Thermochimica Acta, 88 (1985) 433–441
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

LITHIUM SULFATE: CALORIMETRIC DETERMINATION OF THE TEMPERATURES AND ENTHALPIES OF HIGH-TEMPERATURE PHASE TRANSITIONS

G. HATEM

Laboratoire de Dynamique et Thermophysique des Fluides, associé au C.N.R.S., Université de Provence, Centre de Saint-Jérôme, 13397 Marseille Cedex 13 (France)

(Received 27 December 1984)

ABSTRACT

Using a high-temperature Calvet calorimeter as a differential enthalpic analyser Li_2SO_4 was investigated in the temperature range 800–1200 K. One transformation in the solid state was observed at 847 K with a corresponding enthalpy increment of 24.2 kJ mol^{-1}. The solid–liquid transition was found to occur at 1131 K with an enthalpy of fusion of 7.74 kJ mol^{-1}. Furthermore, the analysis of the corresponding thermograms supports the presence of the premelting effect which was evidenced by other techniques. A critical comparison with previous results in the literature is given.

INTRODUCTION

A recent bibliographic survey showed that the values of the temperatures and enthalpies of the solid–solid and solid–liquid transitions of lithium sulfate, Li_2SO_4, are very scattered. However, an accurate knowledge of the entropy increments related to these high-temperature transformations is of much interest, for instance, in:

(1) the use of Li_2SO_4 as an electrolyte for high-energy batteries. Indeed, a plastic phase with a very high ionic conductivity has been found [1];

(2) some projects on thermal energy storage using this material [2], since a fairly large enthalpy increment is related to the high-temperature solid–solid transformation;

(3) thermodynamic calculations where some inconsistencies were reported for Li_2SO_4-containing mixtures [3]; as for us, also in this field, we will use the values of the transformation entropies of Li_2SO_4 to calculate the phase diagrams of the ternary reciprocal molten salt mixtures ($Li^+ + A^+ + F^- + SO_4^{2-}$) (A = Na,K) which have been calorimetrically investigated in a previous work [4].

Therefore, the temperatures and enthalpies of transformation of Li_2SO_4 were measured using differential enthalpic analysis (DEA) which was already shown to be a suitable technique for such determinations.

The present paper reports experimental results together with a statistical estimate of their accuracy and a comparison with those reported in the literature.

EXPERIMENTAL

Apparatus

The apparatus used in this work was a high-temperature microcalorimeter of the Calvet kind [5] which was utilized as a differential enthalpic analyser. We have already described the experimental details and also showed how the great sensitivity of this apparatus allied to its small heating rate allow to detect, separate and estimate the order of magnitude of thermal effects however small and close in temperature [6,7].

For the sake of clarity, we will recall here only certain experimental points of interest to this kind of experiment.

When a thermal effect occurs in the calorimetric cell, the corresponding amount of heat, Q_p, at constant pressure is proportional to the surface of the thermogram, S (recording the EMF of the thermopiles against time)

$$Q_p = KS$$

When the thermal effect is related to a phase transition of the material contained in the calorimetric cell, the above equation can be written as

$$Q_p = KS = n\Delta H_{tr} \qquad (1)$$

where n and ΔH_{tr} are the number of moles and the molar enthalpy of transformation, respectively.

The constant K is obtained during a previous calibration of the calorimeter. This operation is performed with materials having a well-known ΔH_{tr} and with operating conditions similar to those used during the experiment.

Systematic investigations have been carried out in our laboratory [7,8] which have evidenced the importance of an identical location in the calorimeter of the cell containing either the sample or the calibrating material.

The rate of temperature variation (heating or cooling) is linear against time and about 8 K h^{-1}.

Sample preparation

The lithium sulfate used was suprapur (Merck) with the formula ($Li_2SO_4 \cdot H_2O$). The molecule of water was removed using the following thermal treatment: maintainance under vacuum at room temperature for 24 h; heating under vacuum at 450 K for 24 h.

The salt was weighed before and after these operations to control the elimination of the total water. It was then melted under an argon atmosphere. After cooling, only transparent crystals were selected and used. During the experiment Li_2SO_4 was contained in a crucible made of platinum which was closed with a platinum lid.

