was 1.19%. In most cases not enough replication was employed to permit meaningful σ determinations. So as to give some idea of errors, the bar heights on the curve for the solubility in 6.47 m KOH in Fig. 1 are the $\pm 3\sigma$ as determined at 360° and 550 bars in 6.47 m KOH. Phases were identified by x -ray powder diffraction and by petrographic microscopic examination.

The apparatus and procedure used for the growth of sphalerite was the same as that used in the growth of zincite (Laudise *et al.*, 1964). Silver-lined "short" Morey vessels whose inside dimensions were $\frac{7}{8}$ " diameter $\times 2\frac{3}{4}$ " long were used since low pressure growth conditions not requiring Bridgman type closure vessels were suggested from the solubility results. The zinc sulfide nutrient was prepared by hydrothermally recrystallizing sintered pellets of cubic ZnS prepared from special purity ZnS by the St. Joseph Lead Company, Monaca, Pa. Seed crystals were cut from natural sphalerite like that used in the phase equilibria studies. Seeds were oriented by x -ray diffraction.

SOLUBILITY RESULTS

The solubility was determined as a function of temperature at 550 bars in KOH and NaOH of various concentrations, in 8 m CsOH and in a solution saturated with NH_4Cl at 25° C. The results are shown in Figs. 1 and 2. Solubility is reported only for those conditions where ZnS was the stable solid phase and where only one fluid phase was found to co-exist with the solid.

Base concentration is generally reported in terms of molality, m , calculated from the normality, N , by the use of measured densities. Solubilities are reported in terms of wgt. per cent which was calculated

² Natural sphalerite was purchased from Juan Montal, Plaza Sagrado Corazon, 1, Vilafranca del Panades, Spain.

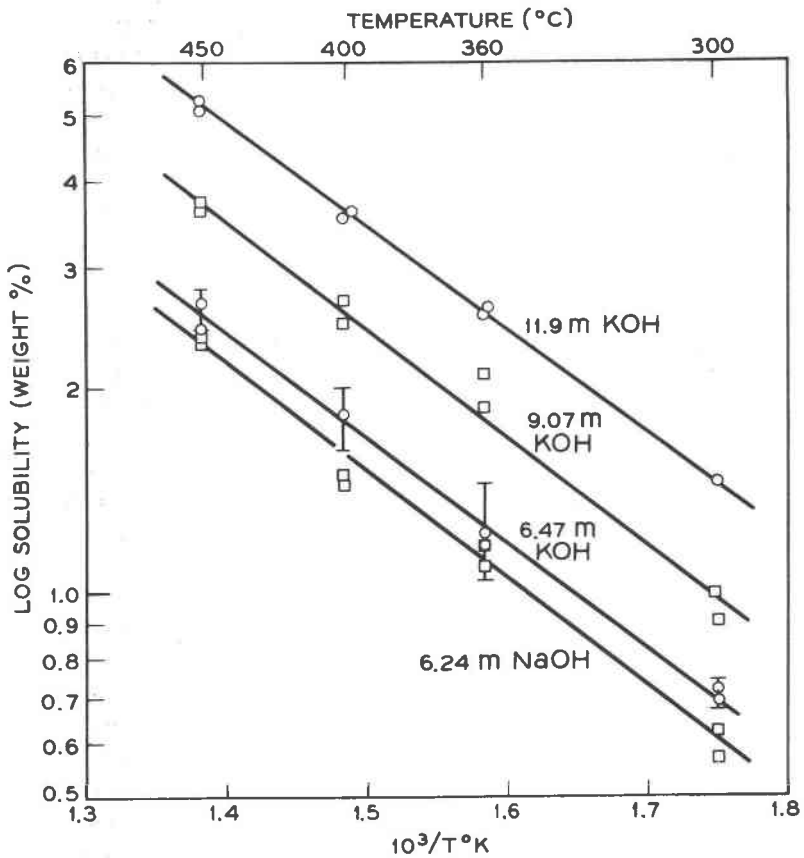


Fig. 1. Wgt. per cent solubility of ZnS vs. the reciprocal of the absolute temperature in KOH and NaOH solutions at 550 bars.

as the wgt. of ZnS lost $\times 100$ / wgt. of water + wgt. of mineralizer. The solubility in 6.47 m KOH was found to be independent of pressure within experimental error between 225 and 1380 bars at 300 and 360° and independent of pressure between 550 and 1380 bars at 400 and 450°.

