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Enthalpies of formation and standard entropies for some potassium Tutton salts

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ABSTRACT

Differential scanning calorimetry (DSC) was used to measure the enthalpies of reaction for the dehydration of the potassium Tutton salts, $K_2M(SO_4)_2 \cdot 6\ H_2O$ with M = Mg, Co, Ni, Cu and Zn. The values determined ranged from 335 kJ mol^{-1} for $K_2Mg(SO_4)_2$ 6 H_2O to 355 kJ mol^{-1} for $K_2Ni(SO_4)_2 \cdot$ 6 H_2O with a measured standard deviation of ± 5 kJ mol^{-1}. Although the information needed to obtain precise values for the enthalpies of formation is not available in the literature for all of these salts, values calculated by modeling the amorphous dehydrated compound as an ideal solid solution produced values within 10 kJ mol^{-1} of the values determined for $K_2M(SO_4)_2 \cdot$ 6 H_2O (M= Mg, Cu, and Zn) where the information needed for this calculate was available. DSC was also used to determine the entropies of reaction for the dehydration of these salts. Since there is little information about the entropies of these compounds in the literature, the entropies of reaction were used with the ideal solution model for the amorphous compound to estimate the standard molar entropies for these salts. The values determined ranged from 490 J K^{-1} mol^{-1} for $K_2Cu(SO_4)_2 \cdot 6\ H_2O$ to 540 J K^{-1} mol^{-1} for $K_2Co(SO_4)_2 \cdot 6\ H_2O$. Since these values are based upon estimated values, they have an estimated error of ± 5 percent.

Introduction

Much of the energy produced from the combustion of fossil fuels in industrial burners is lost as waste heat. Recovering and using this waste heat would significantly reduce the yearly world-wide consumption of fossil fuels [1–6]. The possible use of metal salt hydrates to recover waste heat has been investigated for several years [1–6]. The plan is to use the waste heat to drive the endothermic reactions that remove the waters from the metal salt hydrate to form the anhydrous salt in the charging step. The heat is recovered by adding water to the anhydrous salt to reform the hydrate in the exothermic discharging step. The ideal salt should absorb/ release a large amount of heat per gram of compound to minimize the amount of material needed for the device, be easily synthesized from low cost materials, and be stable through many dehydration/ rehydration cycles. Since Tutton salts are easily synthesized, are robust chemically, and contain six waters of hydration, they are being investigated for possible use in waste heat recovery processes [6–10].

Tutton salts are a large family of compounds with the general formula $M^I{}_2M^{II}(XO_4)_2 \cdot 6\ H_2O$ where M^I is a monovalent cation, M^{II} is a divalent cation, and XO_4 is a divalent anion [6–25]. Since they are readily synthesized by the slow evaporation of stoichiometric solutions containing an equal number of moles of the $M^I{}_2XO_4$ and $M^{II}XO_4$ salts, compounds with $M^I = NH_4$, K, Rb, Cs or Tl, M^{II} = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, or V, and $XO_4 = SO_4$, SeO_4, or CrO_4 have been reported [6–25].

Although thermodynamic parameters such as the enthalpy of reaction (Δ_rH), the entropy of reaction (Δ_rS), and the Gibbs energy of reaction (Δ_rG) for adding or removing the waters of hydration would be useful information for designing waste heat recovery systems using these salts, most of this information has not been reported for any of the potassium Tutton salts. For example, the National Bureau of Standards (NBS) reviewed tabulations of thermodynamic data collected by Wagman et al. [26] only contain the enthalpies of formation (Δ_fH) for the potassium Tutton salts of Mg, Cu, and Zn. This compilation contains no entropy values or Gibbs energies for any of the possible potassium Tutton salts.

In principle, enthalpies of formation can be determined using differential scanning calorimetry (DSC) and the DSCs for several Tutton salts have been reported previously [6-10,17]. Voigt and Goring [17] used DSC to measure the melting points and determined the enthalpies of fusion for 27 Tutton salts. Direct observation by Marcus et al. [20] of four of these salts as they were heated in a glass reaction vessel showed no melting at the reported melting points. They did observe bubbling and concluded these transitions were caused by the loss of water from the salts rather than melting. More recently, DSC of $K_2M(SO_4)_2 \cdot 6\ H_2O$ with M = Mg was reported by Dhundapani et al. [7], with M = Mg, Co, and Cu were reported by Souamti et al. [8], with M= Mg, and Ni

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were reported by Marzougui et al. [9] and with M = Zn was reported by Lim and Kim [10]. While each group established the intermediates formed during the dehydration, no enthalpy values were reported in any of these investigations.

Although all of the potassium Tutton salts have similar structures, the decomposition pathways depend on the metal cation and on the experimental conditions used to make the measurements [7-10, 25]. Our previously published investigation of the reaction pathways established that while $K_2Ni(SO_4)_2 \cdot 6\ H_2O$ lost all six complexed waters in one step and $K_2Cu(SO_4)_2 \cdot 6\ H_2O$ lost four waters in the initial step and two in the second step for all of the conditions tested, the other salts investigated produced different apparent intermediates when different cell configuration, different heating rates, and/ or different sample masses were used [25]. Variable temperature powder X-ray diffraction (pXRD) established the dehydration often formed a phase amorphous to X-rays as an intermediate. This amorphous phase (amorph) became a crystalline solid (xstl) when heated to a higher temperature [25].

DSCs were obtained in static air using various heating rates, sample masses, and pan configurations for $K_2M(SO_4)_2 \cdot 6\ H_2O$ with M = Mg, Co, Ni, Cu, and Zn. There were four main goals for this project. The first was to measure Δ_rH for the dehydration of these salts. This information would establish the maximum amount of heat that could be absorbed or released for a fixed amount of compound in a waste heat recovery device. The values calculated from the enthalpies of formation tabulated by Wagman et al [26] for Mg, Cu, and Zn were used as controls to establish the accuracy of this approach. To the best of our knowledge, the values determined for Co and Ni have not been reported previously and were measured for the first time. The second goal was to use these measurements with tabulated literature values to determine Δ_fH for these potassium Tutton salts. The third goal was to use the observed transition temperatures and the enthalpies of hydration to estimate Δ_rS for the dehydration of these compounds. This would provide data that could be used to estimate Δ_rG and establish the temperature range where a waste heat recovery device using these compounds would be effective. The final goal was to determine the standard molar entropies (S) of these compounds. This goal was hindered by the lack of literature values of S available for the Tutton salts. It was discovered that approximating the amorphous dehydrated compound as an ideal solid solution gave Δ_fH values within kJ mol^{-1} of the accepted values for $K_2M(SO_4)_2 \cdot 6\ H_2O$ with M = Mg, Cu and Zn. Using this model enabled us to establish estimates for the standard molar entropies of these potassium Tutton salts. In ideal cases where the intermediates were largely resolved, Δ_fH and S values for $K_2M(SO_4)_2 \cdot n\ H_2O$ with n < 6 were also determined.

