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

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### ABSTRACT

Melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O)-rozenite (FeSO<sub>4</sub>·4H<sub>2</sub>O) and chalcantite (CuSO<sub>4</sub>·5H<sub>2</sub>O)-bonattite (CuSO<sub>4</sub>·3H<sub>2</sub>O) 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 chalcantite-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, chalcantite, 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).

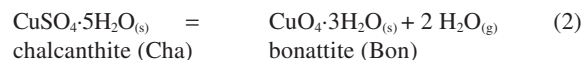
Melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O) and rozenite (FeSO<sub>4</sub>·4H<sub>2</sub>O) are part of a series of Fe<sup>2+</sup> sulfate minerals with varying states of hydration. Other minerals in the series include ferroxahydrate (FeSO<sub>4</sub>·6H<sub>2</sub>O), siderotil (FeSO<sub>4</sub>·5H<sub>2</sub>O), and szomolnokite (FeSO<sub>4</sub>·H<sub>2</sub>O). In addition to melanterite and rozenite, szomolnokite is known to be stable in the system FeSO<sub>4</sub>-H<sub>2</sub>O, but ferroxahydrate and siderotil may require additional components, such as CuSO<sub>4</sub>, 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. Chalcantite (CuSO<sub>4</sub>·5H<sub>2</sub>O) and bonattite (CuSO<sub>4</sub>·3H<sub>2</sub>O) are part of a series

of Cu<sup>2+</sup> sulfate minerals with varying states of hydration that also includes poitevinite (CuSO<sub>4</sub>·H<sub>2</sub>O); anhydrous CuSO<sub>4</sub> 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:



and



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

$$\begin{aligned} \Delta G_r^0 &= -RT \ln K = -nRT \ln (f_{\text{H}_2\text{O}}) \\ &= -nRT \ln [(f_{\text{H}_2\text{O}}^*) \cdot (\%RH)/100] \end{aligned} \quad (3)$$

where  $\Delta G_r^0$  is the standard Gibbs free energy of reaction;  $K$  = equilibrium constant;  $R$  = gas constant;  $T$  = absolute temperature;  $f_{\text{H}_2\text{O}}$  = equilibrium H<sub>2</sub>O fugacity;  $f_{\text{H}_2\text{O}}^*$  = fugacity of pure H<sub>2</sub>O; and  $n = 3$  and  $2$  for reactions 1 and 2, 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

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low of approximately 15% (Pribylov 1969) to a high of approximately 95% (DeKock 1982), with a distinct clustering of estimates between 60 and 80% (Hemingway et al. 2002). On the other hand, most published results for reaction 2 are in good agreement. Preliminary results of this study have been presented earlier (Chou et al. 1998a, 1998b, 1999, 2000).

### EXPERIMENTAL METHODS AND RESULTS

Two experimental methods were used to obtain equilibrium constants for reactions 1 and 2 at 0.1 MPa and between 21 and 91 °C: the gas-flow-cell method and the humidity-buffer method. The humidity-buffer method is more accurate and, therefore, only data obtained by this method between 21 and 70 °C were used to derive thermodynamic properties of the investigated minerals. Even though the gas-flow-cell method is less accurate, it is more efficient for establishing the general trend of equilibrium *RH* values as a function of *T* for each reaction, and, therefore, deserves a brief description.