The dependence of solubility on KOH concentration at 550 bars at several temperatures is shown in Fig. 3.

The solubility in several other mineralizers is listed in Table 1. In most cases the stable phase is probably ZnS but the low solubilities make it difficult to be sure that equilibrium has been obtained in phase equilibria determinations.

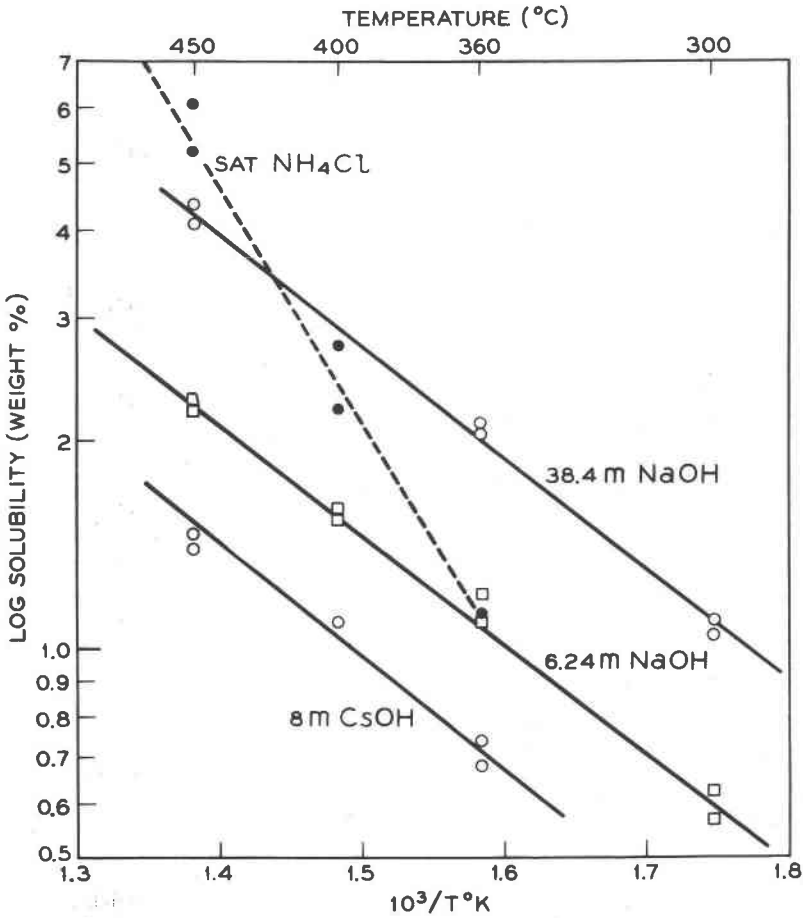


FIG. 2. Wgt. per cent solubility of ZnS vs. reciprocal of the absolute temperature in NaOH, CsOH and NH₄Cl solutions at 550 bars.

