Solubility of Zinc Sulfide in Molten Halide Salts

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ZINC SULFIDE is a phosphor material of relatively simple structure, and its excellent luminescent response under a wide variety of excitation conditions has led to its extensive use. Considerable effort has been devoted to the growth of large single crystals of high purity—mostly by vapor phase methods at high temperatures (*2*). Another method, growth of ZnS crystals from solution, has, in principle, the attractive feature of not requiring a very high temperature; this allows precise temperature control and minimizes the problem of contamination. No attempt to grow large monocrystals by this technique is reported in the literature, although there have been investigations designed to form crystalline ZnS powder from precipitated material. The solubility in water at room temperature is known to be exceedingly small; despite its positive temperature coefficient the solubility is still very small in pure water even near the critical temperature. In experiments in sealed systems, Kremheller and Levine found the solubility of ZnS in pure water to be less than 7×10^{-4} mole per liter at 350° C. (*7*). This value was obtained by determining the loss in weight of natural ZnS (sphalerite) crystals contained in a stainless steel pouch of fine mesh which was suspended for 72 hours in a hydrothermal bomb at 350° C.

Attempts to find suitable nonaqueous solvents for crystallization but not specially for growth of large monocrystals of ZnS were made as early as the last century. Schneider (*11*) formed crystalline ZnS by heating precipitated ZnS with potassium carbonate and sulfur at 400° C. Allen and Crenshaw (*1*) obtained small dodecahedrons of sphalerite when they treated ZnS in molten NaCl at a little above 800° C. in a platinum tube protected from the air by a stream of CO_2; larger crystals were obtained from molten potassium polysulfide at about 350° C. They also obtained crystalline ZnS when precipitated powder was heated with aqueous alkali sulfide at 350° C. in sealed tubes.

There have been two attempts to determine the solubility of ZnS in fused salts which might serve as crystallizing media. In 1912 Houben attempted to determine the solubility of ZnS in molten NaCl (*4*). In this experiment a ceramic crucible was filled with NaCl and brought to temperature. Zinc sulfide was then added and the mixture stirred for 30 minutes. After this, a portion of supernatant solution was withdrawn by means of a quartz tube. This sample was then cooled and dissolved in water, and the precipitate was analyzed for zinc. Houben's values are not reliable, since the solubility was measured out in an open system, thus permitting partial oxidation of ZnS and volatilization of NaCl. His solubility values range from 0.1% by weight at 870° C. to 0.54% by weight at 1220° C. Recently Jander and Weis (*5*) measured the solubility of a number of compounds in $SbBr_3$. They found no detectable solubility of ZnS in this solvent.

This work is an investigation of the solubility of ZnS in molten $ZnCl_2$. Solubilities were determined in several other molten halides for comparison. Zinc chloride was selected for the following reasons:

It has a relatively low boiling point (732° C.) and exists in the liquid form over a suitably wide temperature range [melting point, 318° C. (*8*)]. This temperature range offers such advantage as ease of temperature control, use of quartz containers which permit direct observation of the sample, and minimization of contamination of the sample by containing vessel.

Zinc sulfide can be easily separated from $ZnCl_2$ which is very soluble in water.

Zinc chloride has a common cation with the solute. This eliminates the possiblity of objectionable cation contamination.

EXPERIMENTAL

In devising a method for determining the solubility of ZnS in molten $ZnCl_2$, the volatility of $ZnCl_2$ (*3*) and the susceptibility of ZnS to oxidation at the experimental temperature (*10*) must be considered. It is also necessary to establish that the ZnS which crystallizes is a pure phase and not a solid solution with $ZnCl_2$, since the ionic radii of chloride and sulfur are nearly the same (*9*).

To investigate the existence of solid solution, experiments were performed in which 4 grams of ZnS powder and 10 grams of previously dried $ZnCl_2$ were placed in a quartz vial which was degassed, evacuated, and sealed. The vial was then kept at 700° C. for 4 hours. After slow cooling, the quartz vial was opened and the contents were washed with deionized water until there was no chloride in the washings. Analysis of the residual ZnS showed a chloride content of 0.35 mole %, which can be taken as the upper limit of solid solution.

The following experimental procedure was used to determine the solubility of ZnS in molten $ZnCl_2$. A tared quartz vial (10 cm. long and 2.5 cm. in diameter) was partially filled with $ZnCl_2$ powder; to remove moisture the sample was dried in a vacuum oven at 150° C. The vial was then stoppered, cooled, and weighed. Tared crystals of natural ZnS (sphalerite) were added to the vial, which was then evacuated and sealed. The vial was kept at the desired temperature inside a cylindrical furnace regulated by a stepless controller. After the system inside the vial had reached equilibrium, the vial was quickly removed from the furnace and tilted so that the undissolved crystals (in the bottom of the vial) remained in the elevated bottom part of the vial, held there by surface tension, while the clear solution flowed down to the inverted top part of the vial where it soon froze. By this technique, it is possible to separate neatly practically all the solution from the excess solute. The cooled vial was cut open at an appropriate level, and the crystals were removed, washed with water until free of chloride, dried, and finally weighed. In Figure 1 this is called the "crystal residue" method.

The time necessary to reach equilibrium was determined as follows. Two samples of ZnS crystals in $ZnCl_2$ were heated at 580° C., one for 48 and another for 72 hours. The solubilities were found by the technique described above to be 0.137 and 0.138 molal, respectively, indicating that equilibrium had already been attained in the shorter period. Equilibrium was assumed to occur in all subsequent experiments which were run for approximately 72 hours. Duplicate runs were made in all cases, and the method gave precision to the third decimal place in molality, even when the time allowed for experiments at a given temperature was somewhat varied.