#### Gas-flow-cell method

This method is similar to the one designed by Parkinson and Day (1981) to control precisely the relative humidity for plant growth experiments. Starting materials are mixtures of either reagent grade  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Fisher, lot no. 542299) and its dehydrated product ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ), or reagent grade  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (Fisher, lot no. 782111), and its dehydrated product ( $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ ) with grain size of about 1 mm in diameter. The mixtures were packed in a Pyrex glass tube, 11 mm ID  $\times$  13 mm OD and 180 mm long, and plugged by silica wool at both ends. Dry  $\text{N}_2$  gas was passed through a coil of copper tubing before entering the column. The gas leaving the column was let to a humidity and temperature probe (HMP37E, Vaisala Inc.) before exiting to a water column, in which the flow rates were monitored by counting the number of gas bubbles generated per minute. The copper tubing, sample tube, and the probe were installed in a drying oven, and the temperature was controlled (to  $\pm 0.2$  °C) and measured by three Pt-resistance thermometers (accurate to  $\pm 0.02$  °C) placed in contact with the external wall of the sample tube at the two ends and the center. The sample temperatures inside the tube (accurate to  $\pm 0.2$  °C) as well as %*RH* of the "equilibrated" exiting gas were measured continuously by the humidity-temperature probe and recorded in preset intervals by a data logger, which is an integral part of the probe. Because the inlet gas was preheated before reaching the sample, and also the flow rates were kept low, the temperature differences measured by the probe and the average of those from external thermometers were less than 1 °C. However, due to a temperature gradient in the drying oven, the temperature differences between the two ends of the vertical sample tube ranged from zero near room temperatures to 3 °C at higher temperatures. The maximum temperature difference was minimized to within 1 °C when the sample tube was placed horizontally. The humidity probe was calibrated by the manufacturer by comparing its reading at 0.0 and 75.5% *RH* to a reference humidity instrument. Additional checkpoints at 11.3( $\pm 0.3$ )% (LiCl-saturated solution) and 97.6( $\pm 0.6$ )% *RH* ( $\text{K}_2\text{SO}_4$ -saturated solution) were also provided by the manufacturer. Calibration uncertainty is 0.6% *RH* at 22 °C. Sample

temperature and %*RH* were recorded continuously during each heating and cooling cycle, until the system reached a steady state, normally within 2 to 4 hours after each temperature change. The three external temperatures indicated by the digital Pt-resistance thermometers were recorded manually from time to time.

#### Humidity-buffer method

A weighed amount of sample (typically 100 to 250 mg), either melanterite-rozenite or chalcantite-bonattite mixtures, was loaded into a plastic sample container (8 mm ID  $\times$  10 mm OD and 20 mm tall), which was partially immersed in a humidity buffer, consisting of a binary saturated solution (Fig. 1; Greenspan 1977) in a glass container (17.5 mm ID  $\times$  20 mm OD and 40 mm tall) sealed by a rubber stopper with a septum. Small holes through the cap of the sample chamber allowed the vapor phase of the sample to equilibrate with that of the buffer system at a fixed temperature. To minimize oxidation for experiments containing  $\text{Fe}^{2+}$ , the air in the headspace of the sample-buffer system was evacuated by the use of a syringe. The whole assembly was then immersed in a water bath, the temperatures of which were controlled to  $\pm 0.03$  °C and measured by a Pt resistance probe (accurate to  $\pm 0.02$  °C). The direction of reaction was revealed by the sample mass change (precise to  $\pm 0.05$  mg). Both starting material and experimental products were examined by X-ray diffraction and optical methods, and no unexpected phases were identified. According to Greenspan (1977), uncertainties in predicted %*RH* for the humidity buffers used in the temperature range of this study are no more than  $\pm 0.6$  (see Table 1).

### Results

Experimental results obtained from the gas-flow-cell method are plotted in Figures 2 and 3 for reactions 1 and 2, respectively. Previous published results are also plotted for comparison. Experimental results obtained from the humidity-buffer method are listed in Table 1, and plotted in Figures 4 and 5 for reactions 1 and 2, respectively.

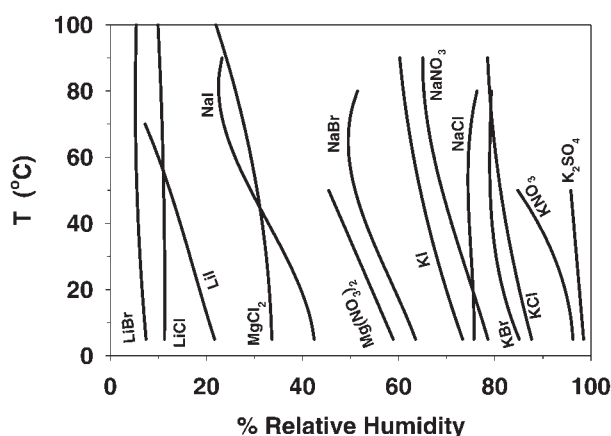


FIGURE 1. Selected humidity buffers from 28 binary saturated aqueous solutions reported by Greenspan (1977) for relative humidities from 3 to 98% at 0.1 MPa. Uncertainties in predicted %*RH* can be as much as  $\pm 2.9$ , but mostly are less than  $\pm 0.5$ .

