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Thermogravimetric Analysis of Cadmium Sulphide—Manganese Sulphide Systems Obtained by Coprecipitation

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CdS-MnS systems obtained by coprecipitation from aqueous solutions of corresponding sulphates by ammonium sulphide were dried for months over Silicagel and then submitted to thermogravimetric analysis. Their content of water and of excess sulphur passes through minima in the critical zone of precipitation, where the precipitates contain very nearly 0.1 mol % MnS. It is believed that the minima correspond to a minimum of specific surface of the precipitates and that this minimum separates the region of formation of CdS:MnS solid solutions from the region towards greater contents of MnS, where coprecipitation of the saturated solid solution CdS:MnS and MnS occurs.

Qualitative analysis of CdS-MnS systems formed by coprecipitation from aqueous solutions of corresponding sulphates by ammonium sulphide¹ has shown that these, *quasi* amorphous, precipitates contain, after months of drying over Silicagel, water and elementary sulphur. To obtain quantitative information about these components and about their thermal behaviour, we submitted the systems to thermogravimetric analysis.

The samples present themselves as compact amorphous conglomerates. The sample holder of the thermobalance was a small platinum cup, suspended on a platinum wire fixed on the beam of a Cahn RG Electrobalance². About 20 mg of sample were used. The temperature rose from $t = 20^\circ\text{C}$ to 650°C as a function of time τ min according to the equation $t = 20 + 0.27 \tau + 0.0053 \tau^2$ in 320 min. The furnace was connected to an oil diffusion pump which maintained a pressure of the order of 10^{-4} Torr. The temperature of the sample and the mass loss were recorded simultaneously at a speed of 1 mm/min. In addition to CdS-MnS precipitates, luminescence grade CdS (LM) and ground crystals of sublimated CdS (SB) were examined.

The thermograms are represented in Figs. 1 and 2 in form of logarithm of percent mass loss *vs* temperature. It is seen that, in general, the curves do not present marked »knees«. Nevertheless some thermograms show three separate temperature intervals of pronounced mass loss. In the case of sample L (Fig. 2), for example, these intervals are: 20° to 80° ; 180° to 320° and over 500°C . We ascribe the first mass loss to water, the second to sulphur and the third to sublimation of CdS. The last attribution is corroborated by the thermograms of pure CdS (LM and SB, Fig. 1) which show that up to 500°C the mass loss of CdS, under our conditions of operation is negligible. Taking into consideration the form of all other thermograms it

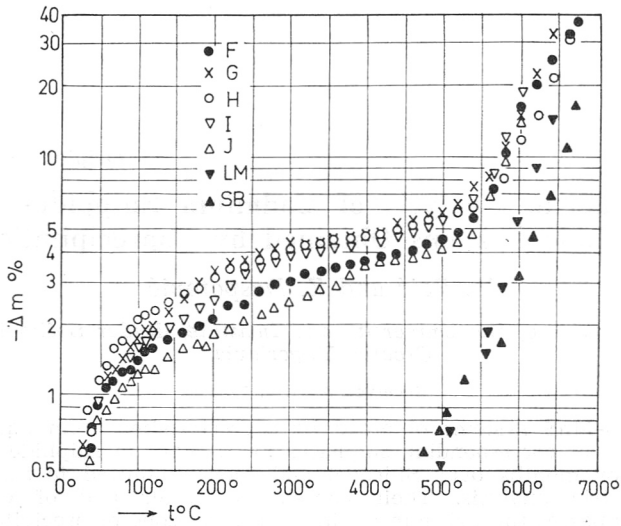


Fig. 1. Thermograms of coprecipitated CdS-MnS systems F to J, the compositions of which are given by the ordinate of curve (III), Fig. 3; Curves LM and SB relate to luminiscent grade CdS and to crushed CdS crystals, respectively prepared by sublimation in vacuo of LM.

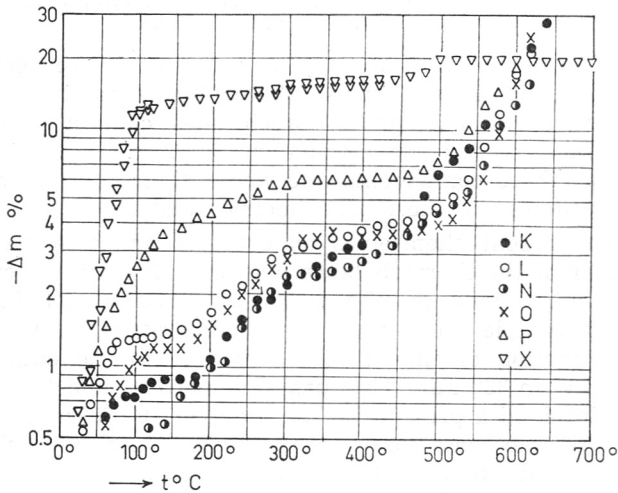


Fig. 2. Thermograms of coprecipitated CdS-MnS systems K to X, the compositions of which are given by the ordinates of curve (III), Fig. 3.

seems reasonable to attribute the mass losses in the intervals 20° to 100° C and 100° to 460° C to water and to elementary sulphur, respectively.