Experimental

Each Tutton salt was prepared by the slow evaporation of an aqueous solution prepared by mixing equal volumes of solutions prepared by dissolving 0.01 moles of K_2SO_4 and 0.01 moles of MSO_4 (M = Mg, Co, Ni, Cu, or Zn) in 50 cubic decimeters of deionized water [7–25]. This solution was evaporated to dryness in an open container held at room temperature (~ 295 K) for several days. The larger crystals that formed were removed manually, rinsed with deionized water, dried, ground using an agate mortar and pestle, and stored in capped vials for later use. Infrared spectra (IR) in KBr pellets, powder x-ray diffraction (pXRD), and thermogravimetric analysis (TG) were used to identify the salt. Additional experimental details and the results of these analyses were presented previously [25].

TG was done using a Mettler Toledo TGA/SDTA 851e. Carefully weighed 5 to 10 mg samples of the compound were placed in 70 μL alumina crucibles with (capped) and without (uncapped) the alumina covers that come with the crucibles. Heating rates of 2, 5, and 10 K min^{-1} were used to determine the effect the heating rate had on the apparent decomposition path min^{-1} way. TG were collected under flowing nitrogen and under flowing air (80 mL/min) to determine if there was an interaction with the carrier gas. Buoyancy corrections were made by subtracting the TG obtained for an empty crucible using the same experimental conditions from the TG of the sample. A detailed analysis of the TG data obtained has been published previously [25].

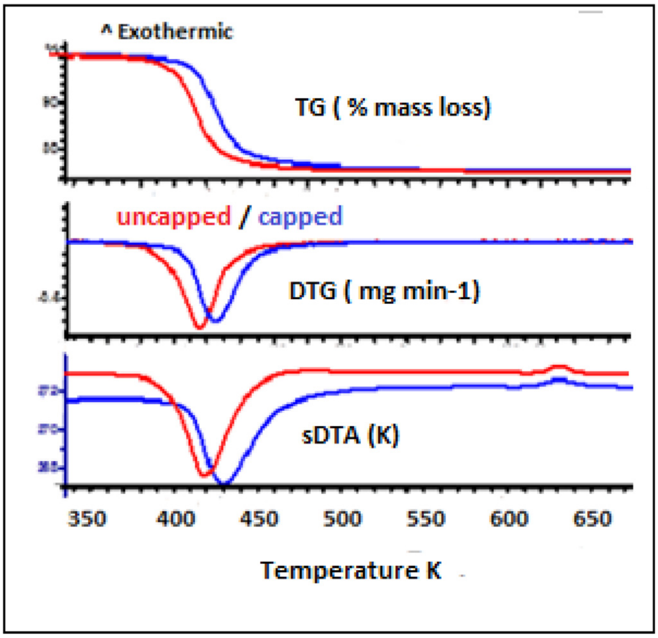

Fig. 1. The TG, DTG, and sDTA observed for $K_2Ni(SO_4)_2 \cdot 6\ H_2O$ for a 5 mg sample in flowing nitrogen for uncapped and capped cells heated at 5 K min^{-1}. The sDTA indicates there are energy change at 630 K where the TG and the DTG show no mass loss.

All DSC were collected by heating samples placed in press sealed Al pans in static air using a Mettler Toledo DSC 822e. Each pan had from one to eight (8) holes punched in the top using the scriber obtained from Mettler Toledo to change the cell configuration to more closely match the capped and uncapped TG cell configurations. Since the scriber has straight sides, each hole was nearly identical and the total area of the opening was directly proportional to the number of holes punched in the cap. Sample sizes ranging from 2 mg to 15 mg and heating rates of 2, 5, and 10 K min^{-1} were used to match the sample sizes and heating rates used in the TG investigations. The instrument was calibrated using high purity In, Sn, Pb, and Zn. The samples were base line corrected and analyzed using the Star software that comes with the instrument. Since the experiments using extra holes had unidentified potential systematic errors in the measurements, only the standard one-hole experiments were used to determine the measurements reported here. The reliability of these measurements was determined by comparing the results to the literature values reported for the Mg, Cu and Zn salts [26] and for the first-row transition metal oxalates reported previously [27].

Results and discussion

Consistent with previous observations, [9,12,25] the six waters of hydration of $K_2Ni(SO_4)_2 \cdot 6\ H_2O$ were lost in one endothermic transition for every set of experimental conditions tested as shown in Figs. 1 and 2. The only effects of perforating the cap were to move the apparent transition to lower temperatures and the small initial endothermic transition at 380 K became more prominent in the perforated pans. Since this is less than one percent of the total area of the curve, this initial transition may be from the loss of physisorped water or from a slight impurity rather than loss of water from $K_2Ni(SO_4)_2 \cdot 6\ H_2O$. The exothermic transition at 630 K was assigned to the amorphous - crystalline transition in dehydrated $K_2Ni(SO_4)_2$ previously since there is no corresponding mass loss in the TG as shown in Fig. 1 and the pXRD in this temperature region was consistent with this assignment [25].

