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Melting of Tutton's salts studied by DSC

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Abstract

The melting behaviour of 27 Tutton's salts $[M^I_2M^{II}(SO_4)_2 \cdot 6H_2O]$ has been investigated by DSC. The melting point T_F and the enthalpy of fusion $\Delta_F H$ of these double salts were determined by the same method. The Tutton's salt with the cations $M^I = NH_4$ and $M^{II} = Zn$ offers a remarkably high value of $\Delta_F H$ (285 J/g). From the DSC curves, conclusions have been drawn concerning the mechanism of fusion. The investigated Tutton's salts melt more or less incongruently. The melting process occurs in either one or two steps. In a two-stage melting mechanism the salt first melts with settling of a lower double salt hydrate. The second step seems to be the melting or dissolution of this lower double salt hydrate.

INTRODUCTION

Knowledge about the thermal behaviour of salt hydrates is of considerable importance for developing appropriate latent heat storage materials. There is a large range of salt hydrates not so far considered. The alums are the only sulphate double salt hydrates being investigated in respect of their melting behaviour [1]. They have a relatively high enthalpy of fusion, but above the melting point they decompose to a certain extent owing to hydrolysis. The high values of the enthalpy of fusion are correlated to extensive changes in ion coordination.

Tutton's salts represent another group of double salts, for which similar changes in ion coordination can be expected. Thus, high values of phase transition enthalpies can also be envisaged. At the same time, Tutton's salts should show enhanced stability to hydrolysis.

Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, and schönite, $K_2Mg(SO_4)_2 \cdot 6H_2O$, are well known. The general formula of these isomorphic double salts can be written as: $M^I_2M^{II}(XO_4)_2 \cdot 6H_2O$ and is known as Tutton's salt. The monovalent and divalent cations can be substituted in great variety: M^I = K, NH_4, Rb, Cs, Tl; M^{II} = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, V. The anions are variable, too: $XO_4 = SO_4$, SeO_4 or CrO_4 [2, 3].

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All the Tutton's salts crystallize in monoclinic form and have the same space group, C_{2h}^{5} or, rather, $P2_{1/a}$ [3]. Montgomery and Lingafelter [4] describe the structure of $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ as an example. The water molecules are arranged in a nearly regular octahedron around the zinc ion. The axial bond is shorter. Each water molecule forms two hydrogen bonds to the sulphate tetrahedron. The ammonium ion is also hydrogen-bonded to the oxygen atoms of the sulphate groups. The potassium, rubidium and caesium ions occupy the same position as the ammonium ion.

The thermal behaviour of Tutton's salts is relatively unknown up to now. Kohler and Franke determined the melting points by optical observations and investigated the isobaric thermal decomposition of the NH_4 and K salts [5]. Hölemann dealt with the isothermal dehydration of Tutton's salts [6]. Tamme and Kanwischer determined the phase transition enthalpy of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ [7]. A total value of 200 J/g was given.

This paper deals with the series of NH_4, K, Rb and Cs salts which contain the divalent cations Mg, Mn, Fe, Co, Ni, Cu and Zn and the anion SO_4.

EXPERIMENTAL

All Tutton's salts were prepared according to their fields of existence in the phase diagrams [8–18]. The modes of preparation cover three groups of salts. The first group includes double salts which are congruently soluble over a wide temperature range. These are the salts with the cation combinations NH_4–Mg, NH_4–Fe, NH_4–Co, NH_4–Ni, NH_4–Cu, NH_4–Zn, K–Co, K–Ni, K–Cu, K–Zn, Rb–Mg, Rb–Fe, Rb–Co, Rb–Ni, Rb–Cu, Rb–Zn, Cs–Mg, Cs–Mn, Cs–Fe, Cs–Co, Cs–Ni, Cs–Cu and Cs–Zn. The two single sulphates ($M_2^{I}SO_4 : M^{II}SO_4$, molar ratio 1 : 1) were dissolved at high temperature and crystallized by cooling.

The salts of the second group are congruently soluble only in a limited temperature range (≈ 0–30°C). These are the Tutton's salts with the cations NH_4–Mn, K–Fe and Rb–Mn. The single sulphates ($M_2^{I}SO_4$: $M^{II}SO_4$, molar ratio 1 : 1) were therefore dissolved at room temperature. The double salts were crystallized by solvent evaporation under vacuum within the temperature range mentioned above.

The only Tutton's salt investigated which is incongruently soluble at all listed temperatures is $K_2Mg(SO_4)_2 \cdot 6H_2O$. In this case the single sulphates were dissolved in the molar ratio 3 : 1 ($M_2^{I}SO_4 : M^{II}SO_4$) at room temperature and the crystallization took place in an evacuated desiccator.

The water content of the hydrates was determined by drying samples of ≈ 0.5 g at temperatures of 150–160°C to constant weight.

In addition, X-ray powder diffractometry was used to identify the Tutton's salts.

Melting points and the phase transition enthalpies were determined with a DSC92 DSC apparatus (Setaram, France).

