Acquisition and evaluation of thermodynamic data for mirabilite-thenardite equilibria at 0.1 MPa

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ABSTRACT

Mirabilite and thenardite are common minerals found in marine evaporite deposits and also in saline lakes as precipitates. In this study, mirabilite-thenardite equilibria were determined along four humidity-buffer curves at 0.1 MPa and between 285.15 K and 305.15 K. Results for the reaction $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}_{(s)} = \text{Na}_2\text{SO}_{4(s)} + 10 \text{H}_2\text{O}_{(g)}$, based on tight reversals along each humidity buffer, can be represented by $\ln K = 174.032 - 62815.11/T$, where s is solid, g is gas, K is the equilibrium constant and T is temperature in K. Our data are in excellent agreement with several previous vapor-pressure measurements and are consistent with the solubility data reported in the literature. Thermodynamic analysis of these data yields $90.858 \text{ kJ} \cdot \text{mol}^{-1}$ for the standard Gibbs free energy of reaction, which is in good agreement with the values of $90.69 \text{ kJ} \cdot \text{mol}^{-1}$ and

90.34 kJ·mol⁻¹ calculated from the thermodynamic data compiled and evaluated previously from two sources.

Key Words: Mirabilite; Thenardite; Humidity buffer; Thermodynamic properties

1. Introduction

Saline lake depositions are the evaporation products under specific geographical and geological environments. They are characterized by multi-stage and long period of salt formation, continuous sedimentation, and cyclicity of salinization-desalinization. In fact, salt sediments occurred not only in the hot and dry circumstances but also in the cold and dry environments. The salt species and assemblages of salt sediments are significantly different under these two different climatic conditions. With the changes of environmental temperature (T) and humidity, phase transitions of some inorganic salts and their hydrates can occur.

Mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and thenardite (Na_2SO_4) are common salts found in marine evaporite deposits. Recently, there are also evidences to support the presences of mirabilite on the surface of Mars and also on the surface of Jupiter's satellite Europa [1]. The rhythmic of mirabilite layer deposition and the composition of sediments are good indicators for the changes in ancient and present climates and environments on Mars and Earth. In order to better define these environmental conditions, information on the stabilities of mirabilite and thenardite in terms of T and relative humidity (RH) is needed. In this study, we reviewed all available data related to the stability of minerals in the

system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ and found that they were not consistent. Therefore, we provided a new set of data, based on our reversal experiments using the humidity buffer technique [2-4].

Figure 1. T -Composition phase diagram of the binary system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ at 0.1 MPa. Stable phase boundaries: —, metastable phase boundaries: E_1 and E_2 are the mirabilite-ice-L and the $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ -ice-L eutectics, respectively. P_1 and P_2 are the peritectics $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}_{(s)} \leftrightarrow \text{Na}_2\text{SO}_{4(s)} + \text{L}$ and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}_{(s)} \leftrightarrow \text{Na}_2\text{SO}_{4(s)} + \text{L}$, respectively. TH = thenardite; MI = mirabilite; L = aqueous solution; s = solid. Also shown are the stability fields for the metastable assemblages (given in parentheses).

2. Dehydration equilibrium

The stability of mirabilite and thenardite can be related by the reaction:

mirabilite thenardite

where (s) and (g) are solid and gas, respectively. Published estimates for the equilibrium relative humidity (*RH*) at 298.15 K under 0.1 MPa pressure range from 78 to 82.5% for this reaction. To evaluate these data, the humidity-buffer technique [2-4] was used in this study to determine equilibrium constants for this reaction between 275.15 K and 305.15 K at 0.1 MPa. Reversals were obtained along four humidity-buffer curves. This technique has been applied to determine the equilibria between melanterite [$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$] and rozenite [$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$] [5], chalcantite [$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$] and bonattite [$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$] [5], epsomite [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$] and hexahydrate [$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$] [6], morenosite ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) and retgersite ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) [7], bieberite [$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$] and moorhouseite [$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$] [8], goslarite [$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$] and bianchite [$\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$] [9], hexahydrate [$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$] and starkeyite ($\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) [10], and kornelite ($\text{Fe}^{+3}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$) and pentahydrated ferric sulfate ($\text{Fe}^{+3}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$) [11]. It should be emphasized that Reaction 1 of this study does not involve an aqueous phase. However, as will be presented later, in the presence of an additional aqueous phase at equilibrium at 0.1 MPa, the system becomes invariant with defined equilibrium temperature and humidity.