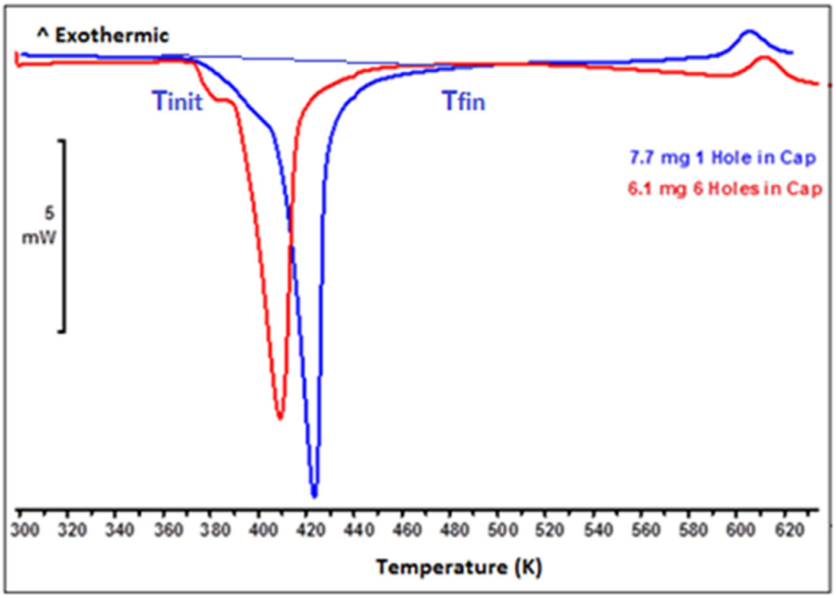

Fig. 2. The DSC observed for $K_2Ni(SO_4)_2 \cdot 6\ H_2O$ in a normal (1 hole) and a ventilated (6 holes) aluminum cell. Both were heated at 2 K min^{-1} in static air. The baseline correction and the integration limits used to obtain Δ_rH from the one-hole measurement is shown in the figure.

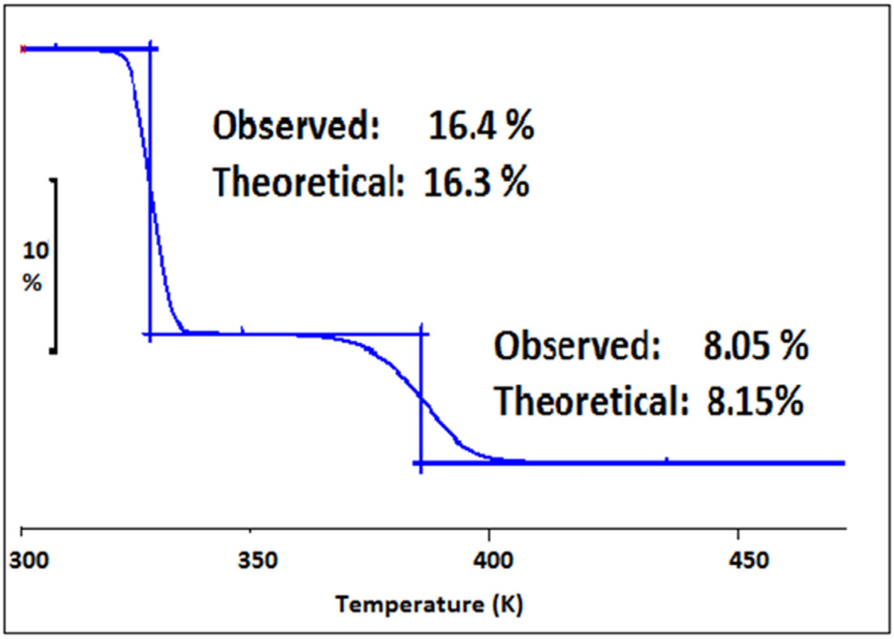

Fig. 3. The TG observed for $K_2Cu(SO_4)_2 \cdot 6\ H_2O$ for a 5 mg sample heated at 10 K min^{-1}. The observed mass losses are compared to the theoretical mass loss for 4 and 2 waters respectively in the figure.

As shown in Figs. 3 and 4, two clearly resolved endothermic transitions were observed for $K_2Cu(SO_4)_2 \cdot 6\ H_2O$ for all of the conditions tested. The first transition at temperatures less than 370 K is from the loss of four waters while the remaining two waters are lost in the second step near 400 K as shown in Fig. 3. Perforating the cell changes the apparent temperature ranges but does not change the number of intermediates observed as discussed in detail previously [25].

The TG for $K_2Zn(SO_4)_2 \cdot 6\ H_2O$ reported by Lim and Lin indicated the six waters were lost in one step while the DSC they presented indicated the waters were lost in two steps [10]. As shown in Figs. 5 and 6, similar results are found here. The TG for a 5 mg sample in an uncapped cell indicates all six waters are lost in one step (see Fig. 5). However, the patterns observed for the DSC for 10 mg samples one-hole pans change as the heating rate is increased. Most of the energy change occurs during the transition near 380 K with a small shoulder at 390 K containing less than 2% of the total area when the sample is heated at 2 K min^{-1}. The shoulder moves to a higher temperature and gets larger when the sample is heated at 5 K min^{-1}. Heating at 10 K min^{-1} produces a pattern similar to the DSC reported by Lim and Lin.

Several decomposition pathways have been reported for $K_2Mg(SO_4)_2 \cdot 6\ H_2O$ [7,8,17, 25].. The DSC reported by Voigt and Goring [17] and the TG-DTA determined by Dhandapani et al. [7] indicated the water was lost in one step. However, the DSC reported by Dhandapani et al. [7] indicated three well resolved transitions while four water loss transitions were reported by Souamti et al [8]. As shown in Figs. 7, the mass loss for 5 mg sample in uncapped cell occurs in one step while four partially resolved intermediates can be identified for a 10 mg sample in a capped cell. In both cases, the total mass loss is consistent with the loss of the six waters of hydration. The most reasonable explanation for this is that increased water vapor pressure in the cell caused by placing a cap on the cell stabilized the intermediates [25].