For the measurements, 15–20 mg of the prepared substance was transferred to a sealable steel crucible. Al_2O_3 was used as reference sample. The DSC curves were recorded under the following conditions: heating and cooling rates, 2 K/min; temperature range, 20–200°C.

The software provided by Setaram was used for the determination of the enthalpy of fusion and of the onset temperature.

Metal standards (In, Sn, Pb, Zn, Hg) were used to calibrate the DSC apparatus in respect of enthalpy and temperature.

The total uncertainty of the enthalpy values was estimated to $\approx 10\%$. This includes uncertainties from sample preparation, differing peak widths because of varying melting kinetics, and so on. The reproducibility for one and the same sample under identical conditions is better than 3%.

RESULTS AND DISCUSSION

Figures 1–4 and the corresponding Tables 1–4 summarize representative results from melting curves recorded by DSC. The melting points, the water contents and the phase transition enthalpies of Tutton's salts are listed in the relevant table.

The DSC curves show that the Tutton's salts melt more or less incongruently in one-stage and two-stage melting processes. A long drawn out effect

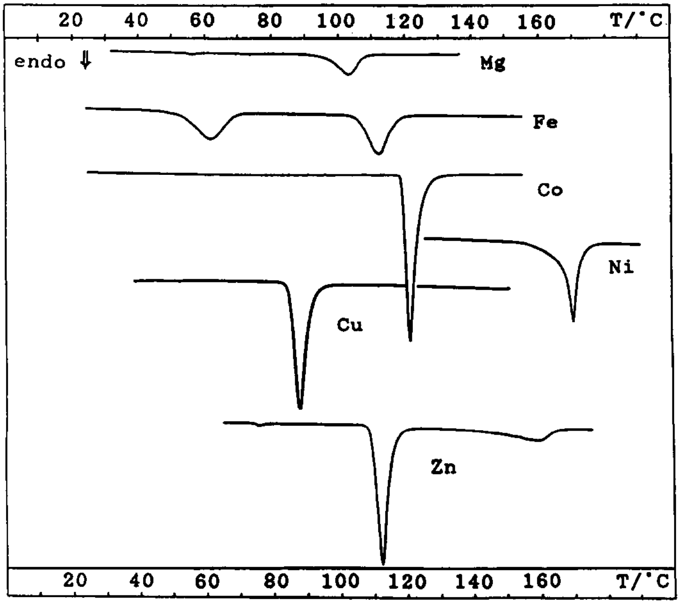

Fig. 1. DSC curves of the series of potassium salts (see Table 1).

after the main peak exists in some cases. The melting curve changes when heating the same sample a second time.

The course of the DTA melting curve determined by Tamme and Kanwischer (Fig. 5) was confirmed by our DSC measurement. The two

TABLE 1

Melting points and phase transition enthalpies of the series of potassium salts

Double salt	T(on)/(°C)		$\Delta_F H$/(J/g)	
	I	II	I	II
Mg: $K_2Mg(SO_4)_2 \cdot 6.22\,H_2O$	54.7	96.6	1.3	49.8
Fe: $K_2Fe(SO_4)_2 \cdot 6.28\,H_2O$	52.8	105.8	46.7	50.6
Co: $K_2Co(SO_4)_2 \cdot 6.27\,H_2O$	119.2		145.6	
Ni: $K_2Ni(SO_4)_2 \cdot 6.10\,H_2O$	166.9		129.0	
Cu: $K_2Cu(SO_4)_2 \cdot 6.21\,H_2O$	81.8		132.2	
Zn: $K_2Zn(SO_4)_2 \cdot 5.98\,H_2O$	109.3	146.8	147.3	45.2

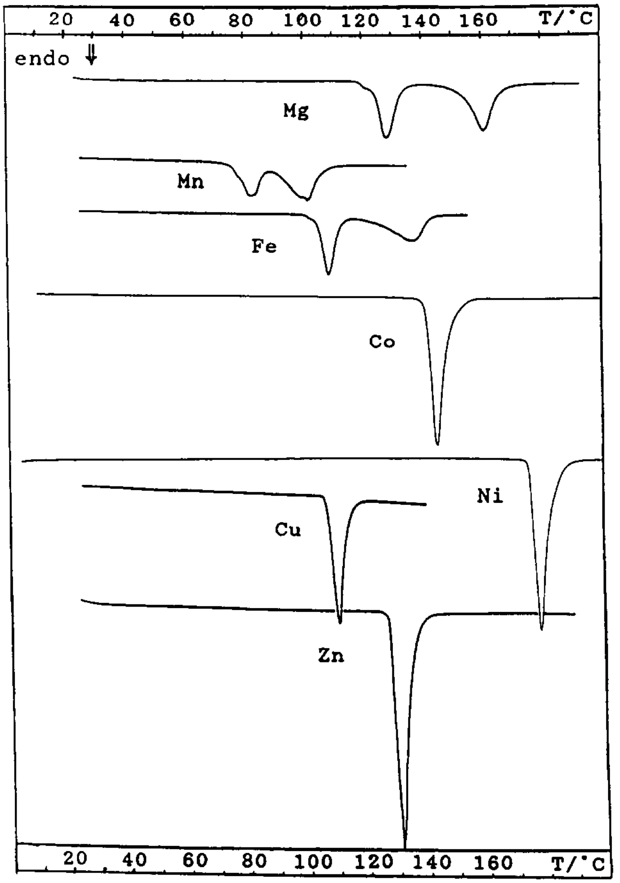

Fig. 2. DSC curves of the series of ammonium salts (see Table 2).

