Thermodynamics and crystal chemistry of rhomboclase, (H₅O₂)Fe(SO₄)₂·2H₂O, and the phase (H₃O)Fe(SO₄)₂ and implications for acid mine drainage

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Abstract

The system Fe_2O_3-SO_3-H_2O contains the most important minerals of acid mine drainage (AMD), iron oxides, and iron sulfates. For geochemical modeling of the AMD systems, reliable thermodynamic data for these phases are needed. In this work, we have determined thermodynamic data for the most acidic sulfates rhomboclase [$(H_5O_2)Fe(SO_4)_2$·$2H_2O$ or $(H_3O)Fe(SO_4)_2$·$3H_2O$] and the phase $(H_3O)Fe(SO_4)_2$. The actual compositions of the studied phases are $(H_3O)_{1.34}Fe(SO_4)_{2.17}(H_2O)_{3.06}$ (molecular mass of 344.919 g/mol) and $(H_3O)_{1.34}Fe(SO_4)_{2.17}$ (289.792 g/mol). Structural details for both phases were refined from synchrotron powder X-ray diffraction data. Enthalpies of formation were determined by acid-solution calorimetry. Low-temperature heat capacity was measured for rhomboclase by relaxation calorimetry but a critical analysis of entropies for several oxysalts showed that these data are too high. Entropies for both phases were estimated from a Kopp-rule algorithm. The enthalpies of formation and entropies were combined with previously published temperature-relative humidity brackets to generate an internally consistent thermodynamic data set for rhomboclase: $\Delta_fH°$ = –3202.03 kJ/mol, $S°$ = 378.7 J/(mol·K); and for $(H_3O)_{1.34}Fe(SO_4)_{2.17}$: $\Delta_fH°$ = –2276.25 kJ/mol, $S°$ = 253.2 J/(mol·K). Solubility experiments at room temperature and at T = 4 °C agree well with previously reported data in the system Fe_2O_3-SO_3-H_2O. An inspection of the extended Pitzer model for Fe^{3+}-SO_4 solutions shows that this model reproduces the general topology of the phase diagram, but the position of the calculated solubility curves deviates substantially from the experimental data. Solid-state ²H MAS NMR spectra on deuterated rhomboclase show two isotropic chemical shifts $\delta_{iso}(^2H)$ = of 8 ± 1 and 228 ± 1 ppm, assigned to $D_5O_2^+$ and Fe-OD₂ groups, respectively. Canonical ensemble (NVT) molecular dynamics simulations for $(H_3O)Fe(SO_4)_2$ at T = 300 K showed that the H_3O^+ groups maintain their trigonal pyramidal geometry and perform different types of motion.

Keywords: Rhomboclase, acid mine drainage, thermodynamics, hydrogen mobility