GROWTH RESULTS

Table 2 lists the experimental conditions of several typical ZnS growth runs, and Fig. 4 shows the rate as a function of Δt, the temperature difference between the dissolving and growth regions of the autoclave. Better quality growth was obtained in 10.8 m than in 5.4 m KOH. Better rates and quality were obtained in KOH than other hydroxides and NH₄Cl. The (110) direction was used for most studies but examination of the habit of grown crystals showed that (111) is probably more rapid. Temperature differentials much above 20° resulted in considerable

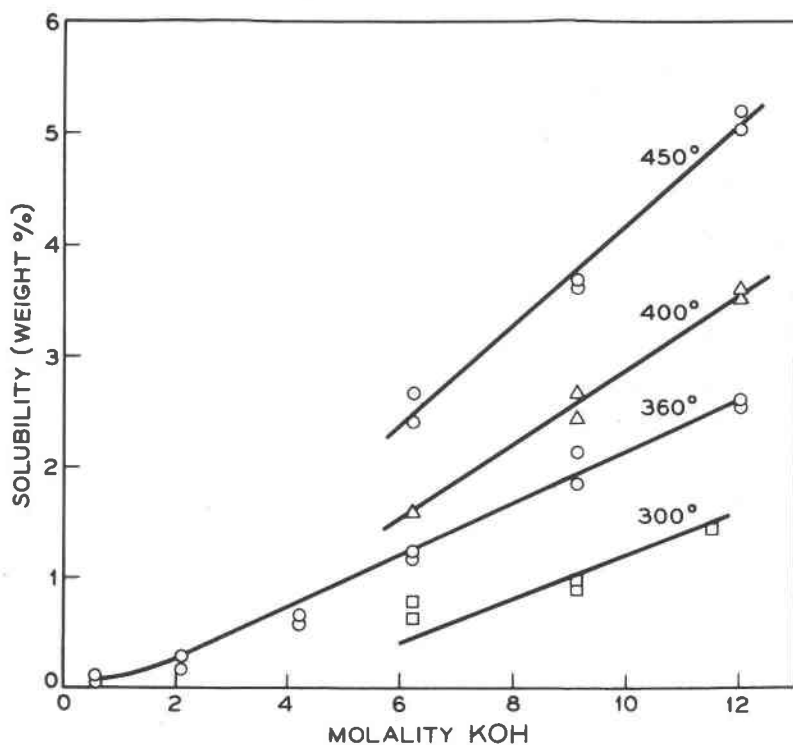


FIG. 3. Wgt. per cent solubility of ZnS vs. molality of KOH at several temperatures and 550 bars.

TABLE I. (PRESSURE 550 BARS)

Mineralizer	Temp ° C.	Solubility wgt. %
6N ZnCl	450	0.08
	360	0.04
6N KF	450	0.10
	360	0.20
NaBO ₂ Saturated at 25°	450	0.375
	360	0.175
6N K ₂ CO ₃	450	0.64
	360	0.20
NaCl Saturated at 25°	450	0.08
	360	0.05
LiCl Saturated at 25°	450	0.28
	360	0.11
4.65 N LiOH	450	0.59
	360	0.40

TABLE 2.

Crystallization Temperature (t_c)	Δ ($t_{dissolving} - t_c$)	Mineralizer	Per cent fill	Growth Rate ¹ on (110) seed
350° C.	30	5.4 m KOH	80%	16 mil/da. (0.4 mm/da.)
350° C.	15	5.4 m KOH	80%	4 mil/da. (0.1 mm/da.)
350° C.	10	5.4 m KOH	80%	1.4 mil/da. (0.035 mm/da.)
350° C.	10	10.8 m KOH	80%	1.2 mil/da. (0.03 mm/da.)

¹ Growth rate was measured by determining the increase in thickness of a (110) seed plate over a given period of time. It is thus twice the rate in (110).

spontaneous nucleation. The quality and rate did not seem to be particularly fill dependent provided the fill was great enough to fill the autoclave completely with the liquid phase at the temperature of the run. Increasing temperature increased rate but also resulted in more frequent autoclave leakage. Dissolving of the seeds was a severe problem. In long autoclaves it was particularly difficult to prevent seed loss even with presaturation of solutions so that finally it was decided to study growth only in short autoclaves. Presaturation at 90° and slow warm-up with large Δt 's helped prevent seed loss. The habit was the same as reported