The DSC observed for $K_2Mg(SO_4)_2 \cdot 6\ H_2O$ changes as the sample size is changed as shown in Fig. 8 for different sample sizes heated in static

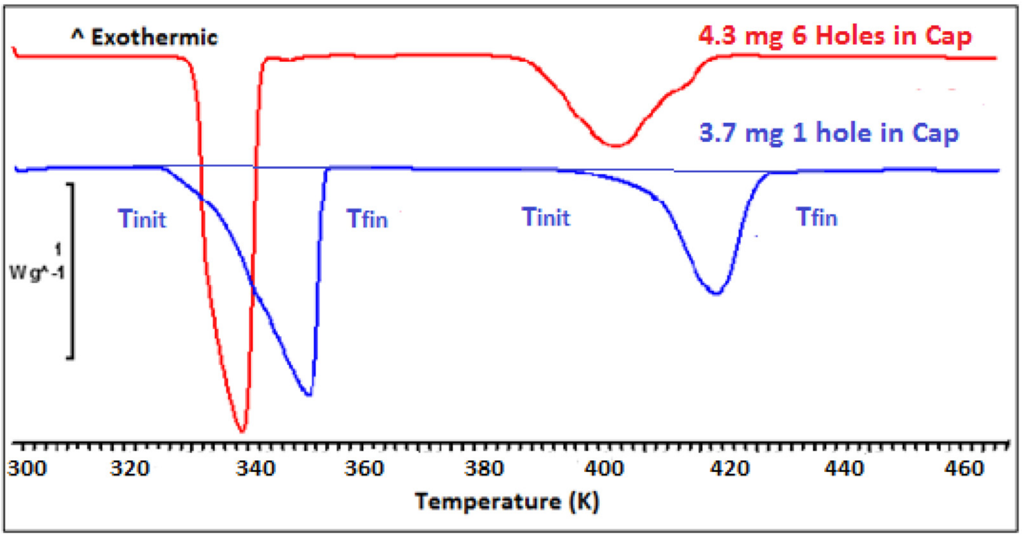

Fig. 4. The DSC observed for $K_2Cu(SO_4)_2 \cdot 6\ H_2O$ in a normal (one-hole) and a ventilated (6 holes) aluminum cell. Both samples were heated at 2 K min^{-1} in static air. The sample sizes are given in the figure. The baseline correction and the integration limits used to obtain Δ_rH for the one-hole measurements are shown in the figure.

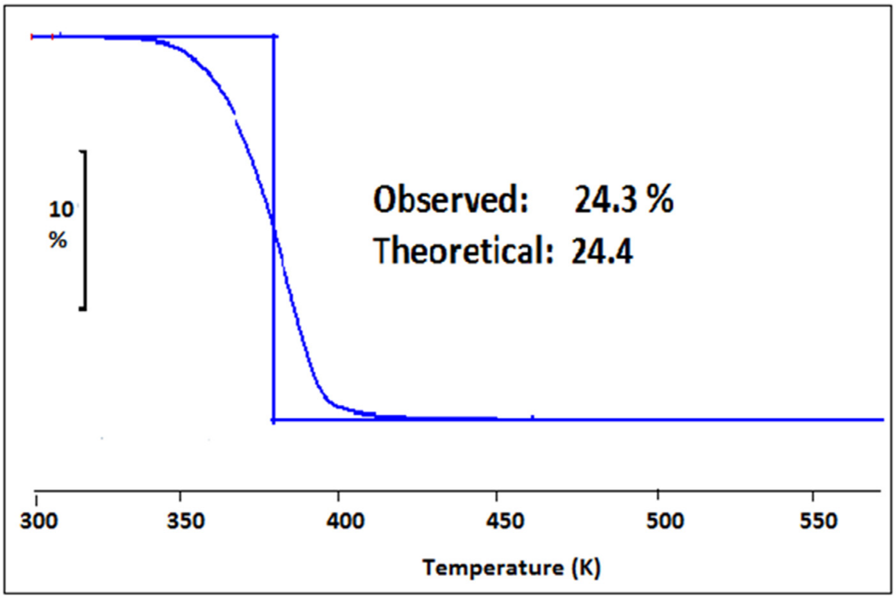

Fig. 5. The TG observed for $K_2Zn(SO_4)_2 \cdot 6\ H_2O$ for a 5 mg sample heated at 10 K min^{-1} in an uncapped cell. The observed mass loss is compared to the theoretical mass loss for 6 waters in the figure.

air in a one-holed pan at 2 K min^{-1}. While most of the energy change occurs in one transition for a 1 mg sample, three partially resolved transitions are observed for a 5 mg sample and three clearly resolved reaction steps are observed for the 11 mg sample. A possible explanation for this are that the transport of the water vapor is hindered as the sample gets larger as it reacts with the larger surface area of the sample. This stabilizes the intermediate enough that it can now be observed.

As illustrated in Figs. 9 and 10, the TG and DSC observed for $K_2Co(SO_4)_2 \cdot 6\ H_2O$ also depend on the experimental conditions. As shown in Fig. 9, all six waters are lost in one step for 5 mg samples in an uncapped cell while the waters are lost in three largely resolved approximately equal steps for 5 mg samples in a capped cell. The effect of increasing the sample size on the DSC is given in Fig. 10. For 2 mg samples, the DSC indicates that most of the water is lost in two transitions in an approximate 2 to 1 ratio. The low energy transition splits into two nearly resolved transitions for 5 mg samples and into three unresolved transitions for 11 mg samples. The exact identity of the intermediates in this region could not be established. Souamti et al. [8] reported the loss of three waters by 375 K and a total of four waters by 389 K and some of the observed patterns are consistent with this conclusion. When the

Table 1
Enthalpies of reaction determined for $K_2M(SO_4)_2 \cdot 6\ H_2O$ are compared to those calculated from the data tabulated by Wagman et al. [26] and the DSC reported by Voigt and Goring (VG) [17]. All values are in kJ mol^{-1}. The experimental uncertainty in the measured values for this work is ± 5 kJ mol^{-1}

Metal (M)	This Work	Wagman	VG	VG(corrected)[a]
Mg	335	334	20	286
Co	350	—	64	328
Ni	355	—	56	322
Cu	345	349	58	322
Zn	350	349	85	349