TABLE 2

Melting points and phase transition enthalpies of the series of ammonium salts

Double salt	T(on)/(°C)		$\Delta_F H$/(J/g)	
	I	II	I	II
Mg: $(NH_4)_2Mg(SO_4)_2 \cdot 6.29\,H_2O$	124.0	153.0	112.5	130.5
Mn: $(NH_4)_2Mn(SO_4)_2 \cdot 6.05H_2O$	74.1	88.9	202.4	
Fe: $(NH_4)_2Fe(SO_4)_2 \cdot 6.07H_2O$	104.7	124.3	215.0	
Co: $(NH_4)_2Co(SO_4)_2 \cdot 6.10H_2O$	142.2		238.5	
Ni: $(NH_4)_2Ni(SO_4)_2 \cdot 5.96H_2O$	175.2		272.2	
Cu: $(NH_4)_2Cu(SO_4)_2 \cdot 6.19\,H_2O$	107.0		170.2	
Zn: $(NH_4)_2Zn(SO_4)_2 \cdot 6.03\,H_2O$	125.7		285.7	

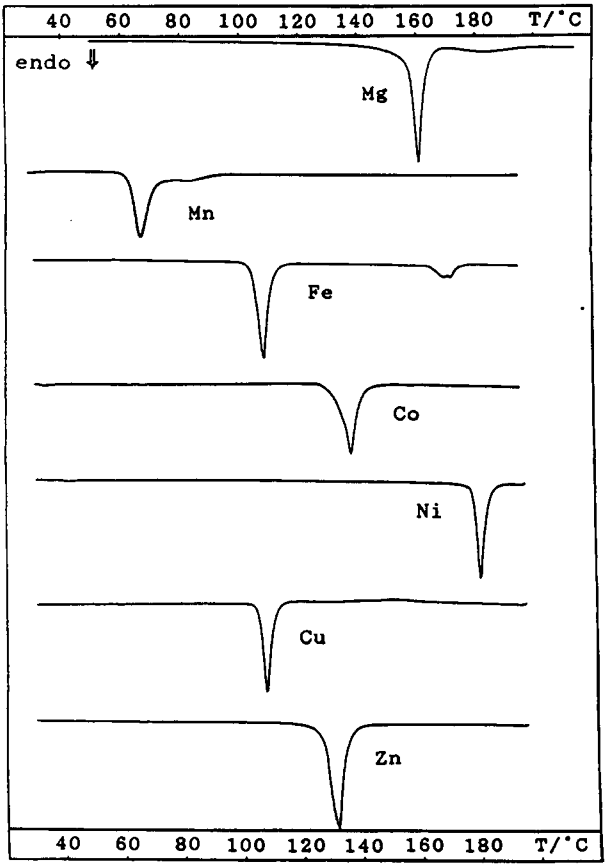

Fig. 3. DSC curves of the series of rubidium salts (see Table 3).

TABLE 3

Melting points and phase transition enthalpies of the series of rubidium salts

Double salt	T(on)/(°C)		$\Delta_F H$/(J/g)	
	I	II	I	II
Mg: $Rb_2Mg(SO_4)_2 \cdot 5.98H_2O$	137.9	154.1	141.6	12.1
Mn: $Rb_2Mn(SO_4)_2 \cdot 6.05H_2O$	62.1		138.5	
Fe: $Rb_2Fe(SO_4)_2 \cdot 6.27H_2O$	104.5	164.7	111.8	22.9
Co: $Rb_2Co(SO_4)_2 \cdot 6.03H_2O$	133.6		131.3	
Ni: $Rb_2Ni(SO_4)_2 \cdot 6.17H_2O$	178.4		115.8	
Cu: $Rb_2Cu(SO_4)_2 \cdot 6.08H_2O$	101.6		121.9	
Zn: $Rb_2Zn(SO_4)_2 \cdot 6.04H_2O$	127.0		200.1	