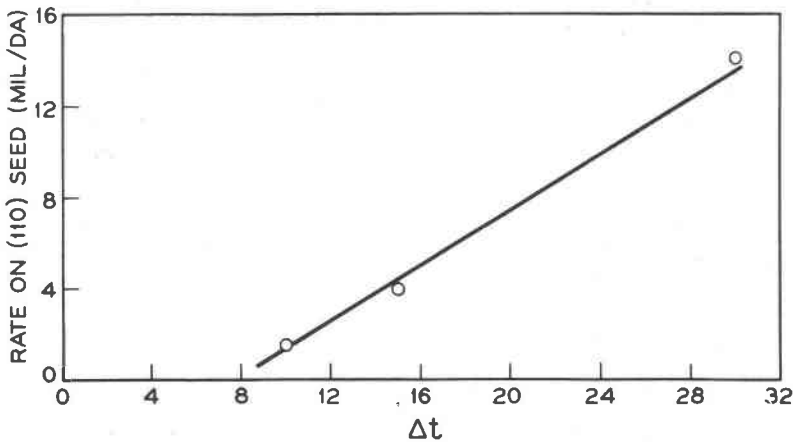


FIG. 4. ZnS Growth Rate vs. Δt , the temperature difference between the dissolving and growth region of the autoclave (conditions: 5.40 molal KOH, 80% fill, 350° crystallization temperature and (110) seed).



FIG. 5. ZnS crystal grown hydrothermally.

previously (Laudise and Ballman, 1960) but the macroscopic quality as shown in Fig. 5 was greatly improved. The tendency for spontaneous nucleation were also improved from the conditions previously reported. A detailed study of optical perfection will be reported elsewhere.

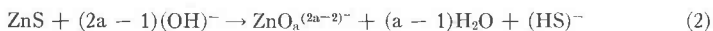
DISCUSSION OF SOLUBILITY

In pure water the dissolving reaction for ZnS may be written by analogy with our previous work (Laudise and Kolb, 1963).

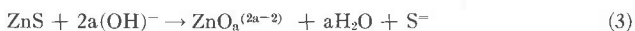


The solubility in water is less than 0.1 wgt. % at 360° and 550 bars and the weight loss technique using small capsules does not have sufficient precision for solubility determinations which might be used to validate Eq. (1) to be made.

In basic media a reasonable solubility reaction would be



which could proceed further



The possibility of a reaction involving the formation of H_2S is unlikely in such strongly basic media and indeed the odor of H_2S could never be detected when an autoclave was opened. The equilibrium constants for

Eq. (2) and (3) are in terms of concentrations

$$K_2 = \frac{(\text{ZnO}_n^{(2a-2)^-})(\text{HS}^-)}{(\text{OH}^-)^{(2a-1)}} \quad (4)$$

$$K_3 = \frac{(\text{ZnO}_n^{(2a-2)^-})(\text{S}^-)}{(\text{OH}^-)^{(2a)}} \quad (5)$$

The thermodynamic equilibrium constants should, of course, be expressed as functions of the appropriate activities. Lacking activity coefficient data, we have used concentrations. While the ZnS concentration is reasonably low the $(\text{OH})^-$ concentration is rather high for this to be a valid assumption. It is therefore somewhat surprising that the K 's calculated by the use of concentrations are quite well behaved. Apparently, the system is closer to ideality than might at first sight be expected.

Since the first ionization constant of H_2S differs by 10^8 from the second, it is likely that the observed solubility is due principally to only one of the equations. Thus, the concentration of the zincate will be equal to either the sulfide or the bisulfide and the equations will reduce to

$$K_2 = \frac{s^2}{(\text{OH}^-)^{(2a-1)}} \quad (6)$$

$$K_3 = \frac{s^2}{(\text{OH}^-)^{(2a)}} \quad (7)$$

where s is the measured solubility.