[a] Corrections made by adding 6 times the enthalpy of vaporization for water

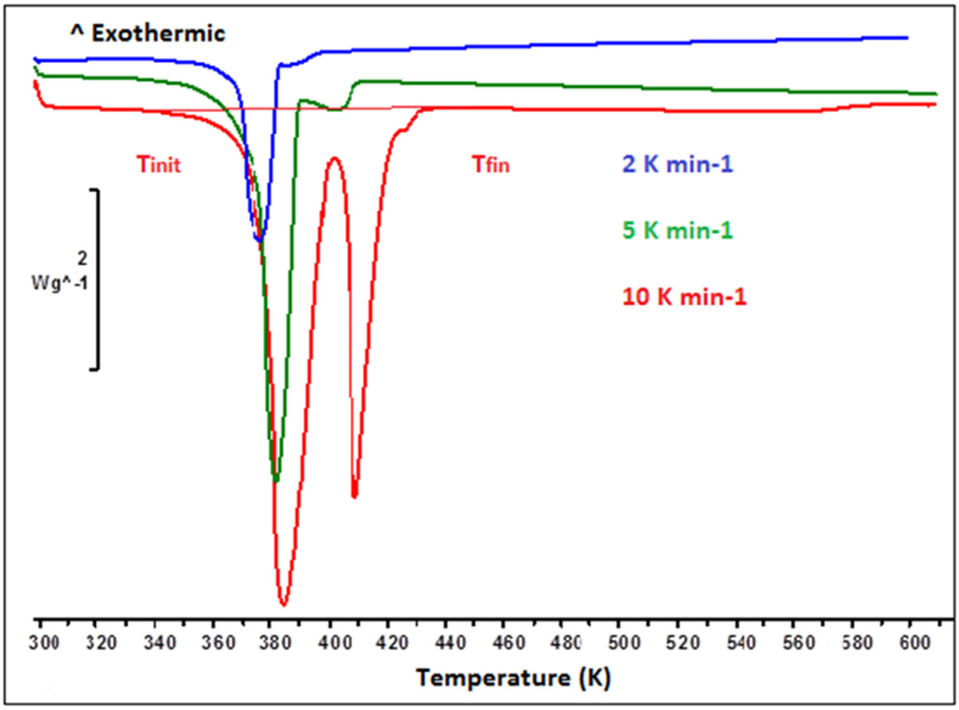

Fig. 6. The DSC observed for $K_2Zn(SO_4)_2 \cdot 6\ H_2O$ in static air one-hole aluminum pan as the heating rate was increased. The sample size was 10 mg. The baseline correction and the integration limits used to obtain Δ_rH for the 10 K min^{-1} measurements are shown in the figure.

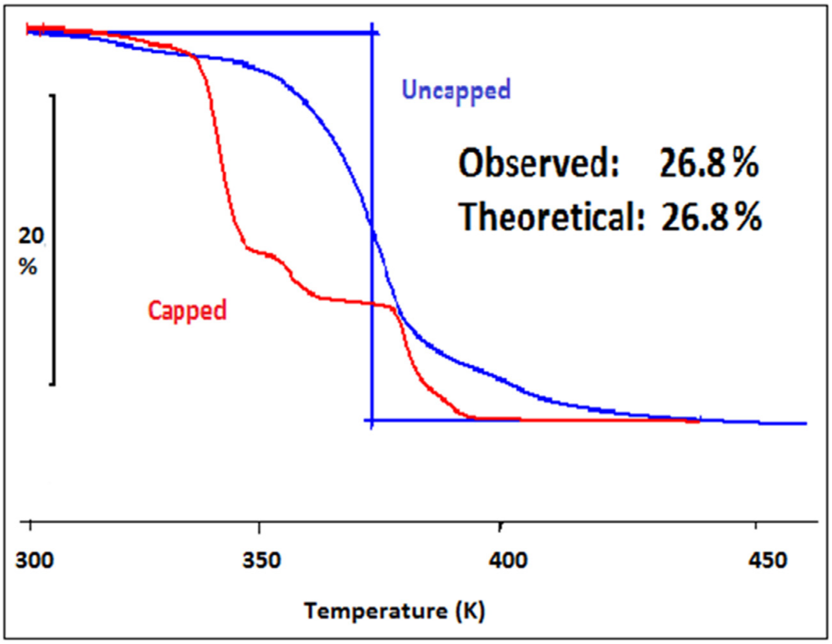

Fig. 7. The TA observed for a 10 mg sample of $K_2(Mg(SO_4)_2 \cdot 6\ H_2O$ in a capped cell and for a 5 mg sample in an uncapped cell. The heating rate was 10 K min^{-1}. The theoretical mass loss is for the loss. of 6 waters.

patterns are mostly resolved for the 5 mg sample, the observed energy changes suggest that two waters are lost in each step consistent with the capped TG results.

Although multiple dehydration pathways have been identified, Hess' Law states that the total energy change for the loss of the six waters is independent of the pathway and the enthalpy of reaction for reaction (1) should be the same for all pathways and can be determined by summing the reaction enthalpies for each step of the multiple step process.

$$K_2M\left(SO_4\right)_2^{\cdot}6H_2O = K_2M\left(SO_4\right)_2(s) + 6H_2O(g) \tag{1}$$

This is equivalent to treating the unresolved transitions as a single transition to determine the enthalpy of reaction. The values determined for Δ_rH of reaction (1) given in Table 1 were determined using this approach following the procedure described in detail previously [27]. Briefly, after applying the linear base line correction indicated in the figures, the DSC software was used to determine the enthalpy change for the transition for temperature ranges shown in the figures. If the intermediates were well resolved, Δ_rH could be determined for each transition as illustrated in Fig. 4. When the intermediates were not resolved, Δ_rH for the total water loss was determined by measuring the total energy release for all process as illustrated in Fig. 6 for the 10 K min^{-1} sample of $K_2Zn(SO_4)_2 \cdot 6\ H_2O$. Since it is not certain if the cells with multiple holes would give correct enthalpies of reaction, only the one-hole experiments were used to collect the data presented in Table 1. The values reported have a measured standard deviation of approximately ± 5 kJ mol-1. Although attributed to melting rather than dehydration, the