Experimental accuracy

The different experimental quantities under examination were measured several times under the same conditions; therefore, for each of them we can calculate [9]:

(1) An arithmetic mean value, $\bar{x}$

$$\bar{x} = (1/n) \sum_{i=1}^{n} x_i$$

(2) A calculated standard deviation, s

$$s = \left[\sum_{i=1}^{n} (x_i - \bar{x})^2 / (n-1) \right]^{1/2}$$

where x_i is the result of the i-th measurement and n the total number of measurements.

(3) A confidence interval where the exact value of x is ascribed to a probability range, in connection with Student's coefficient, t_c. The limits of this interval are: $(\bar{x} - t_c s/\sqrt{n})$ and $(\bar{x} + t_c s/\sqrt{n})$. In the present work, we used the t_c values, given in tables in ref. 10, corresponding to the usual probability 0.95.

In the following, our results are presented under the equivalent form

$$x = \bar{x} \pm t_c s/\sqrt{n}$$

When the quantity to be measured is dependent on many independent experimental parameters, like ΔH_{tr}, we will calculate the relative uncertainty with the following equation which was deduced from a statistical evaluation of experimental errors in calorimetry [11]

$$\begin{aligned}\Delta(\Delta H_{tr})/\Delta H_{tr} &= \left[(\Delta n/n)^2 + (\Delta Q_p/Q_p)^2\right]^{1/2} \\ &= \left[(\Delta m/m)^2 + (\Delta S/S)^2 + (\Delta K/K)^2\right]^{1/2} \qquad (2)\end{aligned}$$

The calculation of $(\Delta K/K)$ is performed in the same way

$$\Delta K/K = \left\{ [\Delta(\Delta H_{tr}(\mathrm{C}))/\Delta H_{tr}(\mathrm{C})]^2 + [\Delta m(\mathrm{C})/m(\mathrm{C})]^2 + (\Delta S/S)^2 \right\}^{1/2} \qquad (3)$$

In this relation, however, $m(\mathrm{C})$ and $\Delta H_{tr}(\mathrm{C})$ are the mass and the molar enthalpy of transformation of the calibrating substance, respectively.

TABLE 1

Calibration of the calorimeter with antimony (a.u. = arbitrary unit)

Number in the set	Melting temp., T (K)	Area of the thermograms (a.u.)	Calibration constant (kJ/(a.u.))
1	903.0	8152	4.86×10^{-2}
2	903.5	8367	4.74×10^{-2}
3	903.5	8530	4.64×10^{-2}
4	903.5	8510	4.65×10^{-2}

RESULTS

Solid–solid transformation

Calibration

The calibrating substance was antimony and was contained in a sealed silica ampoule. This metal has a large undercooling and, accordingly, only heating experiments were selected. Our experimental results are given in Table 1. From the values of the melting temperature reported there for antimony, we found $T_f(Sb_2) = 903.4 \pm 0.4$ K. Since this value is in excellent agreement with that given in the literature (903.5 K [12]), the validity of the experimental technique was concluded for measuring transition temperatures.

The calibration constant, K, was calculated from the value of the enthalpy of fusion reported for antimony by Kubaschewski [12]. The results in Table 1 lead to the value $K = 0.047 \pm 0.0016$ J/(a.u.) (a.u. = arbitrary surface unit).

Temperature and enthalpy of transformation

The experimental results concerning the temperature and enthalpy of the solid–solid high-temperature transformation of Li_2SO_4 are given in Table 2. We obtained the temperature of transition, $T_{tr} = 847.0 \pm 0.4$ K.

TABLE 2

Solid–solid transition of Li_2SO_4: sample weight, 1.92777 g; a.u. = arbitrary unit

Number in the set	Transition temp., T (K)	Area of the thermograms (a.u.)
1	848	9020
2	847	8880
3	847	9165
4	847	8954
5	847	9194
6	847	8810

In Table 3 we report the values found in the literature; it can be noted that the temperatures given in refs. 15, 16, 19 and 20 differ noticeably from the others. The experimental method, the so-called drop method, which was used in ref. 15 is not very suitable for measuring the temperature of a phase transition since the latter is obtained by extrapolation of the experimental temperature ranges before and after the phase transition. Neither does the temperature obtained in ref. 16 have a high accuracy due to the very fast heating rate (600 K h^{-1}) of this thermal analysis. As for the values reported in refs. 19 and 20, the difference can be attributed either to the miscalibration of the detecting thermocouples or the purity of the chemicals which were used.