Since the initial $(\text{OH})^-$ is reduced by the formation of zincate Eqs. (6) and (7) may be rewritten

$$K_2 = \frac{s^2}{[x - (2a - 1)s]^{2a-1}} \quad (8)$$

$$K_3 = \frac{s^2}{[x - 2as]^{2a}} \quad (9)$$

where x is the initial $(\text{OH})^-$ concentration.

It is experimentally observed in Fig. 3 that the solubility of ZnS is small in comparison with $(\text{OH})^-$ concentration. The mole ratio s/x varies from 0.015 to 0.031 at 360° . This suggests that for any reasonable values of a K_2 , and K_3 will reduce to

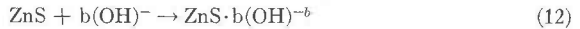
$$K_2 = \frac{s^2}{x^{2a-1}} \quad (10)$$

$$K_3 = \frac{s^2}{x^{2a}} \quad (11)$$

Since s and x are nearly linear as shown in Figure 3 either $2a - 1 = 2$ or $2a = 2$ which leads to $a = \frac{3}{2}$ if Eq. (2) is obeyed or $a = 1$ if Eq. (3) is

obeyed. Thus, Eq. (2) suggests that the species is $(Zn_2O_3)^=$ while Eq. (3) suggests the unrealistic result that the species is ZnO.

Another possible equation is the direct complexing of ZnS



The equilibrium constant will be

$$K_{12} = \frac{(ZnS \cdot bOH^{-b})}{(OH^-)^b} \quad (13)$$

For s and x to be linear $b=1$, which suggests $(ZnSOH)^-$ as the principal species. A dizincate species such as $(Zn_2O_3)^=$ is probably less plausible than a thio-zincate such as $(ZnSOH)^-$.

Log s depends linearly upon the reciprocal of the absolute temperature at constant x since

$$s \simeq x\sqrt{K_3} \quad (14)$$

from Eq. (11) or

$$s \simeq xK_{12} \quad (15)$$

from Eq. (13).

The heat of solution value obtained of 7.2 ± 0.5 kcal/mol seems to be independent of $(OH)^-$ concentration or of the nature of the cation. The error was estimated from the slopes permitted by the bar heights of Fig. 1.

The heat of solution compares with base concentration and cation dependent heats of solution of from 0.4–1.1 kcal/mol obtained for ZnO under similar circumstances. Since the solubility is pressure independent, we may assume that Δv of reaction is negligible. Since the ratio ZnO/x is relatively constant, it is probable that the only one reaction is responsible for dissolving. The solubility is lower than for ZnO which is surprising since ZnS would be expected to be more acidic. It is apparent that a different reaction is responsible for dissolving in NH_4Cl where the slope of log s vs. $1/T$ was larger than in $(OH)^-$. It is not unlikely that zinc amines are formed in NH_4Cl .

DISCUSSION OF GROWTH

More basic media are required for ZnS than for ZnO since the solubility of ZnS is lower than ZnO under similar conditions. The slope of the ZnO solubility curve in 6.47 m KOH at 550 bars is about 0.08 wt. %/10° while that of ZnS in 10 N KOH at 550 bars is 0.19 wt. %/10°. Thus, it is to be expected that the tendency for spontaneous nucleation for a given Δt will be greater for ZnS. Similarly, if the velocity constants are comparable, the ZnS rate will be larger. Since the ZnS rate is only slightly higher, it is probable that the velocity constants are comparable. The ZnS rate is linear with supersaturation as evidenced by its linearity with

Δt . The rate *vs.* Δt curve would probably pass through (0,0) if corrections for the fact that Δt was measured on the outside of the autoclave could be made. The fact that ZnS seeds are more easily lost by dissolving than ZnO even under comparable solubility conditions, is explained by the fact that the ZnS solubility is so low at room temperature that pre-saturation does not place very much material in solution.

The ZnS rate is not pressure dependent, probably because neither solubility nor velocity constant are pressure dependent. The increase in rate with temperature is probably essentially due to the increase of velocity constant with temperature.

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