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Heat of solution of polyhalite and its analogues at $T = 298.15$ K

Georgia Wollmann, Jürgen Seidel, Wolfgang Voigt *

Fakultät für Chemie und Physik, TU Bergakademie Freiberg, 09596 Freiberg, Germany

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ABSTRACT

Calorimetric measurements have been performed to determine the heat of dissolution of polyhalite $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ and its analogues $K_2SO_4 \cdot MSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ (M = Mn, Co, Ni, Cu, and Zn) at $T = 298.15$ K. The dissolution experiments were carried out in $NaClO_4$ solution with varying concentrations (0.5 to 2.0) mol kg^{-1}. All polyhalites dissolve exothermically. Exothermicity increases with concentration of $NaClO_4$. An extrapolation to infinite dilution was done using the SIT model.

Within the limits of experimental uncertainty, the enthalpies of dissolution for the triple salts $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$ with M = Mg, Mn, Ni, and Zn coincide. The value for the cobalt salt is noticeably less exothermic. Dissolution enthalpy of leightonite $K_2CuCa_2(SO_4)_4 \cdot 2H_2O$, which does not crystallize in the polyhalite structure, deviates considerably within the series.

1. Introduction

The mineral polyhalite, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, is abundantly distributed in rock salt formations. Its stability field was examined during the past century with some efforts between $T = (298.15$ and $373.15)$ K [1–4]. Only very few crystallization experiments were performed at $T = 298.15$ K [1,5]. At this temperature, the crystallization field of polyhalite is limited to a small composition range in K_2SO_4–$MgSO_4$-solutions. In addition, the crystallization occurs very slowly [2]. By increasing the temperature, crystallization speeds up and the field of crystallization in the solubility diagram grows enormously.

In the context of waste disposal concepts in rock salt formations, it is of interest to know whether the Mg^{2+} ion in polyhalite can be substituted by other bivalent metal ions and thus polyhalite could serve as a natural heavy metal sink.

D'Ans reported the existence of heavy metal substituted polyhalites $A_2SO_4 \cdot MSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ (A = K, NH_4; M = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd) [6]. Their preparation and thorough characterization were published recently by us [7]. The crystallization fields of these substituted polyhalites are unknown.

We intend to investigate and predict the crystallization fields of the substituted polyhalites $K_2SO_4 \cdot MSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ (M = Mn, Co, Ni, Cu, Zn). In order to accelerate equilibration of the (solid + liquid) equilibrium, the solubilities were determined at $T = 313.15$ K [22]. Solubility constants derived from these results shall be extrapolated to the standard temperature 298.15 K. For this extrapolation, the heat of solution will be used as determined in this work.

In the literature, there is only one measurement reported about the detection of the heat effect by decomposing polyhalite $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$ in water [8].

2. Experimental

2.1. Reagents

The triple salts $K_2MCa_2(SO_4)_4 \cdot 2H_2O$ (M = Mg, Mn, Co, Ni, Cu, and Zn) were prepared as described in [6] and afterwards, checked for phase constituents by Raman spectroscopy and thermal analysis. It is our experience that for typical impurities, such as gypsum, Raman spectra are more sensitive than powder X-ray diffraction patterns. Copper sulfate pentahydrate and potassium sulfate, used in the calorimetric measurements, were re-crystallized. The manganese sulfate monohydrate was prepared by dissolving $MnSO_4 \cdot 4H_2O$ in deionised water (Seralpur Pro 90 CN) at $T = 313.15$ K. The supersaturated solution was stirred for three days. Then, the monohydrate crystallizes, which was afterwards filtered from the solution and air dried. The K_2SO_4, $CuSO_4 \cdot 5H_2O$, and $MnSO_4 \cdot H_2O$ were checked by powder X-ray diffraction and the hydrates additionally by thermal analysis.