All the remaining values range between 846 and 851 K and it is difficult to choose one value from the other temperatures; however, we calculated the mean value and its related confidence interval $T_{tr} = 848.3 \pm 1.5$ K, and it can be stressed that our experimental value pertains to this interval. Also, taking into account that we obtained, under the same experimental conditions, the melting temperature of antimony within 0.1 K of that reported in the literature, it can be concluded that this value (847 K) is the most probable.

We indicated in Table 2 the values of the surfaces of the thermograms corresponding to the transformation of Li_2SO_4; they correspond to the mean value $S = 9003 \pm 161$ a.u. (a.u. = arbitrary unit).

Using eqns. (1) and (2) we obtained for the enthalpy increment related to this transition, $\Delta H_{tr} = 24.1 \pm 0.95$ kJ mol^{-1}. A comparison with the values

TABLE 3

Solid–solid transition of Li_2SO_4: results reported in the literature

Temp., T (K)	Enthalpy (kJ mol^{-1})	Experimental method	Ref.
851	23.54	DTA and DSC	2
	23.0–23.4	Cryoscopy	13
849	25.02	DTA and drop method	14
859	27.32	Drop method	15
865–832	28.45–26.36	DTA	16
848	25.56	Drop method	17
848		TA	18
858		TA	19
842–839	29.12–28.32	TA	20
846		DTA	21
848		–	22
850	21–25 [a]	Cryoscopy	23
847.3		Cryoscopy	24
851		Cryoscopy	25
847	24.24	DEA	This work

[a] Calculated by Grjotheim and Urnes [31].

in the literature (Table 3) indicates that, as for the temperature of transformation, the results obtained in refs. 15, 16 and 20 differ from those reported in the other references. Those values [2,13,14,17,22] are within our confidence interval.

Solid–liquid transformation

Calibration

Since the calibration constant of the calorimeter, K, is temperature dependent it should be determined at a temperature very close to that of the expected phase transition.

Therefore, calibration was carried out with sodium chloride. This salt was enclosed in the same platinum crucible already used for Li_2SO_4. Our experimental results are given in Table 4.

It can be noted that a difference of about 3 K exists between the fusion and solidification temperatures. This difference is probably related to a slight undercooling of the salt, which is not unusual for a solidifying molten salt. Accordingly, we determined the temperature of fusion from the heating thermograms and obtained $T_f = 1073.7 \pm 0.8$ K.

The value given in the JANAF tables (1073.5 K) [26], which compiles several bibliographic references, is in very good agreement with ours. In this temperature range our technique provided a reliable value for the transition temperature under investigation.

Since the constant K was determined from experiments with NaCl samples of different masses, we indicated in Table 4 the corresponding values of (S/n) with S the surface of the thermogram related to the fusion of n moles of NaCl. Using relations (1) and (3), we obtain $K = 0.064 \pm 0.0019$ J/(a.u.).

Temperature and enthalpy of fusion

The results obtained for the solid–liquid phase transition of Li_2SO_4 are reported in Table 5.

TABLE 4

Calibration of the calorimeter with sodium chloride

Number in the set	Transformation temp. (K)		
	Heating	Cooling	$(S/n)\times10^{-5}$
1	1073.5	1069	4.213
2	1072.5	1070	4.444
3	1075	1070.5	4.497
4	1073	1070.5	4.502
5	1074	1070.5	4.391
6	1074	1070.5	4.332

