Solubility and stability of zeolites in aqueous solution: I. Analcime, Na-, and K-clinoptilolite

R.T. WILKIN* AND H.L. BARNES

Ore Deposits Research Section, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

Abstract

The solubilities of analcime and clinoptilolite were determined in dilute, weakly alkaline, aqueous solutions below 300 °C and at vapor-saturated pressures. Analcimes used in this study were from Mont St. Hilaire, Quebec (an₁, Si/Al = 2.02) and Wikieup, Arizona (an₂, Si/Al = 2.55); clinoptilolite samples were from Castle Creek, Idaho (Si/Al = 4.50). The effects of alkali content (Na,K) on clinoptilolite solubility were determined by using cation-exchanged varieties of the Castle Creek material (cp₁, cp₂). In neutral to weakly alkaline solutions, the dominant solubility-controlling reactions of these zeolites are

 $NaAlSi_2O_6 \cdot H_2O(an_1) + 5H_2O(l) \leftrightarrow Na^+ + Al(OH)_4^- + 2Si(OH)_4(aq),$

 $Na_{0.85}Al_{0.85}Si_{2.15}O_{6} \cdot H_{2}O(an_{2}) + 5H_{2}O(1) \leftrightarrow 0.85Na^{+} + 0.85Al(OH)_{4}^{-} + 2.15Si(OH)_{4}(aq),$

 $Na_{1.1}Al_{1.1}Si_{4.9}O_{12} \cdot 3.5H_2O(cp_1) + 8.5H_2O(l) \leftrightarrow 1.1Na^+ + 1.1Al(OH)_4^- + 4.9Si(OH)_4(aq),$

and

 $K_{1,1}Al_{1,1}Si_{4,9}O_{12} \cdot 2.7H_2O(cp_2) + 9.3H_2O(l) \leftrightarrow 1.1K^+ + 1.1Al(OH)_4^- + 4.9Si(OH)_4(aq).$

The logarithm of the equilibrium constants of these reactions were fit to the function: log $K = A + BT + C/T + D \log T$. At 25 °C, log K_{25} values for the Mont St. Hilaire analcime, Wikieup analcime, Na-clinoptilolite, and K-clinoptilolite are -16.1, -15.0, -26.5, and -28.1, respectively. These data were combined with the thermodynamic properties of the aqueous (aq) species Si(OH)₄, Al(OH)⁻₄, Na⁺, K⁺, and liquid water (1) to determine standard Gibbs free energies of formation as a function of temperature. Values of $\Delta G_{\rm f}^{0}$ at 25 °C and 1 bar for the Mont St. Hilaire analcime and Wikieup analcime are -3089.2 and -3044.4 kJ/mol, respectively. The $\Delta G_{\rm f}^{0}$ values for hydrous Na-clinoptilolite and K-clinoptilolite, respectively, are -6267.9 and -6107.4 kJ/mol at 25 °C and 1 bar. The solubility data reported here, and results obtained from previous calorimetric studies, indicate that the aluminosilicate frameworks of analcime and clinoptilolite are stabilized by an increase in Al content.