All salts used in the study ($NaClO_4 \cdot H_2O$ p.a. Fluka, $NaNO_3$ p.a. RdH, K_2SO_4 p.a. Reachim; $CaCl_2 \cdot 2H_2O$ p.a. Fluka, $MgSO_4 \cdot 7H_2O$ p.a. RdH; $MnSO_4 \cdot 4H_2O$ p.a. Merck; $CoSO_4 \cdot 7H_2O$ purr. ABCR; $NiSO_4 \cdot 6H_2O$ p.a. Merck; $CuSO_4 \cdot 5H_2O$ p.a. Fluka; $ZnSO_4 \cdot 7H_2O$ p.a. Fluka) were analyzed by powder X-ray diffraction and thermal analysis. $NaClO_4$ solutions and $NaNO_3$ solutions were prepared by

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* Corresponding author. Tel.: +49 3731 394338; fax: +49 3731 394058.
E-mail address: Wolfgang.Voigt@chemie.tu-freiberg.de (W. Voigt).

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mass. The exact molality of the solutions used was calculated from the mass of the salt and deionised water used for preparation. The sodium perchlorate solutions were analyzed additionally by AAS.

Raman spectra were recorded with a FT-spectrometer RFS 100/S (Bruker). The samples were placed in holders of aluminium and measured from (1200 to 350) cm^{-1} with a 1064 nm laser and a power of 75 mW at 200 accumulation cycles. Thermal analysis was performed with a DTA/TG 22 (Seiko) using (10 to 20) mg of sample in a crucible of platinum at a heating rate of $5\ \text{K} \cdot \text{min}^{-1}$ up to $T = 773$ K under nitrogen flow. The amount of sodium in the $NaClO_4$ solutions was gauged using the atom absorption spectrometer AAS 3 of Carl–Zeiss–Jena at the wavelength 330.3 nm. The solutions were prepared with Cs–La-Buffer by Schinkel and determined with a calibration. The measurements were carried out in an air–acetylene flame with flow rates of $400\ \text{dm}^3 \cdot \text{min}^{-1}$ (air) and $60\ \text{dm}^3 \cdot \text{min}^{-1}$ (acetylene). The error in the resulting molality of the $NaClO_4$ solutions was within ±0.5%.

2.2. Calorimetric experiments

The calorimetric experiments were performed in a Thermal Activity Monitor, TAM II, Thermometric, Sweden equipped with the precision solution calorimeter 2225. The enthalpy values were evaluated using the program Sol-Cal of the TAM software package.

In glass ampoules ($V = 1\ \text{cm}^3$), the salt was weighed in with a microbalance (CC20, $20\ \text{g} \cdot \mu\text{g}^{-1}$, Sartorius). A silicone stopper and beeswax were used to seal the ampoules. The reaction vessel was filled with $100\ \text{cm}^3$ of the appropriate $NaClO_4$ solution or $NaNO_3$ solution, and weighed with an electronic balance (ST 200, 200 g $0.1\ \text{mg}^{-1}$, Ströhlein). The amounts of the polyhalites, potassium sulfate and $NaClO_4$ solution were chosen well below the saturation concentration of $KClO_4$.

All measurements were carried out at $T = 298.15$ K. The reaction vessel containing the ampoule was thermostatted in the calorimeter under a constant stirring speed of 500 rpm. With an electric heater in the reaction vessel, thermal equilibration between the reaction vessel and the thermostat bath was accelerated. After reaching thermal equilibrium, the reaction was started by breaking the ampoule. Since polyhalite and its analogues dissolve slowly main- and after-periods ran for at least 4 h. For K_2SO_4, $CuSO_4 \cdot 5H_2O$, and $MnSO_4 \cdot H_2O$, the duration of the periods were lowered to 90 min. At each $NaClO_4$ concentration at least two measurements were performed. The thermostat stability was 0.1 mK within 24 h and the reaction vessel temperature stability was 0.05 mK within 10 h.

Calibration was performed directly after every dissolution experiment by means of electric heating. The heating power was 100 mW and heating time 50 s.

Before the experiments were carried out, the breaking heat of the ampoule was measured and found to be 0.4% of the total heat effect in the dissolution experiments and was not explicitly considered. The overall accuracy of the calorimeter was verified by measuring the enthalpy of dissolution of ultra pure KCl, which was prepared and characterized as described by Günther *et al.* [9]. The measured molar enthalpy of dissolution was $17.46\ \text{kJ} \cdot \text{mol}^{-1}$. The International Union of Pure and Applied Chemistry (IUPAC) published a recommended reference enthalpy of dissolution of KCl as $(17.584 \pm 0.017)\ \text{kJ} \cdot \text{mol}^{-1}$ [10].