The standard Gibbs free energy of reaction, ΔG_r° , for Reaction 1 was then derived from the equilibrium constant, *K*, using the relation:

$$\Delta G_r^\circ = -RT \ln K$$

$$\begin{aligned}
&= -10 RT \ln (a_{\text{H}_2\text{O}}) = -10 RT \ln (f_{\text{H}_2\text{O}}/0.1\text{MPa}) \\
&= -10 RT \ln [(f_{\text{H}_2\text{O}}^*/0.1\text{MPa}) \cdot RH]
\end{aligned} \tag{2}$$

where ΔG° is the standard Gibbs free energy of reaction, K is equilibrium constant, R is the gas constant ($8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), T is absolute temperature in K, $a_{\text{H}_2\text{O}}$ is the activity of H_2O , $f_{\text{H}_2\text{O}}$ is the equilibrium H_2O fugacity (in MPa), $f_{\text{H}_2\text{O}}^*$ is the fugacity of pure H_2O (in MPa) at T , and RH is the relative humidity ($f_{\text{H}_2\text{O}}/f_{\text{H}_2\text{O}}^*$). The standard states for minerals and H_2O are pure solids and H_2O , respectively, at 0.1 MPa and temperature.

3. Previous work

Phase relations in the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ are shown in Fig. 1. They are mainly based on the solubility data of two stable Na_2SO_4 -bearing minerals, mirabilite and thenardite, and one metastable solid phase, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, in water under 0.1 MPa [12,13]. Solubility relations of mirabilite are shown by the solid curve E_1P_1 , where P_1 is an isobaric invariant point, at which mirabilite coexists with thenardite and solution at 305.53 K [14,15]. Thenardite is stable at higher T and its solubility relations are shown by the solid curve above P_1 [14,15]. Similarly, the solubility relations for the metastable $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ solid phase is shown by the dotted curve E_2P_2 , where P_2 is an isobaric invariant point, at which $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ coexists metastably with thenardite and solution at 296.85 K [14,15]. The points E_1 and E_2 shown in Fig. 1 are the eutectic points, where ice and mirabilite coexist with solution at E_1 and ice and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ coexists with solution at E_2 .

The equilibrium water vapor pressures for the dissociation of mirabilite have been determined previously between 273.15 K and 303.15 K; Pitzer and Coulter [16] reported the vapor pressure of 19.19 mm Hg at 298.15 K, Wuite [17] determined the water vapor pressures between 293.15 K and 297.55 K, and Bell [18] proposed the relationship between vapor pressure and temperature. Gans [15] determined the thermodynamic stability of sodium sulfate heptahydrate. Hamilton [19, 20] obtained a diffraction pattern of hydrate crystals in saturated solution at 287.15 K and Raman spectra of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Diesnis [21] and Liu [22] determined the vapor pressures of saturated aqueous solutions of mirabilite at 293.15 K and 298.15 K and those for thenardite at 313.15 K, 318.15 K, and 323.15 K. Coughlin [23] determined high temperature heat contents of three crystalline modifications of anhydrous sodium sulfate. Figure 2 summarizes all previous and current data related to the mirabilite and thenardite equilibria in terms of temperature and relative humidity at 0.1 MPa. Vapor-pressure measurements were made at 0.1 MPa and 298.15 K by Foote and Scholes [24], Wilson [25], Schumb [26], Norton and Johnstone [27], and Wuite [17], between 273.15 K and 298.15 K by Baxter and Lansing [28], between 273.15 K and 293.15 K by Baxter and Cooper [29], between 290.65 K and 298.15 K by Perman and Urry [30], between 283.15 K and 303.15 K by Bell [18], and between 286.15 K and 298.15 K by Hamad [31].

Thermodynamic data for mirabilite and thenardite derived from calorimetric measurements were evaluated and compiled by Wagman et al. [32] and DeKock [33], and the mirabilite and thenardite phase boundaries based on these data are shown in Fig.

