Formation of Cadmium Sulphide — Manganese(2)Sulphide Solid Solutions by Coprecipitation from Aqueous Solutions of Corresponding Sulphate by Ammonium Sulphide

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When a 0.27 M aqueous solution of (NH₄)₂S, in a quantity 10 mol% short of the stoichiometric value, is added to an aqueous solution of CdSO₄ and MnSO₄ of various compositions, with SO₄²⁻ being 0.3 M, a continuous CdS : MnS solid solution is not formed: saturation is reached for at most about 0.1 mol% MnS, the corresponding relative concentration of MnSO₄ being 4 mol%. With increasing this concentration to 20 mol%, MnS begins to precipitate in substantial amounts, reaching 19.8 mol% for MnSO₄ equal to 50 mol%. Debye-Scherrer diagrams show that the precipitates are quasi amorphous, composed essentially of cubic CdS with certain quantities of hexagonal CdS and MnS. This makes it impossible to distinguish, by these diagrams only, mechanical mixtures from solid solutions.

INTRODUCTION

In order to investigate various physical properties of amorphous cadmium sulphide—manganese(2)sulphide solid solutions, we tried to prepare these compounds by coprecipitation from aqueous solutions of the corresponding sulphates by means of ammonium sulphide¹,²

EXPERIMENTAL

Preparation

In a beaker of 1000 cm³ (Fig. 1), x cm³ 0.3 M aqueous solution of MnSO₄ and 300—x cm³ 0.3 M CdSO₄ were mixed. The relative molar composition of the solution is therefore p_{MnSO₄} = x/3 mol% and p_{CdSO₄} = 100—x/3 mol%. From vessel A (Fig. 1), 300 cm³ 0.27 M aqueous solution of (NH₄)₂S ran into the beaker, at 19 ± 1°C, for 19 ± 1 min. (Chemicals were reagent grade and redistilled water was used for all operations). During the reaction the beaker rotated (~ 1 Hz) which caused a continuous relative motion of the solution of both sulphates to the incoming solution of (NH₄)₂S. The stirring of the liquid was enhanced through an immersed glass rod (B). For complete stoichiometric precipitation of the corresponding sulphides there was a lack of 10 mol% of (NH₄)₂S. The precipitate was separated from the liquid by a centrifuge (~ 25 Hz) after the reaction as well as during washing (ten times with ~ 250 cm³ water). The precipitates were dried in a desiccator over sulphuric acid. When dry, they were kept over Silicagel. The yield of pure CdS obtained by this procedure is 96% of the theoretical amount.

We gave p_{MnSO₄} seventeen different values, from 0 to 100 mol%. During the washing of the precipitates it was observed that a certain quantity of precipitate, especially for p_{MnSO₄} > 20 mol%, passed into a colloidal solution which could not be separated by the centrifuge we used. Furthermore, the yield diminishes
when $p_{\text{MnSO}_4}$ rises: for $p_{\text{MnSO}_4} = 100 \text{ mol}\%$ it is only 50\% of the stoichiometric value. With $p_{\text{MnSO}_4} \geq 40 \text{ mol}\%$ the precipitates take a brownish colour on the surface when not under water. This phenomenon is enhanced during drying. The brownish layer is evidently the result of oxidation of MnS in the presence of moisture and atmospheric oxygen.

These facts indicate the probability that from a certain $p_{\text{MnSO}_4}$ value separate precipitation of the two sulphides occur. This supposition was confirmed by an experiment in which $(\text{NH}_4)_2\text{S} 0.27 \text{ M}$ was added to a $p_{\text{MnSO}_4} = 90 \text{ mol}\%$ solution in small, equal, successive portions, the precipitates being separated after each new addition. The appearance of the successive precipitates shows that the CdS phase precipitates first, followed by the precipitation of the pink modification of MnS, in agreement with the fact that MnS is about four times more soluble in water than CdS\(^3\).

In the light of these observations we considered all precipitates obtained with $p_{\text{MnSO}_4} > 50 \text{ mol}\%$ to be a mechanical mixture of the two sulfides. Therefore we did not investigate them further.

Qualitatively we observed, by gentle heating in a glass tube, that all precipitates contain a small quantity of water and elementary sulphur. A detailed thermogravimetric study of these systems is reported in the next paper. Manganese was determined spectrophotometrically\(^1\). Fig. 2 represents the function $\log(p_{\text{MnS}}) = f(p_{\text{MnSO}_4})$, where $p_{\text{MnS}}$ is the mol $\%$ content of MnS in the precipitate.
Fig. 2. Amount of MnS in the precipitate (logarithmic scale), dried over Silicagel, as function of the relative percentage amount of MnSO₄ in aqueous solution containing a 0.3 M mixture of CdSO₄ and MnSO₄.