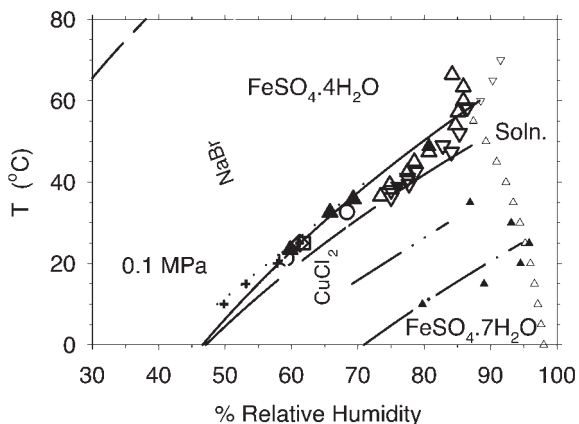
**TABLE 1.** Experimental results from the humidity-buffer method at 0.1 MPa

Humidity buffer	$T$ (°C)*	$f_{\text{H}_2\text{O}}$ (bar)†	%RH‡	ln $K$
<b>(a) Mel (<math>\text{FeSO}_4 \cdot 7\text{H}_2\text{O}</math>)-Roz (<math>\text{FeSO}_4 \cdot 4\text{H}_2\text{O}</math>) Equilibria</b>				
NaBr·2H <sub>2</sub> O (21.30)	0.02535	58.74 ± 0.42	-12.622 ± 0.022	
CuCl <sub>2</sub> ·2H <sub>2</sub> O (32.65)	0.04937	(68.40 ± 0.34)	-10.164 ± 0.015	
NaNO <sub>3</sub>	36.13 ± 0.51	0.05991	71.82 ± 0.32	-9.438 ± 0.066
NaCl	41.04 ± 0.35	0.07804	74.65 ± 0.13	-8.529 ± 0.050
KCl	48.30 ± 0.33	0.11347	81.38 ± 0.30	-7.147 ± 0.050
<b>(b) Cha (<math>\text{CuSO}_4 \cdot 5\text{H}_2\text{O}</math>)-Bon (<math>\text{CuSO}_4 \cdot 3\text{H}_2\text{O}</math>) Equilibria</b>				
MgCl <sub>2</sub> ·6H <sub>2</sub> O [24.06 ± 0.02	0.02997	32.85 ± 0.17	-9.242 ± 0.009	
NaI·2H <sub>2</sub> O [31.47 ± 0.07]	0.04619	36.00 ± 0.42	-8.193 ± 0.017	
NaBr·2H <sub>2</sub> O	51.41 ± 0.08	0.13243	50.69 ± 0.60	-5.402 ± 0.016
KI	68.02 ± 0.09	0.28624	62.16 ± 0.36	-3.453 ± 0.020

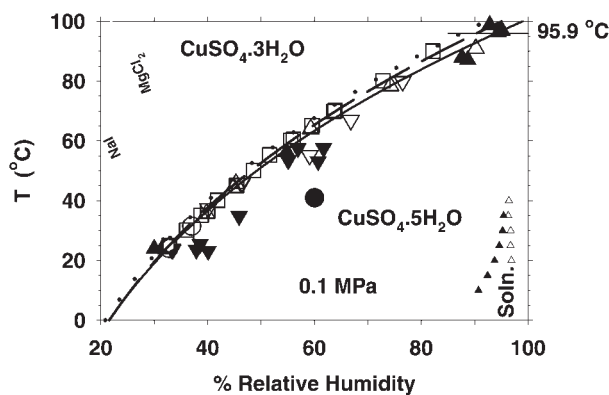
\* Equilibrium  $T$ ; numbers given in parentheses are from Malinin et al. (1979), and those in brackets are from Malinin et al. (1977).

† Calculated from Haar et al. (1984).