2 as dashed and heavy dotted lines, respectively. The location of point A (the star in Fig. 2), a quadruple invariant point (also indicated by P_1 in Fig. 1), is uncertain and other reported positions are shown in Fig. 2 as points A_1 to A_4 . In theory, the phase boundary between $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 in the RH - T space should end at point A.

Figure 2. Experimental results for the mirabilite and thenardite equilibria at 0.1 MPa and phase relations in the binary system

$\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$. Our experimental reversal points along KCl, KBr, NaCl, and KI humidity buffer curves (from Table 3) are shown by the large dots, and the least-squares regression of these data is shown by the solid curve, which intersects the 305.53 K isotherm at point A (the star) with $RH = 87.58$, the isobaric invariant point for the assemblage mirabilite-thenardite-aqueous solution-vapor (point P_1 in Fig. 1; see text for discussion). The mirabilite-thenardite boundaries calculated from [32] and [33] are shown by heavy dotted and dashed lines, respectively. Other experimental data are: [24]: $\circ$, [27]: $\times$, [25]: $\square$, [26]: $+$, [17]: ∇ , [29]: $\blacktriangledown$, [28]: $\blacktriangle$, [18]: $\bullet$, [30]: $\blacklozenge$, [31]: $\diamond$ (thermobarometer) and $\oplus$ (dissociation apparatus), [22]: $\odot$ and thin dotted line, and [21]: $\boxplus$ and thin solid

line. The invariant points A_1 , A_3 are derived from [32] and [33], respectively, and A_2 and A_4 are extrapolated from [21] and [22], respectively. $f_{\text{H}_2\text{O}}$ is the equilibrium H_2O fugacity (in MPa), $f^*_{\text{H}_2\text{O}}$ is the fugacity of pure H_2O (in MPa) at T , and $(10^2 f_{\text{H}_2\text{O}}/f^*_{\text{H}_2\text{O}})$ is relative humidity (%).

4. Experimental method and results

The humidity-buffer technique used in this study was described by Chou et al. [4,11]. Starting materials were either reagent-grade $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ or mixtures of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and its dehydration product, Na_2SO_4 . A weighed amount of the starting material, typically 300 to 700 mg, was loaded into a plastic sample container (8 mm ID x 10 mm OD and 20 mm tall), which was partly immersed in a humidity-buffer solution in a glass container (17.5 mm ID x 20 mm OD and 40 mm tall) sealed with a rubber stopper. The salts used to prepare the four humidity-buffer solutions, each of which is a saturated solution that has well-characterized humidity variations with temperature [4,34], were KI, NaCl, KBr, and KCl (Fig. 2). The materials used in our experiments are listed in Table 1.

Table 1

Property and supplier of materials

Material	Mass fraction purity	Purity analysis method	Supplier
Na_2SO_4	0.998	As stated by the supplier	Acros Organics
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	0.997	Gravimetric method	Present work ^a
KI	≥ 0.99	As stated by the supplier	Sigma-Aldrich
NaCl	0.999	As stated by the supplier	Alfa Aesar
KBr	≥ 0.99	As stated by the supplier	Acros Organics
KCl	0.999	As stated by the supplier	Alfa Aesar
Redistilled water	≥ 0.99	Gravimetric method	Present work ^a

^a Prepared in our laboratory.

The whole assembly was then immersed in a water bath whose temperature was controlled to $\pm 0.03\text{K}$ and was measured by a Pt resistance probe accurate to $\pm 0.02\text{K}$. 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 the fixed temperature. The direction of reaction was determined by the mass change of the sample (precise to $\pm 0.05\text{ mg}$). Both the starting material and experimental products were examined under a microscope and also by using X-ray diffraction and Raman spectroscopy [20], and no unexpected phases were identified. Experimental results are listed in Tables 2 and 3, and are plotted in Fig. 2.

