Determination of melanterite-rozenite and chalcanthite-bonattite equilibria by humidity measurements at 0.1 MPa

I-MING CHOU,1,* R.R. SEAL II,1 AND B.S. HEMINGWAY2

1U.S. Geological Survey, 954 National Center, Reston, Virginia 20192, U.S.A.
2U.S. Geological Survey, 953 National Center, Reston, Virginia 20192, U.S.A.

ABSTRACT

Melanterite (FeSO4·7H2O)-rozenite (FeSO4·4H2O) and chalcanthite (CuSO4·5H2O)-bonattite (CuSO4·3H2O) equilibria were determined by humidity measurements at 0.1 MPa. Two methods were used; one is the gas-flow-cell method (between 21 and 98 °C), and the other is the humidity-buffer method (between 21 and 70 °C). The first method has a larger temperature uncertainty even though it is more efficient. With the aid of humidity buffers, which correspond to a series of saturated binary salt solutions, the second method yields reliable results as demonstrated by very tight reversals along each humidity buffer. These results are consistent with those obtained by the first method, and also with the solubility data reported in the literature. Thermodynamic analysis of these data yields values of 29.231 ± 0.025 and 22.593 ± 0.040 kJ/mol for standard Gibbs free energy of reaction at 298.15 K and 0.1 MPa for melanterite-rozenite and chalcanthite-bonattite equilibria, respectively. The methods used in this study hold great potential for unraveling the thermodynamic properties of sulfate salts involved in dehydration reactions at near ambient conditions.

INTRODUCTION

Efflorescent sulfate salts, such as melanterite, chalcanthite, rozenite, and bonattite, can be important constituents of acid-mine drainage systems. They form during dry periods in sheltered areas through the evaporation of surface or ground waters in the vadose zone. These sulfate salts temporarily store acidity and metals in solid form and can dissolve later during storm events due to their high solubility, with detrimental effects on aquatic ecosystems. The ability to construct geochemical models of the behavior of efflorescent salts in aqueous systems is hindered by a limited and poor understanding of their phase equilibria and thermodynamic properties, among other factors (Jambor et al. 2000 and references therein).

Melanterite (FeSO4·7H2O) and rozenite (FeSO4·4H2O) are part of a series of Fe2+ sulfate minerals with varying states of hydration. Other minerals in the series include ferrohexahydrate (FeSO4·6H2O), siderotil (FeSO4·5H2O), and szomolnokite (FeSO4·H2O). In addition to melanterite and rozenite, szomolnokite is known to be stable in the system FeSO4-H2O, but ferrohexahydrate and siderotil may require additional components, such as CuSO4, to become stable phases (Jambor and Traill 1963). Natural samples of melanterite group minerals contain considerable Cu and Zn in solid solution. Rarely, molar Zn exceeds molar Fe and Cu and the mineral Zn-melanterite is formed (Jambor et al. 2000). Alpers et al. (1994) proposed that seasonal variations in the Cu/Zn ratio of effluent from the Richmond portal at Iron Mountain, California were influenced by the dissolution and precipitation of melanterite. Chalcanthite (CuSO4·5H2O) and bonattite (CuSO4·3H2O) are part of a series of Cu2+ sulfate minerals with varying states of hydration that also includes poitevinite (CuSO4·H2O); anhydrous CuSO4 is the mineral chalcocyanite (Hawthorne et al. 2000; Jambor et al. 2000).

In this study, by using two experimental methods, we determined the equilibrium relative humidity (RH) and refined the thermodynamic relations for two dehydration reactions at 0.1 MPa:

\[
\text{FeSO}_4\cdot7\text{H}_2\text{O}(s) = \text{FeSO}_4\cdot4\text{H}_2\text{O}(s) + 3 \text{H}_2\text{O}(g) \quad (1)
\]

\text{melanterite (Mel)} \quad \text{rozenite (Roz)}

and

\[
\text{CuSO}_4\cdot5\text{H}_2\text{O}(s) = \text{CuO}_2\cdot3\text{H}_2\text{O}(s) + 2 \text{H}_2\text{O}(g) \quad (2)
\]

\text{chalcanthite (Cha)} \quad \text{bonattite (Bon)}

where (s) and (g) are solid and gas, respectively. For both reactions,

\[
\Delta G_r^o = -RT \ln K = -nRT \ln \left( \frac{f_{\text{H}_2\text{O}}}{f_{\text{H}_2\text{O}}^*} \right) = -nRT \ln \left( \frac{f_{\text{H}_2\text{O}}^*}{(\text{RH})/100} \right) \quad (3)
\]

where \(\Delta G_r^o\) is the standard Gibbs free energy of reaction; \(K = \text{equilibrium constant; } R = \text{gas constant; } T = \text{absolute temperature; } f_{\text{H}_2\text{O}} = \text{equilibrium H}_2\text{O fugacity; } f_{\text{H}_2\text{O}}^* = \text{fugacity of pure H}_2\text{O; and } n = 3 \text{ and } 2 \text{ for reactions } 1 \text{ and } 2, \text{ respectively.}

These two reactions were chosen for the present study mainly because both dehydration and hydration reactions are rapid (Mezei et al. 1984) and large discrepancies exist in published results, especially for reaction 1. Estimates in the literature for equilibrium RH for reaction 1 at 25 °C ranges from a