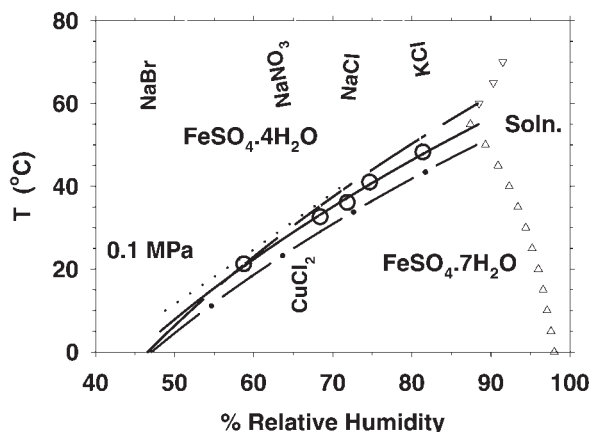
‡ Calculated from Greenspan (1977), except the number in parentheses, which is from Young (1967).



**FIGURE 2.** Comparison of measured %RH values and temperatures for the melanterite-rozenite reaction at 0.1 MPa by the gas-flow-cell method with published results. Data from the present study are shown by large triangles; those pointing up are for heating runs and those pointing down are for cooling, and open and filled triangles are for a vertical and a horizontal sample tube, respectively. The square and diamond at 25 °C represent data from Cohen (1900) and Schumb (1923), respectively. The plus signs between 10 and 25 °C are from Bonnell and Burridge (1934). Note that the data of both Schumb (1923) and Bonnell and Burridge (1934) were reported erroneously for the equilibrium between heptahydrate and hexahydrate. The two circles represent the equilibrium data along the NaBr and CuCl<sub>2</sub> buffer curves obtained by Malinin et al. (1979), and the position of these buffer curves (solid gray lines) are from Greenspan (1977) and Young (1967), respectively. The dashed line above 60 °C is from Pribylov (1969), and the one at lower temperatures is from Hemingway et al. (2002). The dotted, solid, dashed-dot-dot, and dashed-dot lines are from Parkinson and Day (1981), Malinin et al. (1979), Ehlers and Stiles (1965), and DeKock (1982), respectively. The small open triangles are from Reardon and Beckie (1987); those pointing up represent the boundary between melanterite and aqueous solution and those pointing down for the boundary between monohydrate and aqueous solution. According to Bullough et al. (1952), these two boundaries intersect at 56.7 °C, which is very close to the isobaric invariant point at 56.6 °C reported by Linke and Seidell (1958) for the assemblage melanterite-rozenite-aqueous solution. Note that measurements from the present study above 60 °C follow the extension of the boundary between melanterite and aqueous solution. The small filled triangles are measurements of Apelblat (1993) for the boundary between melanterite and aqueous solution; only data between 20 and 30 °C are reliable (see text).



**FIGURE 3.** Comparison of measured %RH values and temperatures for the chalcantite-bonattite reaction at 0.1 MPa by the gas-flow-cell method with published results. Our data are shown by large triangles; those pointing up are for heating runs and those pointing down are for cooling, and open and filled triangles are for a vertical and a horizontal sample tube, respectively. The white hexagon represents the datum of Schumb (1923) at 25 °C and 32.7%RH. The two circles represent the equilibrium data along the NaI and MgCl<sub>2</sub> buffer curves obtained by Malinin et al. (1977), and the position of these buffer curves (solid gray lines) are from Greenspan (1977). The dark solid line represents the boundary between chalcantite and bonattite predicted by Malinin et al. (1977). The dotted and dashed lines were calculated from the data compiled by DeKock (1982) and Wagman et al. (1982), respectively. The dot at 41 °C and 60%RH is from Yang et al. (1994). The thin horizontal line at 95.9 °C shows the temperature of the isobaric invariant point for the assemblage chalcantite-bonattite-aqueous solution reported by Linke and Seidell (1958). The small filled and open triangles are the boundary between chalcantite and aqueous solution measured by Apelblat (1993) and Ishikawa and Murooka (1933), respectively; the data of Apelblat below 20 °C are not reliable (see text).



**FIGURE 4.** Comparison of measured %RH values and temperatures for the melanterite-rozenite reaction at 0.1 MPa by the humidity-buffer method with some published results. Circles represent the data given in Table 1; those along NaBr and CuCl<sub>2</sub> buffer curves are from Malinin et al. (1979), and the rest are from this study. These data can be represented by the solid line (deviations  $\leq 0.95\%$  RH at experimental temperatures) based on the thermodynamic data listed in Table 2. The dotted, dashed, and dash-dot lines are from Parkinson and Day (1981), Malinin et al. (1979), and Hemingway et al. (2002), respectively. All other symbols are the same as in Figure 2.