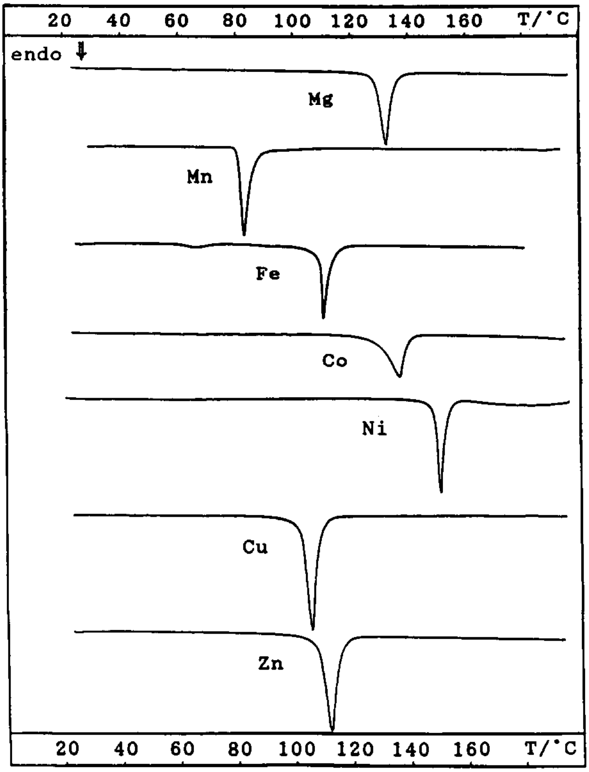

Fig. 4. DSC curves of the series of caesium salts (see Table 4).

endothermic peaks are separated only at the peak maximum. Our enthalpy value (202.4 J/g) agrees with Tamme's result (200 J/g).

The enthalpies of fusion of the Tutton's salts are difficult to compare because of the obviously different melting behaviour. The sums of all

TABLE 4

Melting points and phase transition enthalpies of the series of caesium salts

Double salt	$T(\text{on})/(^\circ C)$		$\Delta_F H/(J/g)$	
	I	II	I	II
Mg: $Cs_2Mg(SO_4)_2 \cdot 6.14H_2O$	128.7		112.0	
Mn: $Cs_2Mn(SO_4)_2 \cdot 5.84H_2O$	81.1		106.0	
Fe: $Cs_2Fe(SO_4)_2 \cdot 5.71H_2O$	59.9	109.6	6.6	87.9
Co: $Cs_2Co(SO_4)_2 \cdot 6.19H_2O$	129.6		105.0	
Ni: $Cs_2Ni(SO_4)_2 \cdot 6.05H_2O$	163.5	178.2	99.7	22.4
Cu: $Cs_2Cu(SO_4)_2 \cdot 5.88H_2O$	102.7		128.3	
Zn: $Cs_2Zn(SO_4)_2 \cdot 6.00H_2O$	108.2		153.4	

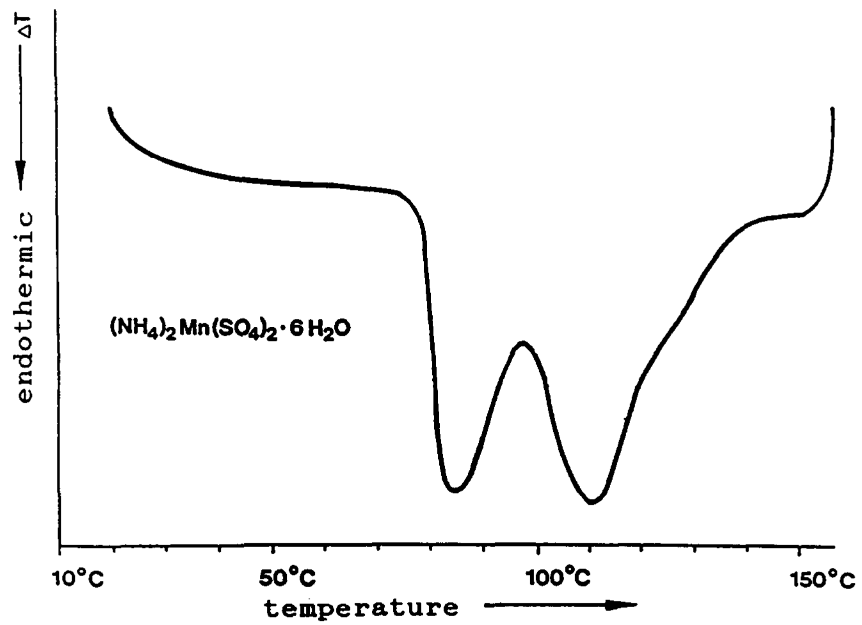

Fig. 5. DTA curve of the Tutton's salt $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ determined by Tamme and Kanwischer [7].

endothermic peaks in each DSC curve cover an enthalpy range of 52–285 J/g. The enthalpy values of the series of ammonium salts are the highest. Thus, the salt $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ shows the remarkable enthalpy of 285.7 J/g, and was therefore picked out for further investigations.

The dependence of the enthalpy of fusion on the number of heating cycles is considered in Fig. 6. The sample contained a 10% excess of water. Therefore the enthalpy of fusion is generally lower than given above.

Obviously the phase transition enthalpy decreases from the first to the sixth cycle. The stratification of a lower hydrate or an anhydrous phase seems to be the reason for the decreasing enthalpy. The fourth, fifth and sixth heating cycles show small endothermic peaks below 100°C, resulting probably from $Zn(SO_4)_2 \cdot 6H_2O$.