Table 2

Experimental results at 0.1 MPa

Run no.	Mass of initial sample ^a /mg	T^b / K	Duration/h	Mass Change/mg	Run no.	Mass of initial sample ^a /mg	T^b / K	Duration/h	Mass Change/mg
KCl buffer									
1	550.43	299.54	48	1.15	19	548.79	301.60	48	-0.05
2	558.70	299.54	48	1.18	20	556.88	301.60	48	-0.02
3	482.71	299.54	48	1.16	21	551.19	(301.75)	72	-0.28
4	493.89	299.54	48	1.12	22	559.62	(301.75)	72	-0.30
5	549.48	300.54	72	0.95	23	483.57	(301.75)	72	-0.26
6	557.83	300.54	72	0.87	24	494.66	(301.75)	72	-0.11
7	481.86	300.54	72	0.85	25	482.67	303.04	48	-1.18
8	493.15	300.54	72	0.74	26	493.55	303.04	48	-1.21
9	548.35	301.10	48	0.44	27	551.58	302.16	48	-0.39
10	556.57	301.10	48	0.31	28	559.88	302.16	48	-0.26
11	549.54	301.35	48	0.19	29	483.87	302.16	48	-0.3
12	557.83	301.35	48	0.27	30	495.01	302.16	48	-0.35
13	481.74	301.35	48	0.26	31	550.91	302.53	72	-1.13
14	493.06	301.35	48	0.60	32	559.32	302.53	72	-1.15
15	549.58	(301.45)	96	0.04	33	483.31	302.53	72	-1.29
16	557.89	(301.45)	96	0.06	34	494.55	302.53	72	-1.1
17	481.78	(301.45)	96	0.04	35	484.63	304.04	48	-1.96

18	493.19	(301.45)	96	0.13	36	495.47	304.04	48	-1.92
KBr buffer									
1	545.82	285.15	48	6.17	20	537.64	298.20	48	0.20
2	570.97	289.15	48	3.08	21	562.75	298.20	48	0.20
3	539.84	295.72	96	6.38	22	615.69	298.20	48	-0.06
4	571.97	295.72	96	5.13	23	546.22	(298.23)	72	-0.43
5	616.82	295.72	96	4.39	24	577.1	(298.23)	72	-0.16
6	540.14	296.32	48	3.57	25	621.21	(298.23)	72	-0.23
7	564.32	296.32	48	7.97	26	615.69	298.30	96	-0.1
8	617.11	296.32	48	5.25	27	616.01	298.60	48	-0.32
9	613.74	297.11	48	1.16	28	543.71	299.09	72	-1.32
10	539.01	297.34	48	1.13	29	622.36	299.09	72	-2.10
11	563.63	297.34	48	0.69	30	542.39	300.09	72	-2.55
12	616.22	297.34	48	0.89	31	576.14	300.09	72	-4.17
13	537.84	297.60	72	1.17	32	620.26	300.09	72	-3.44
14	562.95	297.60	72	0.68	33	548.81	301.35	48	-4.12
15	615.63	297.60	72	0.59	34	571.05	301.35	48	-2.61
16	615.88	(298.10)	96	0.13	35	557.96	301.36	96	-9.15
17	536.23	298.20	48	1.41	36	576.77	301.36	96	-5.72
18	562.72	298.20	48	0.03	37	544.69	301.45	96	-8.46
19	615.59	298.20	48	0.10	38	568.44	301.45	96	-5.72
NaCl buffer									
1	634.62	285.15	48	2.89	18	617.3	292.14	72	0.02
2	510.39	288.15	96	1.96	19	512.99	292.14	72	0.06
3	641.56	288.15	96	1.97	20	366.4	(292.64)	96	-0.10
4	508.98	289.15	48	0.86	21	618.24	(292.64)	96	-0.42
5	616.01	291.16	72	0.51	22	511.28	(292.64)	96	-0.37
6	511.76	291.16	72	0.39	23	641.95	(292.64)	96	-0.54
7	642.64	291.16	72	0.66	24	367.28	293.15	96	-0.14
8	616.49	291.23	48	0.3	25	617.15	293.15	96	-0.66
9	512.35	291.23	48	0.21	26	617.32	293.16	48	-0.45
10	643.53	291.23	48	0.27	27	513.05	293.16	48	-0.43
11	616.99	291.65	48	0.10	28	644.36	293.16	45	-0.49
12	512.82	291.65	48	0.11	29	616.87	294.12	48	-0.86
13	644.17	291.65	48	0.11	30	512.62	294.12	48	-0.86
14	616.79	(291.75)	96	0.20	31	643.87	294.12	48	-1.23
15	512.56	(291.75)	96	0.26	32	513.3	294.63	96	-2.02
16	643.8	(291.75)	96	0.37	33	644.62	294.63	96	-2.67
17	644.36	292.14	72	0	34	622.83	297.11	48	-2.92
KI buffer									
1	642.33	285.15	48	0.45	21	496.42	287.63	72	-0.26