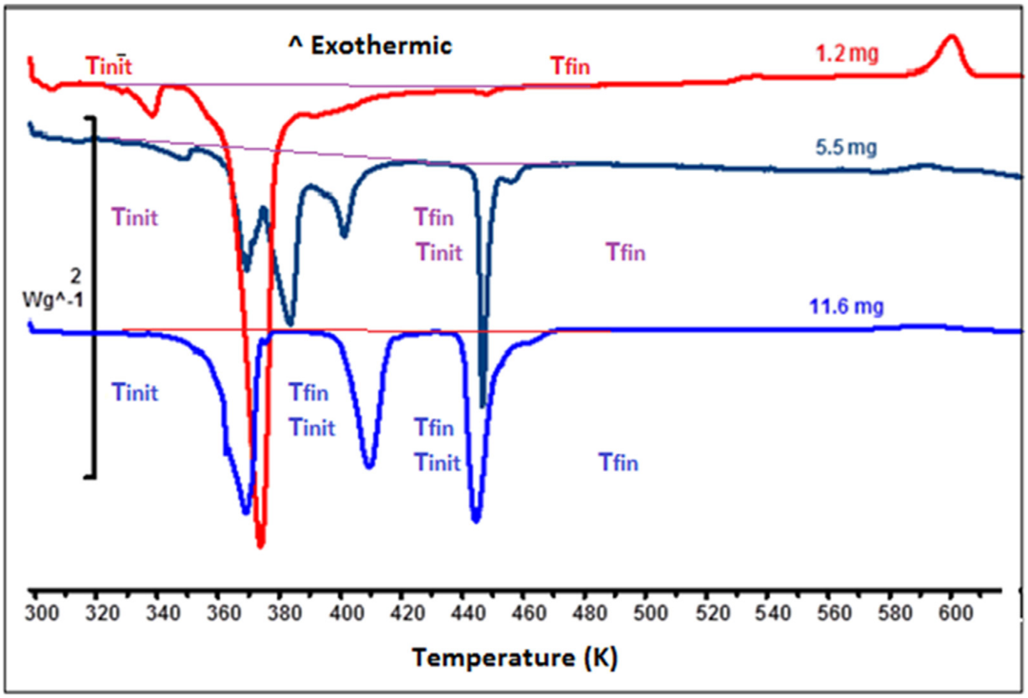

Fig. 8. The DSC observed for $K_2(Mg(SO_4)_2 \cdot 6\ H_2O$ for the sample sizes given in the figure. The heating rate was 2 K min^{-1}. The baseline correction and the integration limits used to obtain ΔrH for these measurements are shown in the figure.

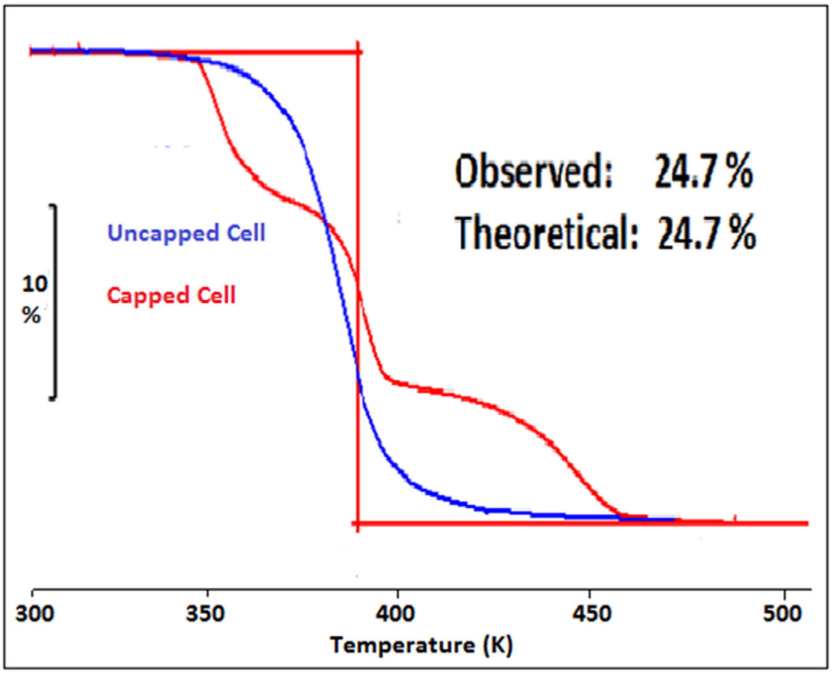

Fig. 9. The TG observed for 5 mg samples of $K_2Co(SO_4)_2 \cdot 6\ H_2O$ at 10 K min^{-1} in a capped and in an uncapped cell. The theoretical mass loss is for the loss of 6 waters.

enthalpies reported by Voigt and Gorman [17] are also given in Table 1. These values are significantly smaller than the values found in this work. Since they used sealed cells, it was assumed that no water evaporated and the final product was a saturated solution rather than the dehydrated salt. Adding the enthalpy of vaporization for six moles of water to account for the energy needed to evaporate the water from this solution produced values in better agreement with the values determined here as shown in Table 1. The remaining differences can be rationalized from errors introduced by not considering the enthalpy changes related to the solution. As shown in Table 1, the values obtained agree to within experimental error for the values calculated from the data tabulated by Wagman et al. [26] for the Cu, Mg, and Zn salts where sufficient data has been tabulated to calculate the expected values strongly supporting the reliability of this approach.

Ideally, the enthalpies of reaction measured for Reaction 1 can be used to determine $\Delta_f H(K_2M(SO_4)_2 6H_2O)$ from equation (2) if $\Delta_f H(K_2M(SO_4)_2)$ and $\Delta_f H(H_2O)$ are known.

$$\Delta_f H\left(K_2M\left(SO_4\right)_2 6H_2O\right) = \Delta_f H\left(K_2M\left(SO_4\right)_2\right) + 6\Delta_f H\left(H_2O\right) - \Delta_r H$$

