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Free energy of formation of zircon and hafnon

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ABSTRACT

The free energy of formation of zircon ($ZrSiO_4$) from its oxides was determined between 1100 and 1300 K by an electrochemical method, in which values of μ_{O_2} defined by the two assemblages Fe_2SiO_4-Fe-SiO_2 (fayalite-iron-quartz) and Fe_2SiO_4-Fe-ZrO_2-$ZrSiO_4$ were each measured using oxygen concentration cells with calcia-stabilized zirconia solid electrolytes. The difference in μ_{O_2} between these two assemblages corresponds to the reaction $ZrO_2 + SiO_2(qz) = ZrSiO_4$. The results, when analyzed using calorimetric data for the entropies and high-temperature heat capacities of $ZrSiO_4$, ZrO_2, and SiO_2(quartz), yields $\Delta_{f,ox}H^0_{298K} = -24.0 \pm 0.2$ kJ/mol for $ZrSiO_4$, in good agreement with the calorimetric value of Ellison and Navrotsky (1992). $ZrSiO_4$ is predicted to decompose to ZrO_2 plus SiO_2 (cristobalite) at 1938 K, assuming a temperature of 1430 K for the martensitic phase transition between the tetragonal and monoclinic forms of ZrO_2 (baddeleyite), with an enthalpy of transition of 8.67 kJ/mol. The same experimental approach was used also to determine the free energy of formation of hafnon ($HfSiO_4$). The entropy of hafnon ($S^0_{298K} = 93.6$ J/mol·K) is similar to that for zircon, but the enthalpy of formation is slightly more exothermic ($\Delta_{f,ox}H^0_{298K} = -25.0 \pm 0.2$ kJ/mol).

The cells with either $ZrSiO_4 + ZrO_2$ or $HfSiO_4 + HfO_2$ produce an anomalous excursion in EMF when the temperature of the α–γ transition in Fe metal at 1184 K is traversed; this excursion takes >12 hours to decay back to the equilibrium value. This behavior is presumably related to strain caused by the volume change of the α–γ transition.

The redetermination of the μ_{O_2} of the Fe_2SiO_4-Fe-SiO_2(qz) equilibrium (the quartz-fayalite-iron or QFI oxygen buffer) carried out in the course of this study gave results in reasonable agreement with previous work, but with a different slope vs. temperature, implying a slightly higher value of S^0_{298K} for Fe_2SiO_4 than the currently accepted calorimetric datum (i.e., 153.5 vs. 151.0 ± 0.2 J/K·mol).

Keywords: Zircon, hafnon, free energy of formation, fayalite, thermodynamic data