

THE PHASE DIAGRAM OF THE SYSTEM $\text{La}_2(\text{SO}_4)_3$ – Ag_2SO_4

D.A. CAMPBELL, Z.M. ZOCHOWSKI and P.A.H. WYATT

Department of Chemistry, The University, St. Andrews, Fife KY16 9ST (Gt. Britain)

(Received 21 February 1983)

ABSTRACT

The phase diagram of the system $\text{La}_2(\text{SO}_4)_3$ – Ag_2SO_4 was studied by DTA, XRD, SEM, and optical methods. One double salt is formed at 67 mole% $\text{La}_2(\text{SO}_4)_3$ and this melts incongruently at $876 \pm 6^\circ\text{C}$. A eutectic is formed at 8 mole% $\text{La}_2(\text{SO}_4)_3$ and at a temperature of $618 \pm 3^\circ\text{C}$. Suppression of decomposition was effected by the sealed tube method, but some reference is made to experiments conducted with a flowing atmosphere of SO_3 , SO_2 and O_2 .

INTRODUCTION

While there exists a quantity of data relating to the individual high temperature behaviour of Ag_2SO_4 and to a lesser extent $\text{La}_2(\text{SO}_4)_3$, phase studies involving the latter are limited to systems such as Rb_2SO_4 – $\text{La}_2(\text{SO}_4)_3$ [1] and Cs_2SO_4 – $\text{La}_2(\text{SO}_4)_3$ [2].

Phase studies of sulphate systems are often complicated by decomposition of the salt, generally at elevated temperatures. According to Conrad et al. [3] Ag_2SO_4 is stable to above 830°C in the liquid phase, while $\text{La}_2(\text{SO}_4)_3$ does not begin to decompose until 900°C , depending on the nature of the surrounding atmosphere [4]. With the present system, two approaches to the problem of decomposition were made. A limited number of experiments were initially conducted using a flowing atmosphere, this being a mixture of SO_2 , SO_3 , and O_2 . (Experimental details are described elsewhere [5].) This technique has the disadvantage that it requires much of the apparatus to be constructed of materials able to resist attack during constant exposure to a highly corrosive atmosphere and this difficulty is increased if the suppression of decomposition requires the use of high pressures.

The second approach is to encapsulate the sample within a closed inert container, initially evacuated. If the container is of small volume, equilibrium decomposition pressures are set up by the decomposition of a negligible amount of substance: in our experiments this, typically, works out at less than 1% of the sample mass. Pressures inside the container never

exceed a few atm (this being limited by the physical strength of the tube) and, apart from suppression of decomposition, there is no detectable effect upon the condensed phase equilibria, as confirmed by other experimental work.

This method has already been used to determine the melting point of CaSO_4 [6] and the advantages are that it is convenient to use with standard DTA apparatus but without risking corrosion damage. It forms the basis of the work reported here.

EXPERIMENTAL

Materials

$\text{La}_2(\text{SO}_4)_3$ was obtained by dehydration of Aldrich Gold label $\text{La}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ (99.999%) by heating at 400°C for 48 h. This material was cooled under vacuum, finely ground, and treated again in the same manner. Complete dehydration was shown by the absence of O–H bands in the IR spectrum of the final material. BDH Ag_2SO_4 (99%) was finely ground but required no further treatment. Mixtures of total mass 200 mg were prepared by grinding the salts together for 10 min under a flowing atmosphere of dry N_2 (to prevent excessive absorption of moisture). The entire sample was transferred to the quartz tube which was evacuated to 0.01 torr and the contents were then heated to 150°C for 2 h prior to sealing. This tube was placed in the sample well of the DTA head and an identical evacuated quartz tube (but containing no reference material) was placed in the reference well. Quartz containers of approximate volume 0.3 cm^3 , length 2 cm, and wall thickness 1 mm were used.

Apparatus

The DTA apparatus comprised a nichrome-wound vertical furnace which was controlled by a Stanton-Redcroft LVP CC220 temperature programmer giving the required heating/cooling rates of $1\text{--}12^\circ\text{C min}^{-1}$ (6°C min^{-1} being typical).