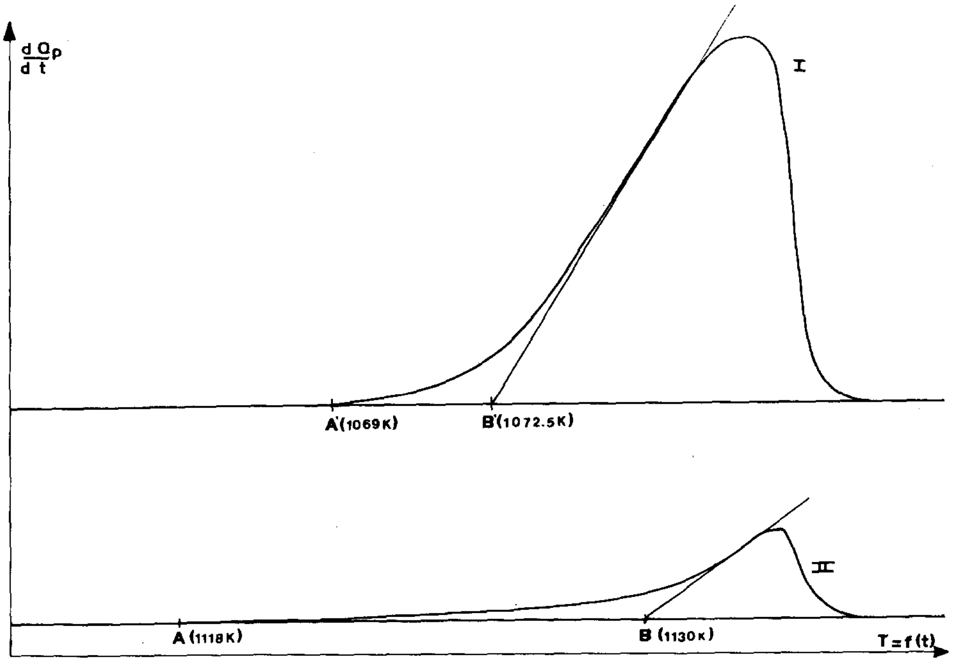

Fig. 1. Thermograms of fusion of: (I) NaCl; (II) Li_2SO_4.

The analysis of the thermograms of fusion of Li_2SO_4 seems to indicate the existence of a premelting phenomenon.

Indeed, the difference of the shapes of the thermograms relative to the fusion of NaCl (curve 1) and of Li_2SO_4 (curve II) is evident from Fig. 1. On the latter, a difference of about 12 K exists between point A (beginning of fusion) and point B (melting point); this difference is only 4 K for NaCl.

This premelting phenomenon has already been observed by several authors using different techniques, such as electrical conductivity measurements [27], Brillouin scattering [28], X-ray diffraction [29], and heat capacity measurements [30], which evidenced a plastic phase before the fusion of Li_2SO_4.

TABLE 5

Melting of Li_2SO_4: sample weight, 2.72503 g; a.u. = arbitrary unit

Number in the set	Melting temp. (K)			Crystallisation	
	Beginning of melting	Melting	Area of the thermograms (a.u.)	T (K)	thermograms thermograms (a.u.)
1	1114	1129	2770	1131	2875
2	1118	1130	2875	1132	2912
3	1118	1130	2780	1132	3000
4	1118	1130.5	2845	1130	3110
5	1118	1129	2830	1130	3088

TABLE 6

Melting of Li_2SO_4: results reported in the literature

Temp., T (K)	Enthalpy (kJ mol^{-1})	Experimental method	Ref.
1126	7.36	DTA/drop method	13
1133	7.65	Drop method	14
1132	–	TA	15
1130	9.33	Drop method	16
1132	–	TA	17
1129		TA	18
1133		DTA	20
1133		–	21
1131	8.20 [a]	Cryoscopy	22
1131	–	Cryoscopy	23
1129	–	Cryoscopy	24
1133	7.74 [a]	Cryoscopy	32
1133	8.26	Cryoscopy	33
1132	7.74	DEA	This work

[a] Calculated by Gryotheim and Urnes [31].

Table 5 also gives the temperatures observed for the beginning of fusion. The mean value obtained for the temperatures of fusion and of solidification, 1129.7 and 1131 K, respectively, are nearly identical.

Since the beginning of solidification is sharper than the beginning of fusion, we think that the value of 1131 K is the more accurate (it should be noted that in the present case no undercooling takes place since the solidification temperature is higher than the fusion temperature). From the values given in Table 5 we obtain $T_f = 1131 \pm 1$ K. The T_f values found in the literature range between 1126 and 1133 K, while the mean value is 1131 K, in excellent agreement with the one we propose in this work.

Due to the premelting phenomenon in Li_2SO_4, the determination of the surfaces of the corresponding heating thermograms was not very accurate. Therefore, the enthalpy of fusion was only obtained from the crystallisation thermograms. From the experimental values reported in Table 5 and using relations (1) and (2), we obtain $\Delta H_f = 7.74 \pm 0.50$ kJ mol^{-1}. All the values from the literature (Table 6), except that given in ref. 17, belong to our confidence interval.

CONCLUSION

Our experimental results, together with those reported in the literature, allowed us to conclude that the most probable values of the temperature and enthalpy increase of the high-temperature phase transitions of Li_2SO_4 are

$T_{tr} = 847 \pm 0.4$ K and $\Delta H_{tr} = 24.2 \pm 0.95$ kJ mol^{-1} for the solid–solid transformation, and $T_f = 1131 \pm 1$ K and $\Delta H_f = 7.74 \pm 0.50$ kJ mol^{-1} for the solid–liquid transformation.

