

On the chemical transport of some binary sulfides

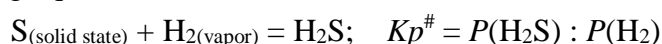
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The present work is concerned with the investigation of the phase diagrams for the systems In–S and Fe–S. It is known that some of these sulphides are promising materials for new technologies, however there are considerable discrepancies concerning the types and temperatures of the solid phase transformations and homogeneity regions of these phases. These discrepancies can be caused by the very low volatility of metal-enriched iron and indium sulphides as well as ambiguous interpretation of the results of electrical measurements. For the scanning of P – T – x diagram of the sulphides systems (In–S and Fe–S) the spectrophotometric technique is elaborated. We suggested studying the equilibria of indium and sulfides with hydrogen as an auxiliary component. It is proved that the equilibrium in this system after introducing hydrogen has to be described by the following equation:



So, there is no noticeable vaporization of chemically bounded indium to the vapor. When the shift of equilibrium (1) takes place, this element should be accumulated (consumed) in the condensed part of the system and cause transformations of some sulfides into other sulfides or changes in their non-stoichiometry.

Vast thermodynamic information about phases of sulphide systems can be received if it is possible to determine $K_P^\#$, which relates pressures of hydrogen and hydrogen sulfide (see eq. 1).

To find the value of $K_P^\#$, one needs to know partial pressure of, at least, one of two molecular forms - H_2 or H_2S . Then the equilibrium pressure of another form (for example, P_{H_2}) can be determined if the pressure of initially introduced hydrogen (P^0) is known. Hydrogen sulfide is known to have an electronic absorption spectrum in the “air” ultraviolet spectral region ($\lambda_{\text{max}} = 196 \mu\text{m}$). This enables quantitative determination of H_2S in the vapor phase by spectrophotometry. The fulfilled experiments give the opportunity of obtaining data about the In-S phase diagram.

The objective of this work is the refinement of the phase diagram of the In–S system within the composition field of 50–60 mol. % and analysis of homogeneity region of the phase $\text{In}_{3-x}\text{S}_4$. Analyzing the $K_P^\#$ – T dependences we assume that the $\text{In}_{3-x}\text{S}_4$, a phase with a broad homogeneity range, has a tendency to decompose into two separate phases in a wide temperature range. Moreover, our results confirm the existence of a narrow two phase field between $\text{In}_{3-x}\text{S}_4$ and $\text{In}_2\text{S}_3'$ at low temperature region.

For the Fe–S system iron(III) chloride can be used as an auxiliary component also. We report initial results from our spectrophotometric study of the equilibrium «solid – vapor» for iron(III) chloride in a wide range of temperatures (150–800 °C). The purpose of this part of the work was to determine (at least qualitatively) the composition of unsaturated vapor of iron(III) chloride. The experiment consisted in scanning *in situ* the absorption spectra of the vapor (wavelength interval 200–800 nm) in two temperature regimes: incremental increasing and decreasing. The presence of some species in unsaturated vapor has been discussed. As metal halides are often used as transport agents for growing sulfides, current results together with some future investigations in this field can find their application, for example, as a base for pyrite production for the needs of technology and energetics.

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