The solidification of $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ takes place incompletely with a high degree of supercooling (Fig. 6). In general, the freezing curves of the investigated Tutton's salts are different. Many of the double salts crystallize like the NH_4–Zn salt, with high supercooling, apart from the NH_4–Cu and the K–Fe salt. Their supercooling is minimal, but solidification is again incomplete (Fig. 7). Another group of Tutton's salts does not show any pronounced crystallization peak. These, for instance, are $Cs_2Mn(SO_4)_2 \cdot 6H_2O$, $Cs_2Co(SO_4)_2 \cdot 6H_2O$, $Rb_2Mg(SO_4)_2 \cdot 6H_2O$ and $Rb_2Mn(SO_4)_2 \cdot 6H_2O$.

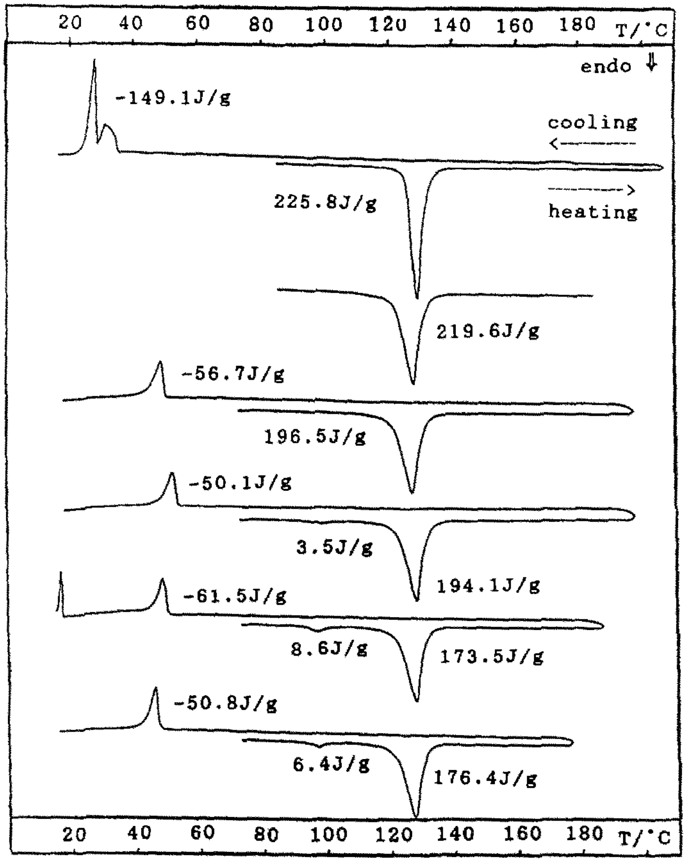

Fig. 6. Heating and cooling cycles of $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$. 1: heating, T(on) = 125.5°C; 2: heating after ≈96 h, T(on) = 121.7°C; 3: heating after ≈196 h, T(on) = 121.6°C; 4: heating after ≈24 h, T(on) = 95.5°C, T(on) = 122.7°C; 5: heating after ≈120 h, T(on) = 93.7°C, T(on) = 121.9°C; 6: heating after ≈24 h, T(on) = 94.2°C, T(on) = 121.5°C.

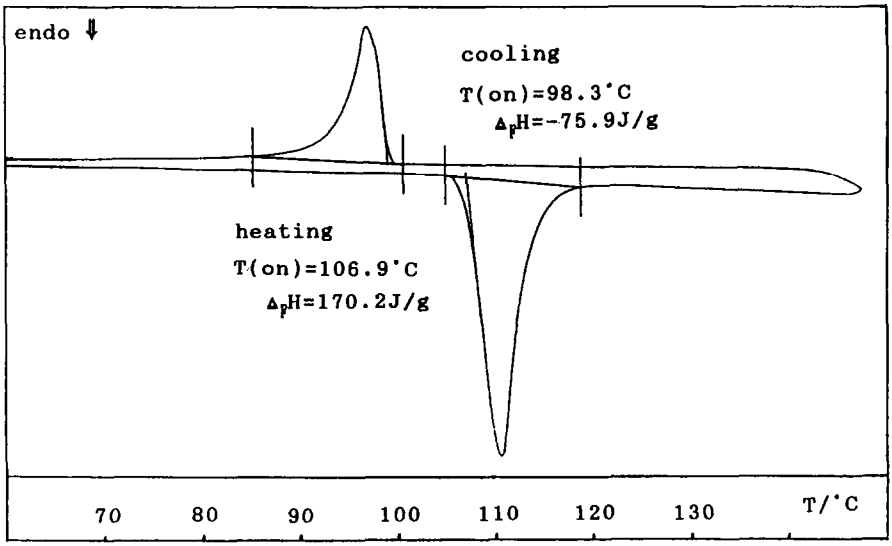

Fig. 7. DSC curve of $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$.

Completely dehydrated $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ rehydrates and forms a Tutton's salt on annealing the sample in a closed DSC crucible below the melting point (115°C, 48 h) (Fig. 8).