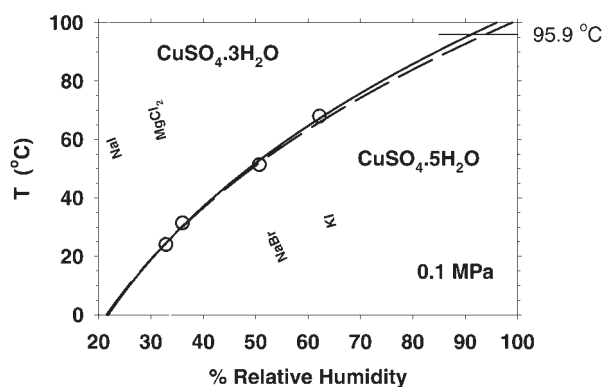


FIGURE 5. Comparison of measured %RH values and temperatures for the chalcantite-bonattite reaction at 0.1 MPa by the humidity-buffer method with those from one published result. Circles represent the data given in Table 1; those along NaI and MgCl<sub>2</sub> buffer curves are from Malinin et al. (1977), and the rest are from this study. These data can be represented by the solid line (deviations  $\leq 1.10\%$  RH at experimental temperatures) based on the thermodynamic data listed in Table 2. This solid line also coincides with the data given by Wagman et al. (1982; see dashed line in Fig. 3). The dashed line is the boundary between chalcantite and bonattite predicted by Malinin et al. (1977). The buffer curves are from Figure 1. The thin horizontal line at 95.9 °C marks the temperature for the presence of an aqueous phase (Linke and Seidell 1958; for details, see Fig. 3).

## DISCUSSION

The changes of temperature and humidity as recorded continuously from the humidity-temperature probe exposed to the NaBr-saturated solution are shown in Figure 6. These results demonstrate the minimum period of time required for the humidity buffer as well as the humidity sensor to reach a stable (or near equilibrium) condition after each temperature change. As the temperature increased from 24.6 to 40.3 °C, the %RH dropped from about 58.5 to near the equilibrium value of 53.1 within 8 hours, and as the temperature dropped from 53.3 to 40.3 °C, the %RH increased from about 50.0 to near 53.1 within 8 hours. The reversal of the humidity as temperature changes from either direction demonstrated that the humidity buffer functioned well. In the present study, the durations of experiment after each temperature change are at least 10 hours, and more than 24 hours in most cases.

As shown in Figure 2, the measured %RH for the melanterite-rozenite assemblage (large triangles) are within a band between those predicted by Malinin et al. (1979; dark solid line) and Hemingway et al. (in press; long dashed line at %RH > 45), except those above 60 °C, where aqueous solution exists. The equilibrium boundaries between melanterite and aqueous solution (small triangles pointing up) and the monohydrate (szomolnokite) and solution (small triangles pointing down) are taken from those predicted by Reardon and Beckie (1987) from solubility data. In the present study, the bend of the %RH-T trend above 60 °C was quite obvious, indicating the presence of the aqueous phase, and the new trend followed that of melanterite-solution boundary at higher temperatures. This observation is consistent with the estimated temperature

