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A thermodynamic model for silica and aluminum in alkaline solutions with high ionic strength at elevated temperatures up to 100 °C: Applications to zeolites

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Abstract

In this study, a thermodynamic model for silica and aluminum in high ionic strength solutions at elevated temperatures up to 100 °C is constructed. Pitzer equations are utilized for the thermodynamic model construction. This model is valid up to ionic strengths of ~24 molal (m) in NaOH solutions with silicate concentrations up to ~1.5 m. The speciation of silica (including monomers and polymers) and aluminum at elevated temperatures is taken into account. Also, the equilibrium constants for silicic acid and its polymer species (H_4SiO_4, $H_5Si_2O_7^-$, $H_4Si_2O_7^{2-}$, and $H_5Si_3O_7^{3-}$) at elevated temperatures up to 100 °C, are obtained based on theoretical calculations. Using this thermodynamic model, thermodynamic properties, including equilibrium constants, and respective reaction enthalpies are obtained for sodium silicates, zeolite A, and the amorphous form of zeolite A, based on solubility experiments at elevated temperatures. The equilibrium constants for zeolite A and amorphous precursor of zeolite A regarding the following reactions up to 100 °C,

$$NaAlSiO_4{\cdot}2.25H_2O(cr) + 4H^+ = Na^+ + Al^{3+} + H_4SiO_4(aq) + 2.25H_2O(l) \quad (1)$$

and

$$NaAlSiO_4{\cdot}2.25H_2O(am) + 4H^+ = Na^+ + Al^{3+} + H_4SiO_4(aq) + 2.25H_2O(l) \quad (2)$$

can be expressed as follows

$$\log K_1 = \frac{7963 \pm 327}{T} - 16.46 \pm 0.96 \quad (3)$$

and

$$\log K_2 = \frac{12971 \pm 160}{T} - 30.80 \pm 0.50 \quad (4)$$

where T is temperature in Kelvin.

The enthalpy of formation from elements, Gibbs free energy of formation from elements, and standard entropy derived for zeolite A and the amorphous form of zeolite A with the chemical formulas mentioned above at 25 °C and 1 bar are –2738 ± 5 kJ/mol, –2541 ± 2 kJ/mol, 373 ± 10 J/(K·mol); and –2642 ± 3 kJ/mol, –2527 ± 2 kJ/mol, and 648 ± 10 J/(K·mol), respectively. The enthalpy of formation from elements for zeolite A derived in this study based on solubility experiments in hydrothermal solutions agrees well with those obtained by calorimetric measurements and by theoretical calculations.

Keywords: Pitzer equation, solution chemistry, sodium silicates, hydrothermal synthesis