REFERENCES

1 L. Nilsson, Thesis, Chalmers University of Technology, Gothenburg, 1981.
2 K. Schroeder and C.A. Sjoblom, High Temp.- High Pressures, 12 (1980) 327.
3 A.D. Pelton, C.W. Bale, and P.L. Lin, in Calculation of Thermodynamic Equilibria in the Carbonate Fuel Cell, Vol. 1, Prepared for J. Ackerman, The U.S. Department of Energy Contract No. DE-AC02-79ET15416, 1981.
4 G. Hatem, Thesis, University of Provence, Marseille, 1980.
5 E. Calvet and H. Prat, Microcalorimetrie, Masson, Paris, 1955.
6 J.P. Bros, Y. Fouque, M. Gaune-Escard, W. Szczepaniak and A. Bogacz, J. Chim. Phys., 10 (1982) 79, 715.
7 Y. Fouque, M. Gaune-Escard, W. Szczepaniak and A. Bogacz, J. Chim. Phys., 4 (1978) 75, 360.
8 W. Lukas and M. Gaune-Escard, J. Chem. Thermodyn., 14 (1982) 593.
9 G. Hatem and M. Gaune-Escard, J. Chem. Thermodyn., 16 (1984) 897.
10 M.R. Spiegel, Theory and Problems of Statistics, McGraw-Hill, New York, 1972.
11 G. Hatem, Precision des Mesures des Enthalpies de Mélange en Calorimetrie Isotherme, A.F.C.A.I. Publication, 1983.
12 O. Kubaschewski, Z. Elektrochem., 54 (1950) 275.
13 I. Kostenska, Proc. VIII konf. otermickej analyse, Vysoke Tatry, 1979.
14 R.P. Clark, J. Chem. Eng. Data, 20 (1975) 1, 17.
15 N. Voskresenskaya and N. Banashek, Anal. Akad. Nauk. SSSR, 25 (1954) 150.
16 C. Rama Mohan Rao and P. Narain Mehotra, J. Appl. Chem. Biotechnol., 28 (1978) 608.
17 L. Denielou, Y. Fournier, J.P. Petitet and C. Tequi, Rev. Int. Hautes Temp. Refract., 8 (1971) 119.
18 K. Huttner and G. Tamman, Z. Anorg. Chem., 43 (1905) 215.
19 D. Marotta and E. Paterno, Atti. Accad. Lincei, 21 (1912) 93.
20 A. Hare, Philos. Mag., 6 (1924) 48, 412.
21 K. Schroeder, A. Kvist and H. Ljungmark, Z. Naturforsch., Teil A, 27 (1972) 1252.
22 R. Arunsson, B. Heed, B. Jansson, A. Lunden, L. Nilsson, K. Schroeder, C.A. Sjoblom, J.O. Thomas and B.C. Tofield, in J. Mundy and P. Vashista (Eds.), Proc. Conf. on Fast Ion Transports in Solids, Geneva, 1979.
23 O. Schmitz-Dumont and I. Heckermann, Z. Anorg. Allg. Chem., 260 (1949) 49.
24 S. Julsrud and O.J. Kleppa, Acta Chem. Scand., Ser. A, 34 (1980) 655.
25 E.I. Speranskaya and A.G. Bergman, Izv. Sekt. Fiz.-Khim. Anal., Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR, 26 (1955) 1980.
26 JANAF, Thermochemical Tables, 2nd edn., National Bureau of Standards, 37, 1971.
27 A.R. Ubbelohde, The Molten State of Matter Interscience, New York, 1978.
28 R. Aronsson, H.E.G. Knape and L.M. Torell, Phys. Lett. A, 73 (1979) 3, 210.
29 T. Forland and J. Krogh-Moe, Acta Chem. Scand., 11 (1957) 3, 565.
30 C.A. Sjoblom, High Temp.-High Pressures, 8 (1976) 499.
31 K. Grjotheim and S. Urnes, Z. Elektrochem., 60 (1956) 626.
32 E. Kordes, G. Ziegler and H.J. Proeger, Z. Electrochem., 58 (1954) 168.
33 R. Riccardi, Gazz. Chim. Ital., 91 (1961) 1469.