2	642.78	285.15	48	0.76	22	504.79	287.63	72	-0.13
3	643.54	286.16	96	0.09	23	558.56	287.63	72	-0.25
4	496.65	286.35	48	0.06	24	643.73	287.63	72	-0.33
5	504.76	286.35	48	0.26	25	497.18	287.66	48	-0.22
6	557.36	286.35	48	0.37	26	504.92	287.66	48	-0.08
7	643.68	286.35	48	0.34	27	557.56	287.66	48	-0.14
8	495.91	(286.66)	96	0.10	28	497.52	288.15	96	-0.34
9	503.62	(286.66)	96	0.15	29	505.41	288.15	96	-0.49
10	556.68	(286.66)	96	0.31	30	558.39	288.15	96	-0.83
11	641.72	(286.66)	96	0.25	31	495.95	288.65	96	-0.04
12	643.63	(286.66)	48	0.05	32	504.32	288.65	96	-0.7
13	643.68	286.94	96	0.05	33	557.75	288.65	96	-1.07
14	643.66	287.05	96	-0.04	34	642.89	288.65	96	-1.17
15	496.77	(287.16)	96	-0.10	35	498.26	289.15	48	-0.29
16	504.66	(287.16)	96	-0.03	36	506.39	289.15	48	-0.39
17	557.34	(287.16)	96	-0.10	37	497.97	289.15	48	-0.45
18	496.96	287.36	96	-0.15	38	506	289.15	48	-0.59
19	504.84	287.36	96	-0.08	39	571.89	297.11	48	-6.26
20	557.42	287.36	96	-0.13	40	565.63	297.11	48	-7.24

Expanded uncertainty $U(M) = 0.10$ mg, $U(T) = 0.04$ K and $U(P) = 0.00005$ MPa (0.95 level of confidence).

^a Starting material consisted of a mixture of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and Na_2SO_4 . Buffer solutions are saturated solutions.

^b Values in parentheses were used to bracket the reaction.

Table 3

Equilibrium temperature (T), vapor pressure of pure H_2O ($f_{\text{H}_2\text{O}}^*$), relative humidity (RH) and equilibrium constants (K) of reaction (1) at 0.1 MPa

Humidity buffer	T^a / K	$f_{\text{H}_2\text{O}}^*{}^b / \text{MPa}$	$RH^c / \%$	$\ln K^d$
KI	286.91	0.0015746	71.26	-44.90
NaCl	292.20	0.0022049	75.51	-40.95
KBr	298.17	0.0031730	80.89	-36.63
KCl	301.60	0.0038835	83.85	-34.25

Expanded uncertainty $U(T) = 0.33$ K, $U(P) = 0.00005$ MPa, $U(RH) = 0.05\%$, and $U(\ln K) = 0.21$ (0.95 level of confidence)

^a Mean of the two experimental temperatures shown in parentheses for each buffer listed in Table 2.

^b Calculated from [38].

^c Calculated from [34].

^d The uncertainties were derived from those associated with the listed equilibrium T for each buffer system, assuming no uncertainties

associated with $f_{\text{H}_2\text{O}}^*$.

5. Thermodynamic analysis

Equilibrium constants and ΔG_r° values for reaction (1) were obtained from our experimental data using Eq. (2) and were listed in Tables 3 and 4, respectively. Fig. 3 shows the relation between $\ln K$ and $1/T$ for reaction (1); our reversal data can be represented by $\ln K = 174.032 - 62815.11/T$. The standard enthalpy of reaction, ΔH_r° , was calculated according to the relation:

$$\partial (\ln K) / \partial (1/T) = - \Delta H_r^\circ / R \quad (3)$$

The calculated values of ΔH_r° for reaction (1) were listed in Table 4 together with the entropy of reaction, ΔS_r° , as calculated from the relation:

$$\Delta G_r^\circ = \Delta H_r^\circ - T \Delta S_r^\circ \quad (4)$$

Although the ΔG_r° and ΔH_r° values obtained in this study were precise, the value for ΔS_r° involves large uncertainties because it was calculated from the difference of two large numbers for ΔG_r° and ΔH_r° .