The T and ΔT signals from the Pt–Pt/13% Rh differential thermocouple were recorded on a Linseis twin-pen chart recorder. The ΔT signal required prior amplification and this was provided by a custom-built DC amplifier (gain: $\times 1000$). The thermocouples were referenced to an ice/water junction.

Direct observations of samples at high temperatures were made using a custom-built furnace with two optical ports at 180° to each other. Samples were viewed in situ using a travelling microscope of low magnification, while furnace control was achieved as before, although only the temperature of the sample was monitored.

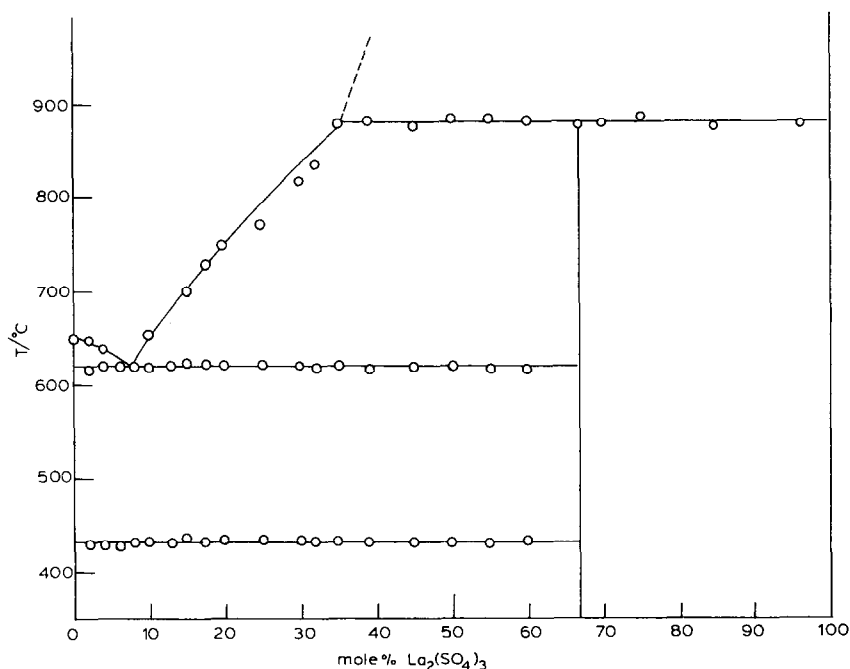


Fig. 1. Phase diagram of the system $\text{La}_2(\text{SO}_4)_3$ - Ag_2SO_4 .

RESULTS

The phase diagram obtained by DTA is shown in Fig. 1 and its main features are described below. The diagram records the transitions obtained on heating, at rates of 6°C min^{-1} , except the right-hand liquidus line which was obtained on cooling.

The morphological $\beta \rightarrow \alpha$ transition of Ag_2SO_4 [3,7] occurs at $433 \pm 3^\circ\text{C}$ on heating but exhibits supercooling and transforms at $407 \pm 6^\circ\text{C}$ during cooling. This transition is evident on heating and cooling cycles at all compositions in the range 1–61 mole%; [all compositions are expressed in terms of mole% $\text{La}_2(\text{SO}_4)_3$]. The pure Ag_2SO_4 melts at 665°C . A double salt [$2 \text{La}_2(\text{SO}_4)_3 \cdot \text{Ag}_2\text{SO}_4$; see below] is formed and this melts incongruently at $878 \pm 6^\circ\text{C}$ over the composition range 34–95 mole%. On cooling the reverse reaction exhibits supercooling and occurs at $844 \pm 5^\circ\text{C}$.

A eutectic of composition 8 mole% is formed between the double salt and Ag_2SO_4 and is detected at $618 \pm 3^\circ\text{C}$ on heating (1–61 mole%). On cooling, however, two exotherms are associated with the transition (see later).

