

High Temperature Thermodynamics of Phosphoric Acid in Aqueous Solution

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Knowledge of the thermodynamic properties of phosphoric acid in aqueous solution at superambient conditions is both of technological and geochemical interest. Namely, the Gibbs energy of formation at the standard state of infinite dilution is needed as a function of temperature and pressure for characterizing chemical and phase equilibria in hydrothermal solutions. Such thermodynamic surfaces can be constructed by integrating the standard molar heat capacities and volumes determined in an extended range of temperatures and pressures. We have measured the densities and heat capacities of dilute solutions of phosphoric acid (0.1 to 1 molal) using flow vibrating tube densitometry [1] and differential Picker type calorimetry [2] at temperatures up to 623 K and pressures to 30 MPa. These values were combined with the literature data on the dissociation constants of phosphoric acid and its thermal and volumetric properties; here the heat capacity values reported earlier by Sharygin *et al.* [3] were of particular interest. The simultaneous treatment of these different thermodynamic data by the SOCW model [4] and consideration of the partial dissociation of phosphoric acid at temperatures below 473 K allowed us to obtain a consistent description of the standard thermodynamic properties of formation up to at least 673 K.

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