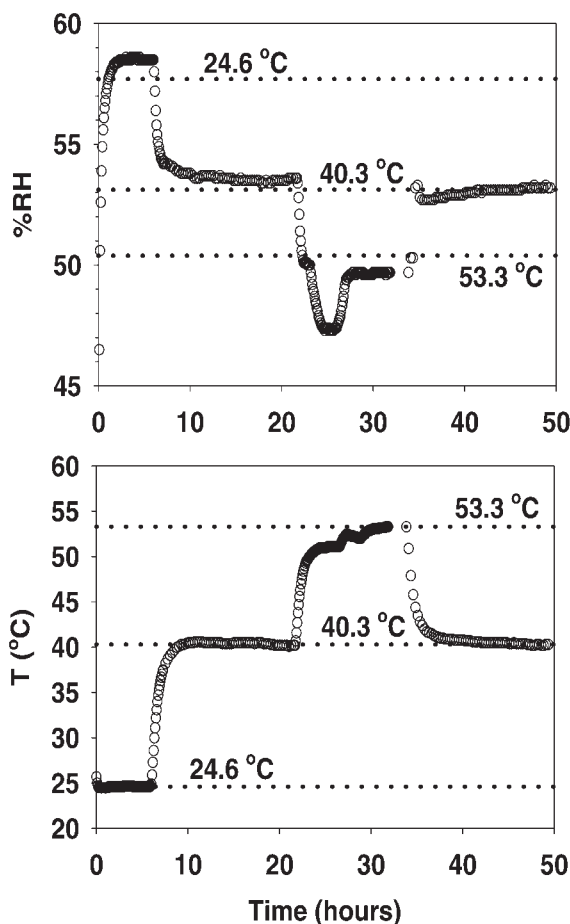


FIGURE 6. Response of humidity to the temperature change as recorded (every five minutes) by the humidity-temperature probe exposed to the vapor phase above an aqueous solution saturated with NaBr. The horizontal dotted lines in the top diagram indicate the equilibrium %RH for the marked temperatures. Note the reversal of %RH at 40.3 °C.

of 56.6 °C reported by Linke and Seidell (1958) based on previous experimental data for the coexistence of melanterite-rozenite and aqueous solution between 56 and 63 °C (Fraenckel 1907; Kobe and Frederickson 1956). At lower temperatures, our data are also in good agreement with those reported by Parkinson and Day (1981; dotted line), Cohen (1900; square at 25 °C), and Schumb (1923; diamond at 25 °C). Insignificant differences were observed in the measured values of %RH between the sample tube in horizontal (filled large triangles) and vertical positions (open large triangles).

The data collected by the gas-flow-cell method were not used for thermodynamic analysis because of large temperature uncertainties in the measurements presented in Figure 2. Instead, results obtained by the humidity-buffer method shown in Figure 4 (open circles) were used. The temperatures in these experiments were well controlled ( $\pm 0.03$  °C) and the reaction reversals were well defined. For example, Figure 7 shows the mass changes of melanterite-rozenite mixture (143 to 225 mg) equilibrated with KCl-saturated buffer at various temperatures for durations between 46 to 50 hours. The equilibrium tem-

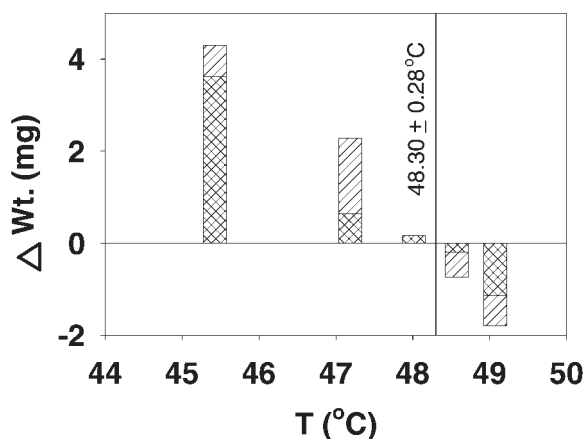


FIGURE 7. Experimental results using the humidity-buffer method, showing weight changes of the melanterite-rozenite mixtures (143 to 225 mg) equilibrated with the KCl buffer at fixed temperatures for 46 to 50 hours. Two samples were run at each temperature and patterns indicate different samples; both of those runs at 48.02 °C had the same weight change. The equilibrium point was bracketed between 48.02 and 48.57 °C. Results are listed in Table 1.

perature for reaction 1 along KCl buffer curve was thus defined at  $48.30 \pm 0.28$  °C, as the reaction was bracketed between 48.02 and 48.57 °C. The data along NaBr and  $\text{CuCl}_2$  buffer curves were taken from Malinin et al. (1979), and those along  $\text{NaNO}_3$ , NaCl, and KCl buffer curves were determined in this study (Table 1 and Fig. 4). Again, the regression line of these data (dark solid line in Fig. 4) is in good agreement with the equilibrium curves predicted by Malinin et al. (1979; dashed line), Parkinson and Day (1981; dotted line), and Hemingway et al. (in press; dashed dot line), and also consistent with the invariant point for the assemblage melanterite-rozenite-aqueous solution suggested by Linke and Seidell (1958) at 56.6 °C.