The observed enthalpy value is similar to that for the salt with 10% excess of water. However, the anhydrous compound and water were mixed in a

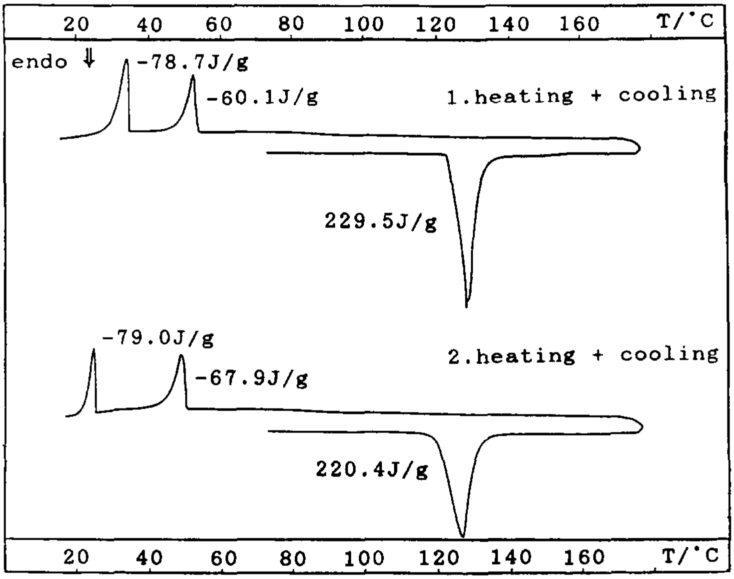

Fig. 8. DSC curves of $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ after rehydration of dried salt. 1: heating, T(on) = 124.4°C; 1: cooling, T(on) = 53.6°C, T(on) = 35.1°C; 2: heating, T(on) = 120.0°C; 2: cooling, T(on) = 50.4°C, T(on) = 25.6°C.

stoichiometric ratio. Therefore the rehydration seems to be incomplete because of the lower value of enthalpy compared with that of the stoichiometric Tutton's salt. Including the uncertainty of the enthalpy values ($\approx 10\%$), the degree of hydration reaches ≈ 70–80%.

The appearance of the intermediate and final products of the melting process of each Tutton's salt can be inferred from the DSC curves of the Tutton's salts in relation to identification by X-ray powder diffraction, and from phase diagram data of the ternary aqueous systems. In Fig. 9 a classification scheme according to the supposed melting behaviour is suggested. Figure 9(a) shows the one-stage melting salts, which can form solid

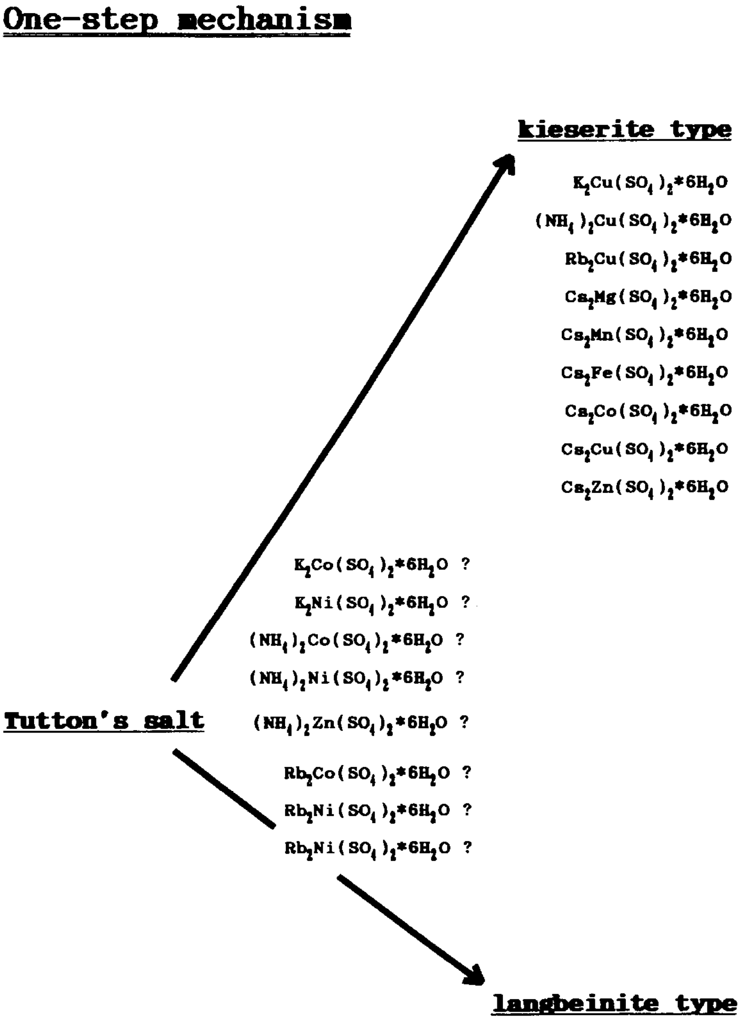

Fig. 9(a). Classification of the Tutton's salts according to melting behaviour: one-step melting salts.