3. Results and discussion

The calorimetric data obtained are listed in tables 1 to 5 and plotted in figures 1 to 3. All polyhalites dissolve exothermally. With increasing $NaClO_4$ concentration, the integral molar heat of dissolution becomes more exothermic for all polyhalites, by about $-15\ \text{kJ} \cdot \text{mol}^{-1}$ within the concentration range from (0.5 to 2.2) mol $NaClO_4 \cdot \text{kg}^{-1}$ H_2O. The slope of the regression lines in the SIT plot (figure 4) is more or less the same for all polyhalites.

In order to find out whether the strong concentration dependence could be caused by hydrolytic or ion association effects of the bivalent metal sulfates, additional calorimetric experiments were conducted with $MnSO_4 \cdot H_2O$ and $CuSO_4 \cdot 5H_2O$. From all ions considered in this study, hydrated cupric ions possess the largest acidity constant [11]. Ion association constants are given in [12,13].

As can be seen in figure 2, the dissolution enthalpies of $CuSO_4 \cdot 5H_2O$ and $MnSO_4 \cdot H_2O$ hardly vary within the concentration range. Therefore, the conclusion can be drawn that the increasing exothermicity is not caused by the bivalent metal sulfates. Determinations of the integral dissolution enthalpies of potassium sulfate in sodium perchlorate solutions, ranging from (0.097 to 0.52) $\text{mol} \cdot \text{kg}^{-1}$, showed the same strong concentration dependence on $NaClO_4$ concentration as the polyhalites (figure 3). To ensure that no precipitation of potassium perchlorate occurs, which might cause this result, the integral dissolution enthalpies of potassium sulfate were determined also in sodium nitrate solutions of (0.47 and 3.3) $\text{mol} \cdot \text{kg}^{-1}$ (table 5). Again, within the concentration range considered, the dissolution enthalpies become more exothermic by about $-14\ \text{kJ} \cdot \text{mol}^{-1}$. Thus, the slope of the dissolution enthalpies of the polyhalites is related with K_2SO_4 as a constituent of polyhalite. However, the type of ion interaction

TABLE 1

Molar heat of dissolution $\Delta_{sol}H$ of Mg- and Mn-polyhalite in aqueous $NaClO_4$ solutions at $T = 298.15$ K.

$\bar{m}^a$/103 g	$\bar{m}_{sol}{}^b$/g	$m_{sol}{}^c/(\text{mol} \cdot \text{kg}^{-1})$	$\Delta_{sol}H/(\text{kJ mol}^{-1})$	$\bar{m}^a/10^3$ g	$\bar{m}_{sol}{}^b$ /g	$m_{sol}{}^c/(\text{mol} \cdot \text{kg}^{-1})$	$\Delta_{sol}H/(\text{kJ} \cdot \text{mol}^{-1})$
		Mg-polyhalite				*Mn-polyhalite*	
98.428	103.372	0.517	–28.21	98.099	103.332	0.491	–27.56
98.614	103.379	0.517	–28.67	99.294	103.360	0.491	–27.95
98.630	103.353	0.517	–28.38	99.312	106.534	0.908	–34.30
100.602	106.204	0.879	–33.32	95.485	106.475	0.908	–34.10
97.876	106.158	0.879	–33.05	98.789	109.710	1.41	–37.83
100.778	109.281	1.30	–38.26	97.284	109.740	1.41	–38.59
94.766	109.528	1.30	–38.14	97.493	109.897	1.41	–38.32
101.853	112.171	1.75	–41.96	99.626	112.354	1.80	–41.85
100.846	112.433	1.75	–42.34	100.094	112.000	1.80	–41.64
101.013	114.268	2.05	–44.49	100.029	112.539	1.80	–42.23
93.745	114.232	2.05	–44.57	98.420	114.966	2.23	–44.72
				100.299	115.031	2.23	–44.54
				100.201	115.014	2.23	–44.88

[a] Mass of polyhalite.

[b] Mass of $NaClO_4$ solution.

[c] Molality of $NaClO_4$ solution.