DISCUSSION

Powder X-ray diffraction patterns of treated and untreated mixtures (67 mole%) were obtained (Philips 1040 diffractometer) and are shown in Fig. 2

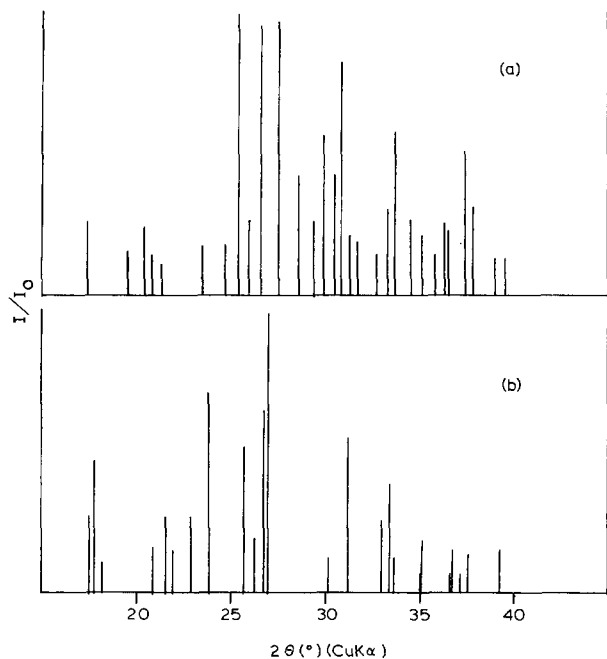


Fig. 2. X-Ray powder diffraction patterns of (a) heated, and (b) unheated mixtures [67 mole% $\text{La}_2(\text{SO}_4)_3$].

as evidence of double salt formation. One complication is that $\text{La}_2(\text{SO}_4)_3$ obtained by dehydration of the nonahydrate is not isolated in its most stable crystalline form. The anhydrous material when examined by cross-polar microscopy [8] had the appearance of a glass. However, if some Ag_2SO_4 is added to the $\text{La}_2(\text{SO}_4)_3$ and this mixture (96 mole%) is then heated to above the incongruent melting point and held there for 170 h before being slowly cooled, ($< 1^\circ\text{C min}^{-1}$) the particles assume a regular crystalline appearance. Under the cross-polars these exhibit extinction which implies a non-cubic structure. The XRD pattern is slightly modified also. (Compare also ref. 5 where similar behaviour is shown by BeSO_4 .) The unheated sample of Fig. 2(b) is a 67 mole% mixture of recrystallized $\text{La}_2(\text{SO}_4)_3$ and Ag_2SO_4 . This mixture was maintained at 1000°C for 240 h then cooled at a rate of $0.6^\circ\text{C min}^{-1}$ to provide a sample whose XRD is shown in Fig. 2(a). The formation of one double salt is indicated by other observations.

Both eutectic and the Ag_2SO_4 morphological transition terminate at 61 mole% where, even though very weak, they persist even after five heating/cooling cycles. Any double salt must therefore lie at a composition greater than 61 mole%. Allowing for the fact that under our experimental conditions Ag_2SO_4 cannot be detected in mixtures more dilute than 5 mole% Ag_2SO_4 , this puts the composition of the double salt at approximately 67 mole%. Another indication is the appearance, on first heating only, of an

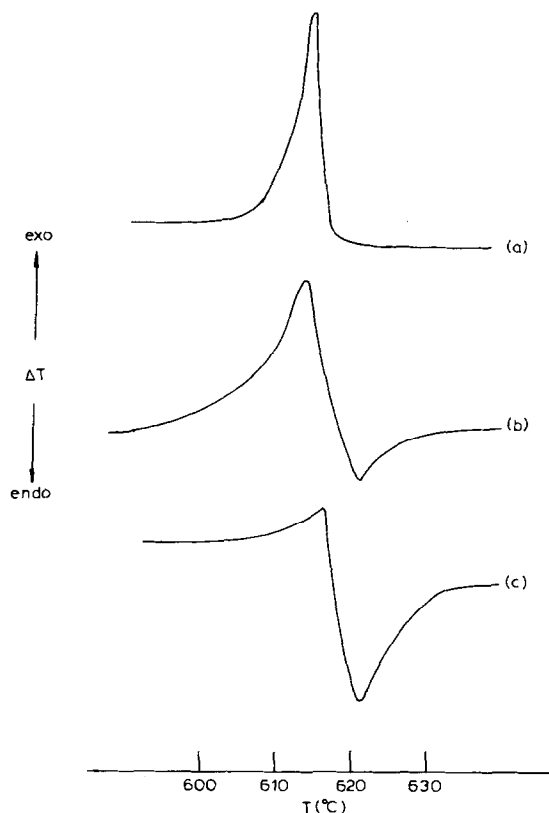


Fig. 3. DTA traces showing variation of relative magnitudes of exotherm and eutectic endotherm obtained on first heating of mixtures of composition 40 mole% (a), 35 mole% (b), and 9 mole% (c).