**X-Ray Examination**

The diffractographic method was used with X-rays monochromatised by reflection (CoKα radiation, λ = 1.7902 Å). Four typical diffractographic curves are shown in Fig. 3. Preparation G (p_{MnS} = 0.0366 mol %) shows only the three strongest lines of cubic β-CdS. Preparation K (p_{MnS} = 0.105 mol %), basically β-CdS, contains a small quantity of hexagonal α-CdS. In preparation N (p_{MnS} = 0.464 mol %) there is more α-CdS than in K. Preparation X, obtained with p_{MnSO₄} = 100 mol %, corresponds to the pink β-hexagonal modification of MnS as it presents the same type of Debye-Scherrer pattern as α-CdS. This fact and width of lines of all X-ray diagrams makes it impossible to decide by these means whether a preparation is a solid solution of the two sulphides or a mechanical mixture. At the same time it shows that all preparations are nearly amorphous.
DISCUSSION

The function \( \log p_{\text{MnS}} = f(p_{\text{MnSO}_4}) \) (Fig. 2) presents three remarkable \( \log p_{\text{MnSO}_4} \) sections:

(i) In the interval \( 0 < p_{\text{MnSO}_4} < 4 \text{ mol}\% \), \( p_{\text{MnS}} \) grows rapidly from 0 to about 0.1 mol\% MnS. In our opinion, in this region the precipitates are solid solutions of the two sulphides. The amount of MnS is not a linear function of \( p_{\text{MnSO}_4} \), which is also shown in Fig. 4: the function 100 \( p_{\text{MnS}} / p_{\text{MnSO}_4} = f(p_{\text{MnSO}_4}) \) is not constant in this interval of \( p_{\text{MnSO}_4} \), but decreases rapidly.

(ii) From \( 4 < p_{\text{MnSO}_4} < 20 \text{ mol}\% \), \( p_{\text{MnS}} \) remains approximately constant. It means, we believe, that the CdS : MnS solid solution has reached its saturation for at most about 0.1 mol\% MnS.

(iii) For \( p_{\text{MnSO}_4} > 20 \text{ mol}\% \) the content of MnS of the precipitates rises more rapidly than exponentially. The function in Fig. 4 also rises from the very low minimum at \( p_{\text{MnSO}_4} = 20 \text{ mol}\% \). It means that in this region, with growing \( p_{\text{MnSO}_4} \), larger and larger amounts of MnS are precipitated. Thus a mechanical mixture of CdS and MnS is formed, CdS containing at most about 0.1 mol\% MnS in the solid solution.
CONCLUSIONS

In our conditions of operation a solid solution of MnS in CdS contains at most about 0.1 mol% MnS. This saturation concentration is reached when the aqueous solution of the mixture of corresponding sulphate contains about 4 mol% MnSO₄. Further increase in this content does not, at first, increase the amount of manganese in the precipitate. Notable precipitation of MnS follows the precipitation of CdS when the relative amount of MnSO₄ in aqueous solution reaches 20 mol%. The order of precipitation, except for the formation of the dilute solid solution, corresponds to the solubilities of CdS and MnS in water at 18°C. At high temperatures, H. Wiedemeier and A. Khan⁵ as well as W. R. Cook⁶ showed that there exists a considerable solubility of MnS in CdS and to a smaller extent, of CdS in MnS. Since the crystalline structures of the two kinds of solid solutions are different, there exists a considerable miscibility gap.

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IZVOD

Stvaranje čvrstih otopina kadmijskih sulfida i manganovog sulfida koprincipalim od sulfata sa amonijevim sulfidom

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Dodaje se vodenim otopinama CdSO₄ + MnSO₄ različitih sastava, no kojima je SO₄²⁻ stalno 0,4 M, jednaki volumen vodene otopine (NH₄)₂S 0,27 M, ne stvara se neprekinut niz čvrstih otopina CdS : MnS: dolazi do zasićenja kad talog sadrži najviše 0,1 mol % MnS. Tada relativna koncentracija MnSO₄ iznosi 4 mol %. Ako relativna koncentracija MnSO₄ naraste na 20 mol %, MnS se taloži u znatnoj količini od 18,8 mol % kad je relativna količina MnSO₄ jednaka 50 mol %. Debye-Scherrer dijagrami pokazuju da su talozi gotovo amorfniji i da sadrže pretežno kubični CdS s primjesama heksagonalnog CdS i MnS. Samo pomoću tih dijagrama nije moguće razlikovati mehaničke smjese od čvrstih otopina.