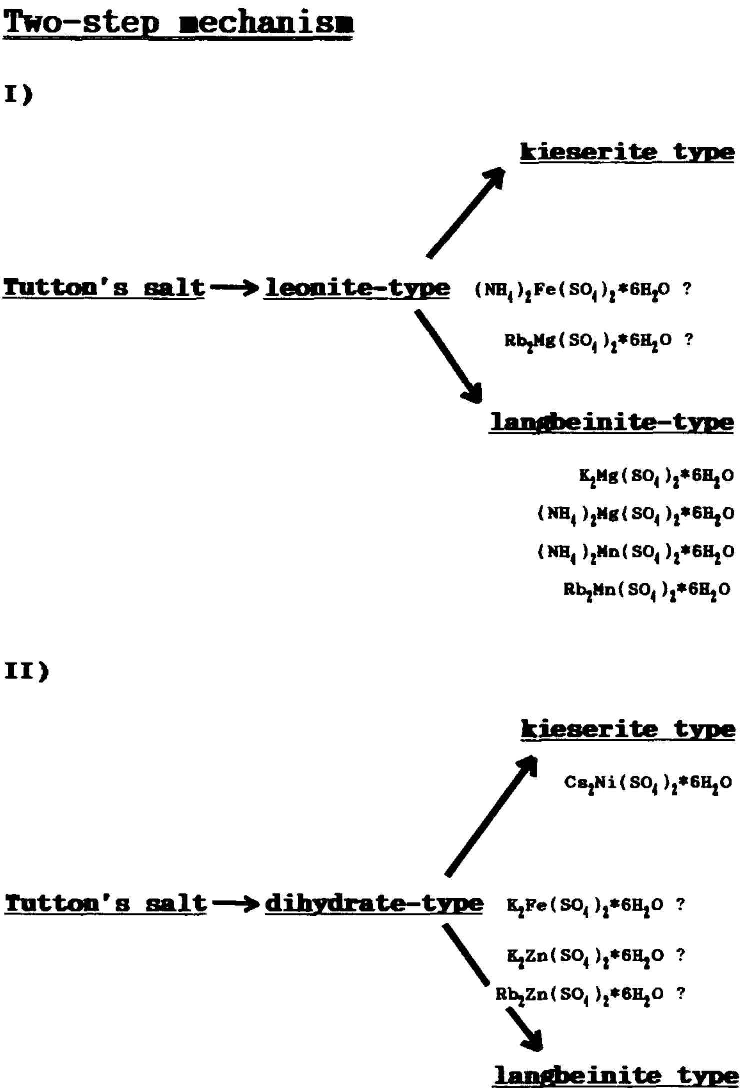

Fig. 9(b). Classification of the Tutton's salts according to melting behaviour: two-step melting salts.

phases of kieserite or langbeinite type. It is known that the caesium ion cannot fit into the langbeinite structure. Copper sulphate does not form langbeinites either. In these cases kieserite will be the phase formed. For the remaining one-stage melting Tutton's salts, it is difficult to decide whether the kieserite or the langbeinite structure is formed. According to the ternary phase diagrams, kieserite will be the stable salt up to 100°C. Often the formation of langbeinite is kinetically inhibited. Therefore, we assume that above 100°C the salts in the first column are converted into kieserite form.

This was confirmed by us after isolation and identification of $ZnSO_4 \cdot H_2O$ as the melting product of $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$.

There is a second group of Tutton's salts, the two-stage melting salts, which is shown in Fig. 9(b). The two-stage melting process proceeds with the formation of a lower double salt hydrate, either a salt of leonite type $M^{I}_{2}M^{II}(SO_4)_2 \cdot 4H_2O$ (I) or of the type $M^{I}_{2}M^{II}(SO_4)_2 \cdot 2H_2O$ (II). The respective type of the potassium and ammonium salts can be supposed by excluding the non-existent double salt hydrates. For instance, we isolated and identified $K_2Zn(SO_4)_2 \cdot 2H_2O$ as an intermediate melting product. The crystal type of the intermediate melting products of the rubidium and caesium salts is inferred by assuming a similarity to the potassium and ammonium salts.

In the second stage, the lower hydrate melts with settling out of the corresponding kieserite or langbeinite.

Figure 9(b), I shows the salts with intermediates of leonite type. According to the ternary phase diagrams, $K_2Mg(SO_4)_2 \cdot 6H_2O$, $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ and $Rb_2Mn(SO_4)_2 \cdot 6H_2O$, in the second melting stage, form products of the langbeinite type. The salt $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ also forms the langbeinite-type product. We have isolated and identified langbeinite as the melting product after the second stage. The Tutton's salts forming a dihydrate are listed in Fig. 9(b), II. Only for $Cs_2Ni(SO_4)_2 \cdot 6H_2O$ can the type of final product be decided unambiguously.

Our investigation also shows a correlation between ionic radius, electron configuration of M^{2+} and the melting point of the Tutton's salts.