Results obtained by the gas-flow-cell method for reaction 2, shown as large triangles in Figure 3, are in good agreement with the measured value of Schumb (1923; white hexagon) at 25 °C and those of Malinin et al. (1977) along the NaI and  $\text{MgCl}_2$  buffer curves (circles near room temperature). Results of this study at higher temperatures are also in good agreement with the measured values of Carpenter and Jette (1923; squares), and the predicted values of Malinin et al. (1977; solid dark curve), Wagman et al. (1982; dashed curve), and DeKock (1982; dotted curve). However, the %RH at 41 °C reported by Yang et al. (1994; dot) is too high. Again, the difference observed in the measured %RH values between the sample tubes in horizontal (filled large triangles) and vertical position (open large triangles) was insignificant. Results of this study are consistent with the temperature of 95.9 °C reported by Linke and Seidell (1958; thin horizontal solid line in Fig. 3) for the invariant point of the assemblage chalcantite-bonattite-aqueous solution, based on the experimental data of Agde and Barkholt (1926) and Miles and Menzies (1937), and are also consistent with the measured boundary between chalcantite and aqueous solution at lower temperatures [(Apelblat (1993) and Ishikawa and Murooka (1933) shown respectively as filled and open small triangles in Fig. 3)]. It should be noted that the %RH

values reported by Apelblat (1993) for aqueous solutions saturated with metal sulfate are reliable only at or near 25 °C. Again, because of large temperature uncertainties in our measurements presented in Figure 3, these data were not used for thermodynamic analysis. Results obtained by the humidity-buffer method shown in Figure 5 (open circles) were used for the thermodynamic analysis. The data along NaI and  $\text{MgCl}_2$  buffer curves were taken from Malinin et al. (1979), and those along NaBr and KI buffer curves were determined in the present study (Table 1 and Fig. 5). The regression line (dark solid line) coincides with the data given by Wagman et al. (1982), but deviates slightly from the dashed line predicted by Malinin et al. (1977).

#### THERMODYNAMIC ANALYSIS

Equilibrium constants and  $\Delta G^\circ$  values for reactions 1 and 2 were obtained using Equation 3, and these values were listed in Tables 1 and 2, respectively. Figures 8 and 9 show the rela-

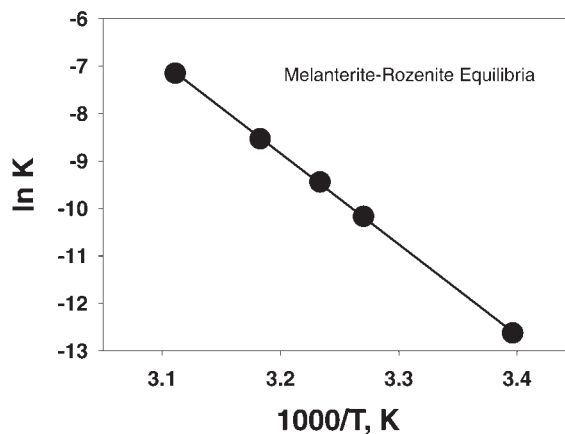


FIGURE 8.  $\ln K$  vs.  $1/T$  plot for the melanterite-rozenite equilibria. Dots show the data from Table 1, and the solid line is a least-squares fit of the data ( $r^2 = 0.9998$ ).

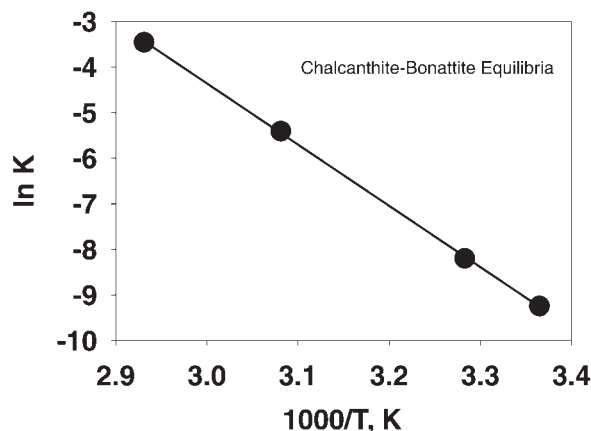


FIGURE 9.  $\ln K$  vs.  $1/T$  plot for the chalcantite-bonattite equilibria. Dots show the data from Table 1, and the solid line is a least-squares fit of the data ( $r^2 = 0.9998$ ).

