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Heat capacities and thermodynamic functions of TiO_2 anatase and rutile: Analysis of phase stability

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Abstract

At high temperature, coarse-grained (bulk) rutile is well established as the stable phase of TiO_2, and nanophase anatase, thermodynamically stable relative to nanophase rutile, transforms irreversibly to rutile as it coarsens. The lack of experimental heat-capacity data for bulk anatase below 52 K lends uncertainty to its standard entropy and leaves open a slight possibility that anatase may have a thermodynamic stability field at low temperature, as suggested by some theoretical calculations. In the present study, the molar heat capacities of rutile and anatase were measured from 0.5 K to about 380 K. These data were combined with previously measured high-temperature heat capacities, and fits of the resulting data set were used to generate $C^{\circ}_{P,\mathrm{m}}$, $\Delta_0^{\mathrm{T}}S^{\circ}_{\mathrm{m}}$, $\Delta_0^{\mathrm{T}}H^{\circ}_{\mathrm{m}}$, and $\Delta_0^{\mathrm{T}}G^{\circ}_{\mathrm{m}}$ values at smoothed temperatures between 0.5 and 1300 K for anatase and 0.5 and 1800 K for rutile. Using these new data and the enthalpy of transformation between anatase and rutile at 298 K, the change in Gibbs free energy for the transition between anatase and rutile from 0 to 1300 K was calculated. These calculations reveal that the transformation from bulk anatase to bulk rutile is thermodynamically favorable at all temperatures between 0 and 1300 K, confirming that bulk anatase does not have a thermodynamic stability field. Implications for the natural occurrence of these two minerals in terrestrial, lunar, and planetary settings are discussed. In particular, anatase requires low-temperature aqueous conditions for its formation and may be a reliable indicator of such conditions in both terrestrial and extraterrestrial settings.

Keywords: Rutile, anatase, TiO_2, heat capacity, thermodynamics, phase transformation