Electromotive Force Measurements in High-Temperature Systems

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1. Introduction

Stability of phases existing in chemical systems is determined by its Gibbs free energy designated as G. The relative position of Gibbs free energy surfaces in the G-T-X (composition) space determines stability ranges of respective phases yielding a map called the phase diagram. Since the knowledge of phase equilibria is essential in designing new materials, determination of Gibbs free energy for respective phases is being continued on both theoretical as well as experimental ways. While in principle chemical potentials of pure substances are needed to derive Gibbs free energy of formation of the stoichiometric phases, it is not the case for the phase (solid or liquid) with variable composition. As an example, in Fig 1, ΔG_m for three different systems is shown. Fig.1a shows free energy of formation of the intermetallic, stoichiometric Mg₂Si phase recalculated per one mole of atoms (Turkdogan, 1980). Fig1b illustrates Gibbs energy of formation of one mole of liquid In-Pb solution (Hultgren, 1973). Finally, Fig.1c demonstrates Gibbs energy of formation of the solid phase, wustite ('FeO') (Spencer & Kubaschewski, 1978).

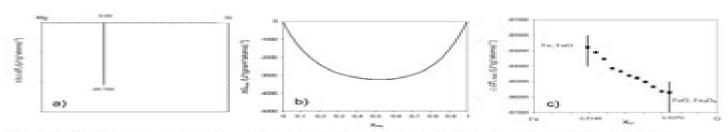


Fig. 1. Gibbs free energy of formation of a) stoichiometric Mg₂O phase, b) liquid In-Pb solution, c) solid phase 'FeO' wustite.

In the last two cases experimental information about chemical potentials of both components in the solution (partial Gibbs energies) was necessary to obtain ΔG_m vs. composition dependencies at fixed temperature.

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