Table 4

Comparison of the derived values of Gibbs free energy (ΔG_r°), enthalpy (ΔH_r°) and entropy (ΔS_r°) of the reaction with literature values for the mirabilite-thenardite equilibrium at 298.15 K and 0.1 MPa

$\Delta G_r^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta H_r^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	$\Delta S_r^\circ / (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	Reference
90.858	522.28	1446.99	this study
90.69	522.18	1447.22	[32]
90.34	521.44	1445.91	[33]
90.63	521.74	1444.74	[31]
91.19	521.95	1444.78	[35]
91.12	521.24	1442.64	[16]
91.16	-	-	[25]

91.19	-	-	[28]
92.22	-	-	[30]

Expanded uncertainty $U(\Delta G_r^\circ) = 0.021 \text{ kJ}\cdot\text{mol}^{-1}$, $U(\Delta H_r^\circ) = 3.37 \text{ kJ}\cdot\text{mol}^{-1}$, and $U(\Delta S_r^\circ) = 11.34 \text{ kJ}\cdot\text{mol}^{-1}$ (0.95 level of confidence)

Data from the present study are in excellent agreement with most of the previous vapor-pressure measurements [16, 25, 28, 30, 31, 35], as shown in Table 4 and Figs. 2 and 3. The results also agree well with the thermodynamic data evaluated and compiled by Wagman et al. [32] and DeKock [33]. Our ΔG_r° value is about 0.17 and 0.52 $\text{kJ}\cdot\text{mol}^{-1}$ higher than the values recommended by Wagman et al. and DeKock, respectively; no estimated uncertainty was given by Wagman et al., and our value is still within the uncertainty of DeKock's estimate, which is more than 1 $\text{kJ}\cdot\text{mol}^{-1}$. Extrapolating our mirabilite and thenardite boundary shown in Fig. 2 to 305.53 K, we predict 87.58 %RH at the invariant point for the assemblage mirabilite-thenardite-aqueous solution-vapor, which is in good agreement with the extrapolated values based on the previous vapor pressure measurements of saturated solutions (within 2 %RH; Fig. 2).

Figure 3. Plot of $\ln K$ vs. $1/T$ for the mirabilite and thenardite equilibria. Our experimental reversal points along KCl, KBr, NaCl, and KI humidity buffer curves (from Table 3) are shown by the large dots, and the least-squares regression of these data is shown by the solid line, which intersects the 305.53 K isotherm at point A (★) with %RH = 87.58, the isobaric invariant point for the assemblage mirabilite-thenardite-aqueous solution-vapor (see text for discussion). Other experimental data are: [32]: ×, [33]: ···, [18]: ---, [28]: ○, [29]: ▲, [30]: ☆, [31]: —· (thermobalance) and —·· (dissociation apparatus), [24]: ◇, [25]: ▽, [26]: +, and [27]: △.

6. Discussion

The results of this study and those of Chou et al. [6-10] further confirm the conclusion of Hemingway et al. [36] that the Gibbs free-energy contribution for each water of crystallization in hydrated sulfate salts, except for the first water, is near $-238.0 \text{ kJ} \cdot \text{mol}^{-1}$. The Gibbs free-energy contribution for each water of crystallization can be calculated

from the experimental results of this study for mirabilite and thenardite equilibrium by the equation:

$$\Delta G_{\text{xw}, 298\text{K}}^{\circ} = - (\Delta G_{\text{r}, 298\text{K}}^{\circ} - n\Delta G_{\text{f}, \text{H}_2\text{O}, 298\text{K}}^{\circ})/n \quad (5)$$

where $\Delta G_{\text{xw}, 298\text{K}}^{\circ}$ is the Gibbs free-energy contribution for each additional water of crystallization at 298.15 K, $\Delta G_{\text{r}, 298\text{K}}^{\circ}$ is the Gibbs free energy of the reaction at 298.15 K, $\Delta G_{\text{f}, \text{H}_2\text{O}, 298\text{K}}^{\circ}$ is the Gibbs free energy of formation from elements for water vapor at 298.15 K, and n is the stoichiometric coefficient for water in the dehydration reaction.