The results of this method for determining the solubility of ZnS in molten $ZnCl_2$ were further checked by using a different technique as follows. Vials were prepared as above,

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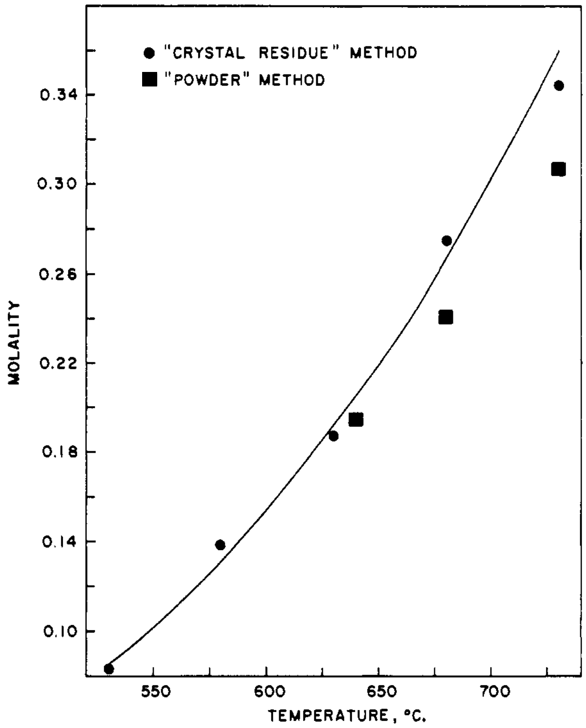

Figure 1. Solubility of zinc sulfide in molten zinc chloride

except that a weighed quantity of highly purified ZnS powder was used instead of sphalerite crystals. The vial containing the sample was sealed and put into a cylindrical furnace, and the temperature was raised 10° every 2 hours until the solid phase disappeared and a clear solution remained. The vial was cooled and the determination repeated, starting from a temperature 10° below that previously determined as being the approximate saturation temperature. Samples were agitated by rocking and kept at temperature for up to 8 hours. If ZnS dissolved at this temperature within 8 hours, the vial was cooled and the process repeated again by bringing the system to 10° below the temperature used before. Observations were made visually by lifting the cover (a firebrick) of the furnace and illuminating the vial with focused beam of light. In this way, it was possible to obtain approximate solubility values to within 10°. These values ("powder" method, Figure 1) agree with the more accurate values obtained by the other method.

RESULTS AND DISCUSSION

Table I summarizes the results of the measurements of the solubility of ZnS in $ZnCl_2$. The solubility of ZnS was investigated in molten NaCl, KCl, $ZnBr_2$, ZnI_2, and mixtures of $ZnCl_2$ and alkali halides using the same experimental procedures. The results of solubility determinations are given in Table II with, two values of ZnS in $ZnCl_2$ for comparison. The solubility of ZnS decreases as one goes from $ZnCl_2$ to ZnI_2—i.e., from a more ionic to a more covalent solvent. In the strongly ionic solvents, NaCl and KCl, the solubility is considerably smaller than in $ZnCl_2$. These results suggested that the solubility of ZnS might be enhanced in solvents having a bonding type intermediate between those of alkali halides and $ZnCl_2$. The mixtures, $ZnCl_2$-NaCl (20 mole %) and $ZnCl_2$-KCl (20 mole %) were also studied. The low melting points of these mixtures offer many experimental advantages; $ZnCl_2$-NaCl (20 mole %) melts at 290° C. and Zn-Cl_2-KCl (20 mole %) melts at 280° C. (*8*). The solubility of ZnS in these mixtures (Table II) is higher than that in pure $ZnCl_2$.

Table I. Solubility of ZnS in Molten $ZnCl_2$, Crystal Residue Method

Temp., ° C.	$ZnS/ZnCl_2$, G./1000 G.	Molality
730	33.6	0.344
680	26.8	0.275
630	18.3	0.188
580	13.5	0.138
530	8.09	0.0831

Table II. Solubility of ZnS in Some Molten Halides

Solvent	ZnS/Solvent, Moles/1000 G.	Temp. ° C.
$ZnCl_2$	0.138	580
$ZnBr_2$	0.0851	580
ZnI_2	0.0132	580
NaCl	0.0152	880
KCl	0.0316	880
$ZnCl_2$	0.344	730
$ZnCl_2$-NaCl (20 mole %)	0.396	700
$ZnCl_2$-KCl (20 mole %)	0.498	700

The logarithm of molality of dissolved ZnS (Table I) plotted against $1/T$ produces a straight line. A least squares analysis of the data gives the following equation for the solubility,

$$\log m = -2.52 \times 10^{3}/T + 2.06$$

where m is the molality of dissolved ZnS and T is the temperature in degrees Kelvin. From this equation the heat of the solution can be calculated if one assumes that the solution is ideal and that ZnS does not ionize. Under these conditions the heat of solution is given by

$$\Delta H_{\text{soln}} = -R\,\frac{d\ln m}{d(1/T)} = 11.5 \text{ kcal./mole}$$

This is also the net amount of heat evolved on crystallization of one mole of ZnS from solution. This value may be compared with the heat of sublimation of ZnS. Using Veselovsky's (*13*) equation as corrected by Spandau and Klanberg (*12*) for ZnS vapor pressure in the 777° to 975° temperature range,

$$\log p = \frac{-13{,}390}{T} + 9.795$$

one obtains for the heat of sublimation

$$\Delta H = RT^2\,\frac{d\ln p}{dT} = 61.3 \text{ kcal./mole}$$

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