EXPERIMENTAL STUDY OF THE THERMODYNAMICS OF SOLID-STATE REACTIONS

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This report presents the most significant results obtained at the Laboratory of Electrochemistry, Thermodynamics, and Mineral Physics at the IEM RAS, using the high-temperature galvanic cell (EMF-method) and a vacuum-block calorimeter. The EMF-method can be illustrated by the example of studies of silver selenide [1]. The reaction of naumannite formation from the elements is realized in an electrochemical cell: (–)Pt | Ag | SE or LE | Ag_2Se, Se | Pt(+), in a wide temperature range determined by the solid (SE – AgI, $RbAg_4I_5$, AgCl) or liquid electrolyte (LE – molten salts or glycerol solution) used. Thermodynamic properties of phases and phase relations in binary and ternary silver-containing systems have been determined over a wide range of temperatures and atmospheric pressure [2-5]. Experiments at hydrostatic argon pressure up to 0.7 GPa were carried out in high-pressure gas vessels developed by the IEM RAS [6, 7]. Another important variation of the EMF-method is the use of oxygen-conducting solid electrolytes [8], which is widely used to study the thermodynamic properties of oxide systems. At the Laboratory, this method has been applied to the study of natural objects: oxygen fugacity above the bulk sample was determined for some chondrites [9], and the $pO_2(T)$ dependence was obtained in high-temperature fumaroles on Kudryavy Volcano (Iturup Island, Kuril Islands) [10]. Standard enthalpies of formation of Sb_2Se_3 and other chalcogenides, pnictides and intermetallics were determined on a unique vacuum-block calorimeter of our own design [11].

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