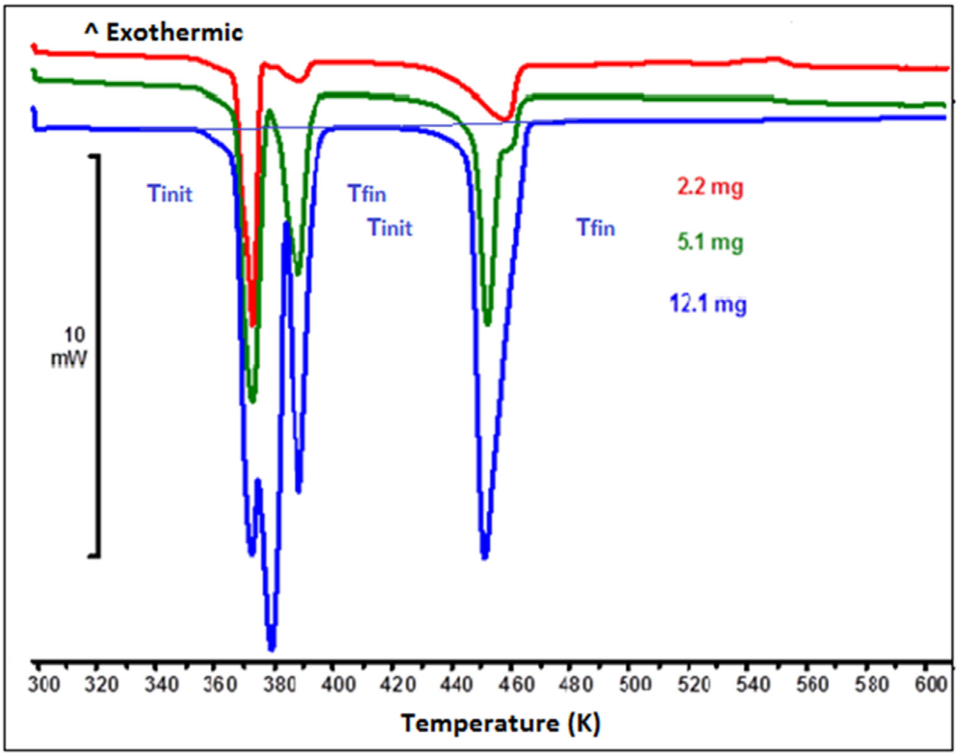

Fig. 10. The DSC observed for increasing sample masses of $K_2Co(SO_4)_2 \cdot 6\,H_2O$ in one-hole aluminum pans. The DSC was taken in static air using a heating rate of 2 K min^{-1}. The baseline correction and the integration limits used to obtain $\Delta_f H$ for the 12.1 mg measurement is shown in the figure. The smaller samples used the same limits.

Table 2
Values determined for the enthalpy of formation ($\Delta_f H$) based on the averages of the measured DSC values obtained using measurements in static air with several different heating rates compared to the values tabulated by Wagman et al. [26] Xstl refers to the solid compound with a definite pXRD diffraction pattern while amorph refers to a phase that was amorphous to X-rays. All values are in kJ mol^{-1}. The experimental uncertainty in the measured values is ± 5 kJ mol^{-1} and ± 10 kJ mol^{-1} for the values using estimated value for $\Delta_f H[K_2M(SO_4)_2$ (amorph)].

Compound	$\Delta_f H$[a]	$\Delta_f H$[b]	Wagman
$K_2Mg(SO_4)_2 \cdot 6\,H_2O$	-4541	-4537	-4540
$K_2Mg(SO_4)_2 \cdot 4\,H_2O$	-3948	-3925	-3922
$K_2Mg(SO_4)_2 \cdot 2\,H_2O$	-3351	-3348	-3344
$K_2Mg(SO_4)_2$ (xstl)	-2755c	-2751	-2755
$K_2Mg(SO_4)_2$ (amorph)	-2726	-2723[c,d]	-2722.6[d]
$K_2Cu(SO_4)_2 \cdot 6\,H_2O$	-4019	-4016	-4024
$K_2cu(SO_4)_2 \cdot 2\,H_2O)$	-2827[c]	-2830	-2827
$K_2Cu(SO_4)_2$ (xstl)	-2224	-2220	-2224
$K_2Cu(SO_4)_2$ (amorph)	-2213	-2209[c,d]	-2209.3[d]
$K_2Zn(SO_4)_2 \cdot 6\,H_2O$	-4233	-4243	-4235
$K_2Zn(SO_4)_2 \cdot 2\,H_2O$	-3038	-3025	-3034
$K_2Zn(SO_4)_2$ (xstl)	-2434[c]	-2444	-2434
$K_2Zn(SO_4)_2$ (amorph)	-2411	-2420[c,d]	-2420.5[d]

[a] Calculated using literature value for $\Delta_f H\,[K_2M(SO_4)_2$ (xstl)]
[b] Calculated using estimated value for $\Delta_f H\,[K_2M(SO_4)_2$ (amorph)]
[c] Assumed value
[d] Estimated from $\Delta_f H\,(K_2SO_4) + \Delta_f H\,(MSO_4)$

Table 3
Enthalpies of formation determined for $K_2M(SO_4)_2 \cdot n\,H_2O$ (M = Co, Ni) based on the assumption that $\Delta_f H[K_2M(SO_4)_2$(amorph)] = $\Delta_f H\,(K_2SO_4) + \Delta_f H\,(MSO_4)$. All values are in kJ mol^{-1} and have an estimated uncertainty of ± 10 kJ mol^{-1} from the uncertainty in the value of $\Delta_f H[K_2M(SO_4)_2$ (amorph)].

n	0(amorph)	0 (xst)	2	4	6
Co	-2326[a]	-2347	-2968	-3567	-4147
Ni	-2310[a]	-2330	—	—	-4138

[a] Assumed

Table 4
Entropies determined for $K_2M(SO_4)_2 \cdot 6\ H_2O$ based on the assumption that $S[K_2M(SO_4)_2(amorph)] = S(K_2SO_4) + S(MSO_4) + R\ln(2)$. All values are in J K-1 mol-1 and have an estimated uncertainty of ± 5 per cent.

n	0(amorph)	0 (xst)	2	4	6
Mg	292[a]	266	351	436	519
Co	299[a]	261	333	414	534
Ni	273[a]	241	—	—	525
Cu	290[a]	264	361	—	487
Zn	292[a]	265	350	—	508

[a] Assumed

(2)

Since values for $\Delta_f H(K_2M(SO_4)_2)$ and $\Delta_f H(K_2M(SO_4)_2^{\cdot}6H_2O)(M = Mg, Cu, \text{and} Zn)$ are tabulated by Wagman et al, [26] these compounds were used as controls to determine the accuracy of this approach. As shown in Table 2, the values determined for the hexahydrates agree to within ± 2 kJ mol-1 for these values. In the cases where the intermediates are resolved, the measured $\Delta_r H$ for these transitions can also be used with the appropriate balanced chemical equation and literature values to determine the enthalpies of formation for these compounds. Even when the transitions were not completely resolved, the average value determined for $\Delta_r H$ by averaging the value measured for the reaction for the loss of water from the starting material to form the intermediate and the loss of water from the intermediate to form the next stable phase provides values within 20 kJ mol-1 for systems with poorer resolved intermediates as shown in Table 2. The uncertainties in the values formed using this procedure are obviously larger than for the well-resolved transitions, but it does provide reasonable estimates that could be used in heat recovery calculations.

