

Observing and Modeling High-Temperature Phase Transformations

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This seminar describes two studies involving different approaches to the elucidation of high temperature phase equilibria and thermochemistry. In the first study,¹ time-of-flight neutron diffraction was used for the first time to observe phase transformations in $^{75}\text{-Ga}_2\text{S}_3$ and MnGa_2S_4 in effusion cells above 1240°C. This study demonstrated that an anomalous temperature dependence of vapor pressure previously observed for these compounds was a manifestation of a phase transformation. By their crystallographic features, the observed phase changes were classified as order-disorder transformations. These ‘premelting’ transitions, occurring approximately 100 degrees below the melting points, could only be discovered by observation of the phases *in situ*. In the direction of decreasing temperature, the disorder-to-order transformation is facile and no rate of cooling could preserve the disordered phase for easy inspection at room temperature. The result of this study was the observation of predicted phases, confirmation of a thermodynamic theory of phase transformations, and the discovery of a relationship between structural changes and vapor pressures that may also apply to other binary chalcogenides.

The second study², which is in progress, employs a purely computational approach to determination of phase equilibria and chemical activity in the salt system $[\text{Na}^+, \text{K}^+/\text{Cl}, \text{S}^{2-}, \text{SO}_4^{4-}, \text{CO}_3^{3-}, \text{OH}]$. The goal of the study is to characterize the salt system in its molten state, given the initial conditions of temperature and pressure. Unlike the first study, ample thermodynamic data are available to allow use of a thermodynamic model for prediction of phases present at equilibrium and the activities of the components. The advantage of a computational approach is that fewer experiments need to be performed. The thermodynamic model employed is the ideal solution with associated species, which account for nonideality. With this model, phase diagrams have been calculated for binary and ternary subsystems of the above salt system with varying degrees of success. In general, melting temperatures and eutectic compositions of simple eutectic binary systems are easily reproduced. Calculations on systems that contain features such as peritectics, solid solubility, intermediate compounds, and complex equilibria revealed only the general shape of the phase diagram, but still predict melting temperatures with good accuracy. Gradually, the calculations will be extended to include all of the salts in the system. The results will be applied to predicting the chemistry of molten salts in industrial settings, where they contribute to corrosion in steel. The activities of molten-salt species, coupled with alloy constituent activities, will be used to understand and predict corrosion in steel and aid selection of corrosion-resistant materials.

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