For reaction (1), $\Delta G_{\text{r}, 298\text{K}}^{\circ}$ is $90.858 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta G_{\text{f}, \text{H}_2\text{O}, 298\text{K}}^{\circ}$ is $-228.6 \text{ kJ}\cdot\text{mol}^{-1}$ and n is 10, therefore, according to Eq. (5), we obtained $-237.68 \text{ kJ}\cdot\text{mol}^{-1}$ for $\Delta G_{\text{xw}, 298\text{K}}^{\circ}$. This result and previous data for $\Delta G_{\text{xw}, 298\text{K}}^{\circ}$ are listed in Table 5, having an average value of $-238.47 \text{ kJ}\cdot\text{mol}^{-1}$ with a maximum deviation of $1.43 \text{ kJ}\cdot\text{mol}^{-1}$. The improved understanding of the free-energy contribution of individual water molecules associated with hydration of efflorescent salts will improve the ability to estimate thermodynamic data for phases in the absence of experimental values. However, considering the relatively large uncertainties associated with the simple linear fits method for the derivation of thermodynamic data, as demonstrated here (Table 5) for some cases, this method should be applied with caution.

Mirabilite and thenardite are relatively rich in nature, especially in saline lake areas. These minerals can be found as saline lake depositions reflecting the variations in climate and environment. Generally, stable and metastable mirabilite layers occur in the sub-arid or arid climate zones of the frigid and sub-frigid to mid-warm zones as a typical cold

phase [37]. The results of this study also showed that the increase in humidity and decrease in temperature favor the stability of mirabilite in sediments, as expected.

Table 5

Derived thermodynamic data for the Gibbs free-energy contribution of water at 298.15 K and 0.1 MPa ($\Delta G_{\text{XW},298\text{K}}^{\circ}$)

Equilibrium	$\Delta G_{\text{XW},298\text{K}}^{\circ}/(\text{kJ}\cdot\text{mol}^{-1})$	Difference ^a $/(\text{kJ}\cdot\text{mol}^{-1})$	Reference
mirabilite–thenardite	-237.68	-0.79	this study
melanterite–rozenite	-238.34	-0.13	[5]
chalcantite–bonattite	-239.90	1.43	[5]
morenosite–retgersite	-237.44	-1.03	[7]
epsomite–hexahydrite	-238.73	0.26	[6]
bieberite–moorhouseite	-238.03	-0.44	[8]
goslarite–bianchite	-238.23	-0.24	[9]
hexahydrite–starkeyite	-239.39	0.92	[10]

^a The difference between the listed value and the average value of $-238.47 \text{ kJ}\cdot\text{mol}^{-1}$ for $\Delta G_{\text{XW},298\text{K}}^{\circ}$.

7. Conclusions

To obtain equilibrium constants for hydration and dehydration reactions near ambient temperature and pressure conditions, two experimental methods were tested previously [5]. One is the gas-flow-cell method and the other is the humidity-buffer method. The humidity-buffer method is more accurate and has been widely used to derive thermodynamic properties of salt minerals. In this study, the equilibrium constants for reaction (1) were determined by measuring the equilibrium humidities using the humidity-buffer method at 0.1 MPa and between 285.15 K and 305.15 K. Mass changes of the solid equilibrium assemblage along four humidity buffers were measured at fixed P – T conditions and our reversal experiments define the stability boundary between mirabilite and thenardite in T – RH space at 0.1 MPa. Our results provide a guide to

evaluate vapor pressure measurements reported previously (Table 2 and Fig. 2). Our data, which agree well with the thermodynamic data compiled and evaluated by Wagman et al. [32] and DeKock [33], predict the position of the isobaric invariant point to be at 305.53 K and 87.58 %*RH* at 0.1 MPa for the assemblage mirabilite-thenardite-aqueous solution-vapor.

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