The contents of water and excess sulphur thus obtained are represented in Fig. 3 as functions of the logarithm of the amount of MnS ($\log p_{\text{MnS}}$) present in water and excess sulphur free material. It is seen that each of these functions passes through a minimum at about 0.1 mol %, which we ascribe to a minimum of the specific surface of the systems. This behaviour is not fortuitous. To support this assertion, we traced, in the same figure,

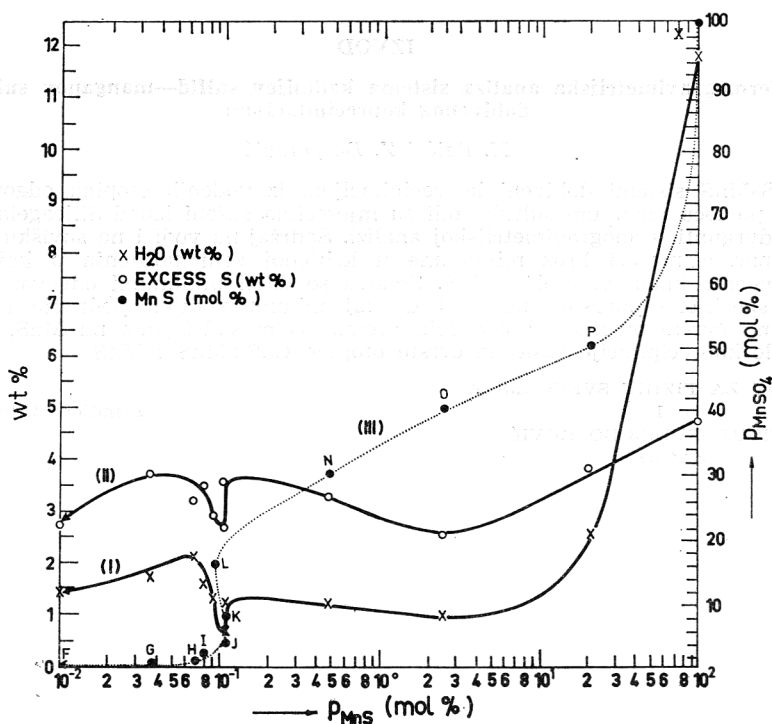


Fig. 3. Curve (I), water, and curve (II), excess sulphur contents (left-hand ordinate) vs logarithm of amount of MnS ($\log p_{\text{MnS}}$) in the system; curve (III), relative molar percent amount of MnSO_4 (p_{MnSO_4}) (right-hand ordinate), in aqueous solution of CdSO_4 and MnSO_4 , vs $\log p_{\text{MnS}}$.

the function $p_{\text{MnSO}_4} = g(\log p_{\text{MnS}})$, where p_{MnSO_4} denotes the relative per cent molar concentration of MnSO_4 in the 0.3 M SO_4^{2-} aqueous solutions of CdSO_4 and MnSO_4 , being always 10 mol % in excess of the added 0.27 M $(\text{NH}_4)_2\text{S}$ solution¹. It is seen that the critical region, between 0.0721 mol % MnS (sample H) and 0.112 mol % MnS (sample J), which separates the p_{MnSO_4} intervals of precipitation of CdS-MnS solid solutions from the coprecipitation of MnS, coincides with this minima. It is worth remarking that in the minimum the specific surface is very sensitive to the amount of MnS in the precipitate: the minimum has a width of only 0.4 mol % MnS.

Up to about 2.5 mol % MnS (sample 0) the functions giving the amounts of water and excess sulphur are *quasi* parallel. With growing p_{MnSO_4} the precipitates contain more and more MnS which retains much more water, but is not so active in favouring the coprecipitation of sulphur.

In our opinion the minimum of specific surface separates the region of precipitation of mainly CdS:MnS solid solutions from the region, towards greater MnS contents, of coprecipitation of the saturated CdS:MnS solid solution and MnS.

REFERENCES

1. M. Paić, *Croat. Chem. Acta* 43 (1971) 169.
2. W. W. Wendlandt, *Thermal Methods of Analysis*, Interscience Publishers, New York, London, Sydney, 1964, p. 58.

IZVOD

**Termogravimetrijska analiza sistema kadmijev sulfid—manganov sulfid
dobivenog koprecipitacijom***M. Paić i Z. Despotović*

CdS-MnS sistemi dobiveni koprecipitacijom iz vodenih otopina odgovarajućih sulfida, pomoću amonijum sulfida, bili su mjesecima sušeni iznad Silicagela i nakon toga podvrgnuti termogravimetrijskoj analizi. Sadržaj na vodi i na suvišku sumpora tih preparata prolazi kroz minimume u kritičnoj zoni taloženja u kojoj talozi sadrže veoma blizu 0,1 mol % MnS. Smatra se da ti minimumi odgovaraju minimumu specifične površine taloga i da taj minimum dijeli područje nastajanja CdS : MnS čvrste otopine od područja prema većim sadržajima na MnS, u kojem dolazi do koprecipitacije zasićene čvrste otopine CdS : MnS i MnS.

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