**TABLE 2.** Derived thermodynamic data (0.1 MPa and 298.15K)

$\Delta G_r^\circ$ (kJ/mol)	$\Delta H_r^\circ$ (kJ/mol)	$\Delta S_r^\circ$ (J/K·mol)	Reference
<b>(a) Mel (FeSO<sub>4</sub>·7H<sub>2</sub>O)-Roz (FeSO<sub>4</sub>·4H<sub>2</sub>O) Equilibria</b>			
29.231 ± 0.050	159.39 ± 0.30	436.6 ± 1.1	This study
29.308	156.02	439.3	Malinin et al. (1979)
28.870	159.97	439.7	Hemingway et al. (2002)
26.080	157.17	439.7	DeKock (1982)
40.124	175.811	445.261	Pribylov (1969)
<b>(b) Cha (CuSO<sub>4</sub>·5H<sub>2</sub>O)-Bon (CuSO<sub>4</sub>·3H<sub>2</sub>O) Equilibria</b>			
22.593 ± 0.040	111.73 ± 0.72	299.0 ± 2.3	This study
22.589 ± 0.205	112.46 ± 3.68	301.5 ± 12.2	Malinin et al. (1977)
22.641	111.70	298.7	Wagman et al. (1982)
22.878	111.79	298.2	DeKock (1982)

tion between  $\ln K$  and  $1/T$  for reactions 1 and 2, respectively, and values of the standard enthalpy of reaction,  $\Delta H_r^\circ$ , were calculated according to the van't Hoff relation:

$$\partial (\ln K) / \partial (1/T) = -\Delta H_r^\circ / R. \quad (4)$$

Values of  $\Delta H_r^\circ$  for reactions 1 and 2 are listed in Table 2. Values of the entropy of reaction,  $\Delta S_r^\circ$ , were calculated from the relation:

$$\Delta G_r^\circ = \Delta H_r^\circ - T \Delta S_r^\circ \quad (5)$$

and are listed in Table 2. These derived thermodynamic data were compared with previously published data in Table 2.

Adopting the value of  $-2507.75 \pm 1.0$  kJ/mol for  $\Delta G_r^\circ$ , which corresponds to the standard Gibbs free energy of formation from elements at 298.15 K and 0.1 MPa, for melanterite suggested by Parker and Khodakovskii (1995), the  $\Delta G_r^\circ$  for rozenite calculated from our  $\Delta G_r^\circ$  datum for reaction 1 at 25 °C is  $-1794.9 \pm 1.3$  kJ/mol. Similarly, adopting the value of  $-1879.75$  kJ/mol for  $\Delta G_r^\circ$  for chalcantite suggested by Wagman et al. (1982), the  $\Delta G_r^\circ$  for bonattite calculated from our datum for reaction 2 at 25 °C is  $-1399.96$  kJ/mol, essentially the same value as suggested by Wagman et al. (1982). However, no uncertainties were assigned by Wagman et al. (1982) to their values.

## SUMMARY

Equilibrium constants for reactions 1 and 2 were determined by measuring the equilibrium humidities using the gas-flow-cell method and the humidity-buffer method at 0.1 MPa and between 21 and 98 °C. The first method measured humidity and temperature of the equilibrium assemblages with a commercially available probe, and the second method measured mass changes of the solid equilibrium assemblages along humidity buffers (Fig. 1) at fixed  $P$ - $T$  conditions. Results obtained by these two methods are similar: the gas-flow-cell method is more efficient but the humidity-buffer method has better temperature control, and therefore only the data obtained by the latter method between 21 and 70 °C were used for thermodynamic analysis.

For reactions 1 and 2, our data at higher temperatures are consistent with those reported by Malinin et al. (1979) and Malinin et al. (1977), respectively, at temperatures below 33 °C, and also consistent with the temperatures (at 0.1 MPa) sug-

gested by Linke and Seidell (1958) for the invariant assemblages melanterite-rozenite-aqueous solution at 56.6 °C and chalcantite-bonattite-aqueous solution at 95.9 °C. Values for  $\Delta G_r^\circ$  and  $\Delta H_r^\circ$  for reactions 1 and 2 were obtained (Table 2) by combining our data with those of Malinin et al. (1977, 1979). 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.

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