Neither $\Delta_f H(K_2M(SO_4)_2)$ nor $\Delta_f H(K_2M(SO_4)_2^{\cdot}6H_2O)$ are reported by Wagman et al [26] for M = Co and Ni. As shown in Figs. 2, 8, and 10, an exothermic transition is observed in the DSC that does not correspond to a mass loss transition (see Fig. 1). Variable temperature pXRD established the transition was from an amorphous phase (to X-rays) to crystalline (xstl) $K_2M(SO_4)_2$ [25]. This exothermic transition is assumed to be reaction (3) and$\Delta_r H$ for this transition is given by equation (4).

$$K_2M(SO_4)_2(\text{amorph}) = K_2M(SO_4)_2(\text{xstl}) \tag{3}$$

$$\Delta_r H = \Delta_f H(K_2M(SO_4)_2(\text{xstl})) - \Delta_f H(K_2M(SO_4)_2(\text{amorph})) \tag{4}$$

While thermodynamic values are not tabulated for the amorphous phases, it was hypothesized that $\Delta_f H(K_2M(SO_4)_2$ (amorph) could be estimated by assuming it was an ideal solid solution (i.e. $\Delta_{mix} H = 0$) of the component salts and Using equation 5. $\Delta_f H(K_2M(SO_4)_2$ (xstl) could be then determined using this value and the measured$\Delta_r H$ for this transition from equation (4).

$$\Delta_f H(K_2M(SO_4)_2(\text{amorph})) = \Delta_f H(K_2SO_4(s)) + \Delta_f H(M(SO_4(s)) \tag{5}$$

This assumption was tested for M = Mg, Cu, and Zn and the results obtained for the hexahydrates and the dehydrated crystalline salts from $\Delta_f H$ of the amorphous salts determined using this approximation are compared to the values from Wagman et al. [26] in Table 2. While ignoring the enthalpy of mixing introduces errors, the estimates obtained using this approximation were often within 10 kJ mol-1 of the measured values. The values obtained for M = Co and Ni using this approximation are given in Table 3. The uncertainties in these values are expected to be similar to the differences between the measured values and the values made using this approximation shown in Table 2.

It is possible to measure the entropies of reaction for these compounds from the DSC data in principle since at equilibrium ($\Delta_r G = 0$),

$$\Delta_r S = \Delta_r H / T \tag{6}$$

For multistep processes, this equation could be applied by using the enthalpy values and the equilibrium temperature for each step in the process and summing these values to find the total entropy change. The main experimental uncertainty when using this approach is establishing the equilibrium temperature. While the peak temperature provides a reasonable estimate, the sample size, number of holes in the pan, and the heating rate change the apparent peak temperatures as shown in the figures. The advantage of this method is that it provides an easy way to estimate the values for $\Delta_r S$, but it is likely to be in error by a few percent.

A second approach for determining $\Delta_r S$ is to numerically integrate the curve formed by dividing the enthalpy by the temperature for points during the transition over the temperature ranges selected for the transition. This has the advantage of not requiring the equilibrium temperature to be established and allowing the total entropy change for non-resolved, overlapping reactions to be measured as one transition. The experimental uncertainty is expected to be smaller using this approach and it was used to determine the values reported here.

Establishing the standard molar entropy for these salts [$S(K_2M(SO_4)_2 \cdot n\ H_2O)$ (n = 2, 4, or 6)] is hindered by the lack of reliable standard molar entropy values for $K_2M(SO_4)_2$ ($S(K_2M(SO_4)_2)$ needed to calculate them for the measured $\Delta_r S$ using equation 7.

$$S(K_2M(SO_4)_2^{\cdot}nH_2O) = S(K_2M(SO_4)_2) + nS(H_2O) - \Delta_r S \tag{7}$$

Since it provided good estimates for $\Delta_f H(K_2M(SO_4)_2$ (amorph)), the ideal solution model was used to estimate $S(K_2M(SO_4)_2$ (amorph) by assuming it was equal to the sum of the component entropies plus $\Delta_{mix} S = R \ln 0.5$. Using this value and determining $\Delta_r S$ for the amorph – xstl transition from the DSC data using equation 6, $S(K_2M(SO_4)_2$ (xstl) could then be determined. Finally, $S(K_2M(SO_4)_2$. n H_2O) could be calculated using equation 7. The values determined are given in Table 4. While these values are reasonable, they may have an error of 5% or more largely from the uncertainty in the value of $S(K_2M(SO_4)_2$ (xstl).

Conclusions

Previous investigation into the dehydrations of some of the potassium Tutton salts reported different intermediates were formed during the dehydration [6–9]. Nearly all of these apparently contradictory conclusions [6–9] were reproduced by changing the cell configuration, the sample mass, and/or the heating rates used to make the measurements indicating that while all of the previously reported observations were correct, they only are accurate for the set of experimental conditions used. This confirms that the dynamics of the dehydration of these salts are complex and parameters such as the way the compound is confined, the sample size and the heating rate will determine which pathway is followed. This complexity will need to be considered when designing devices using these salts for waste heat recovery.

Although the thermal dehydrations of $K_2M(SO_4)_2 \cdot 6\ H_2O$ with M = Mg, Co, Ni, Cu, and Zn) follow a complex mechanism, the enthalpies of reaction for the removal of all six waters were determined by treating a multiple step process as a single step process. The values determined using this approach agree well with the previously determined values for the Mg, Cu, and Zn salts as shown in Table 1. These values can then be used to determine the enthalpy of formation for the compound using Reaction (1) and Equation (2). As shown in Table 2, the values determined agree to within a few kJ mol-1 for the values tabulated by Wagman et al. [26] for Mg, Cu, and Zn.

Previous research has shown that the dehydration initially produces an amorphous compound [25]. Modeling this amorphous compound as an ideal solid solution and using DSC measurements to determine the enthalpy of crystallization for the dehydrated compound provides a way to determine the enthalpies of formation for unknown values of

$K_2M(SO_4)_2$. As shown in Table 2, most of the values determined are within 10 kJ mol-1 of the values determined previously [26]. This approach was used determine enthalpies of formation for the Co and Ni salts that had not been reported previously. The results are given in Table 3. This ideal solution approximation for amorphous $K_2M(SO_4)_2$ was also used to estimate previously unmeasured standard molar entropies for these potassium Tutton salts. The values determined are given in Table 4. While these values may be in error by 5 percent or more, they should be accurate enough to predict the temperature range needed to use these salts for waste heat recovery processes.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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