The melting temperatures of the salts of each investigated series show the same dependence on the nature of the divalent cation, as demonstrated in Fig. 10. The series of the melting points of all the Tutton's salts, as a measure of the lattice stability, corresponds to the change of the ligand field

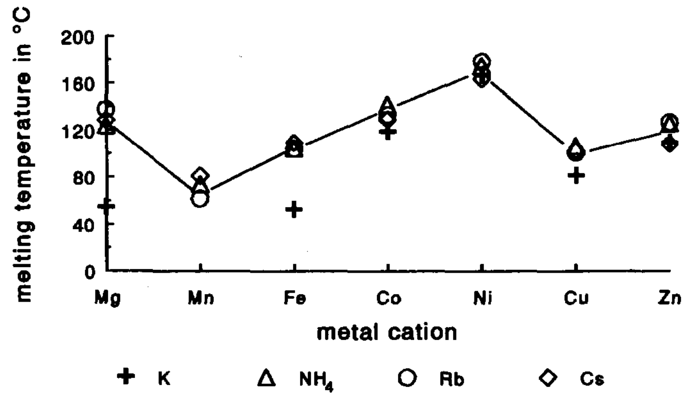

Fig. 10. Melting temperatures of the Tutton's salts in dependence on the divalent cation present; ionic radius (in pm): Mg 72, Mn 83, Fe 78, Co 75, Ni 69, Cu 57$_4$, Zn 73.

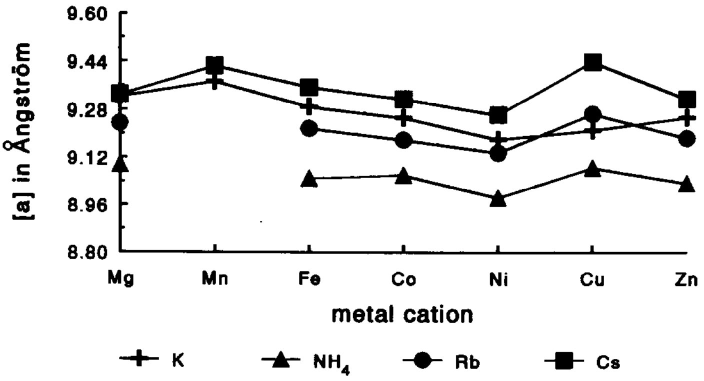

Fig. 11. Lattice constants [*a*] of the Tutton's salts in dependence on the divalent cation present.

stabilizing energy (LFSE) expected for the 3d elements. For high spin complexes, the LFSE is zero for manganese and reaches a maximum value for nickel. Because of the tendency of copper towards square planar coordination, the melting points of the copper salts are lowered.

From the comparison of the Mg^{2+}, Zn^{2+} and Mn^{2+} salts, none of which has any contribution of LFSE, it is concluded that the ionic radius of manganese ions appears to be unfavourable for the structure of Tutton's salts.

This discussion is supported by the variation of the lattice constant [*a*] as shown in Fig. 11. The values of the lattice constant [*a*] are inversely proportional to the melting points, as expected for the lattice energy. The copper salts again behave anomalously.

REFERENCES

1 J. Guion, Thermochim. Acta, 67 (1983) 167.
2 Gmelins Handbuch der anorganischen Chemie, Verlag Chemie, Weinheim, Volumes 27, 52, 56–60.
3 Landold-Börnstein: Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, K.-H. Hellwege (Ed.), Heidelberg/New York, 1982.
4 H. Montgomery and E.C. Lingafelter, Acta Crystallogr., 17 (1964) 1295.
5 K. Kohler and W. Franke, Z. Anorg. Allg. Chem., 331 (1964) 17.
6 H. Hölemann, Z. Anorg. Allg. Chem., 239 (1938) 269.
7 R. Tamme and H. Kanwischer, Report: Entwicklung von Medien für dynamische Latentwärmespeicher im Niedertemperaturbereich, DFVL-FB 84-03, Stuttgart, 1984, pp. 45–47.
8 A. Benrath and A. Sichelschmidt, Z. Anorg. Allg. Chem., 197 (1931) 113.
9 W. Küster and A. Thiel, Z. Anorg. Chem., 21 (1899) 120, 121.
10 A. Benrath, Z. Anorg. Allg. Chem., 208 (1932) 169.
11 Gmelins Handbuch der anorganischen Chemie, Verlag Chemie, Weinheim, Vol. 60, 1965, Part B, pp. 1033–1076.
12 A. Benrath, Z. Anorg. Allg. Chem., 198 (1930) 82.
13 A. Benrath, Z. Anorg. Allg. Chem., 195 (1931) 247.

14 Gmelins Handbuch der anorganischen Chemie, Verlag Chemie, Berlin, Vol. 59, 1932, Part B, p. 1001.
15 A. Benrath, Z. Anorg. Allg. Chem., 202 (1931) 161.
16 J. Locke, Am. Chem. J., 27 (1902) 459.
17 Gmelins Handbuch der anorganischen Chemie, Springer Verlag, Vol. 56, 1976, Part C6, p. 229.
18 W.G. Schewtschuk, D.A. Storojenko and H.M. Lasorenko, Zh. Neorg. Khim., 27 (1982) 520.