exotherm at $615 \pm 1^\circ\text{C}$ seen with mixtures of composition 8–95 mole%. As shown in Fig. 3, the magnitudes of the exotherm and of the eutectic endotherm which immediately follows vary with composition, the endotherm being completely swamped at compositions greater than 40 mole%.

One possible explanation for this latter effect is that heat is evolved when the double salt is formed and the intimate association with the eutectic tends to suggest that liquid plays a mechanistic role in the formation of the double salt. The exotherm is, however, observed at compositions greater than 67 mole%, a region where (in the context of the present phase diagram) liquid would not be expected. At this stage some preliminary scanning electron microscopy was conducted. A sample (67 mole%) was heated to 700°C for 72 h, removed and allowed to cool under dry N_2 . Micrographs showed that the particles had coalesced, producing smooth surfaces of a spheroid appearance, in sharp contrast to the appearance of the starting material. This evidence suggested that liquid was indeed involved in the formation of the

double salt and the fact that the sample had that appearance at the time of removal indicates that the process was still taking place. This is something which might be expected if the rate of formation of double salt was dependent upon the presence of a liquid phase. However, further work and speculation on the nature of this process is outside the scope of the present report.

Eutectic transition

As stated previously, two exothermic heat effects are associated with the eutectic transition on cooling. At $606 \pm 5^\circ\text{C}$ there is a small peak, the intensity of which varies little with composition. At $595 \pm 5^\circ\text{C}$ the larger of the two peaks is detected. The magnitude of this exotherm does vary with composition, being most intense between 4 and 13 mole% and completely engulfing the high temperature transition between 7 and 9 mole%. This "splitting" is observed at cooling rates of between 1 and 6°C min^{-1} and the difference of 10°C is always maintained.

However, when a sample of 13.5 mole% was heated to above the eutectic temperature and slowly cooled ($< 1^\circ\text{C min}^{-1}$) until the first transition was reached and allowed to equilibrate there for 30 min or more, the larger low temperature transition was not detected when cooling was resumed.

A further attempt to investigate this apparent kinetic effect was made using the optical furnace previously described. Mixtures in the composition range 0–80 mole% were examined. On heating, the eutectic transition is characterized visually by a colour change from white to intense yellow as liquid is formed. This is apparent in the composition range 4–55 mole%. The effect is observed over the stated composition range but the colour intensity is dependent on the composition of the mixture relative to that of the eutectic. On cooling, a two-stage process is seen. Again taking 13.5 mole% as an example, as the sample is cooled towards the eutectic, solid is seen floating on a clear yellow liquid; but at 605°C there is a sudden burst of needle-like crystals spreading throughout the yellow liquid. Further cooling causes more crystallization and at 595°C the remaining yellow colour suddenly disappears leaving a completely white solid. If the sample is heated to above the eutectic, cooled slowly ($< 1^\circ\text{C min}^{-1}$) until the first crystallization occurs and held steady at this temperature ($604 \pm 1^\circ\text{C}$) then complete conversion of the yellow medium to the white solid takes place in 30 min. This confirms the kinetic effect inferred from DTA and gives some physical evidence for the nature of the process which is occurring.

The splitting effect was also reproduced in the flowing gas experiments where the salts were contained in Pt cups. Overall, the flowing gas experiments gave similar, but less precise results to those carried out with sealed tubes. The optical furnace gave valuable confirmation of other DTA interpretations, since it permitted direct observation of other phase changes such as incongruent melting.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. G.S. Harris for his advice, Mr. A.S. Edwards for providing assistance with SEM, and Messrs. R.A. Batchelor and A. Reid for XRD work. D.A.C. acknowledges the support of the Science and Engineering Research Council of Great Britain.

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