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Note

THE REVERSIBILITY OF THE $\alpha \rightarrow \beta$ TRANSFORMATION OF $ZnSO_4$

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A high temperature polymorphic transformation of $ZnSO_4$ has been detected by several workers [1—4], but the temperature remains uncertain. The differential thermographs recorded by Nam [3] show a peak at 750°C on both heating and cooling, while the vapour pressure plots of Ingraham and Kellogg [4] show a change of slope at 734°C, from which the $\alpha \rightarrow \beta$ enthalpy change is calculated as 20.1 kJ $mole^{-1}$. At least two studies [5,6] contain no evidence of a transformation.

The major obstacle in a DTA study in the transformation temperature region is the onset of a two-step decomposition of $ZnSO_4$ ($\rightarrow ZnO \cdot 2\,ZnSO_4 \rightarrow ZnO$), for which reported values vary from 680°C to 850°C [5,3]. In this work, a flowing atmosphere of SO_3 suppresses the decomposition, with the result that the sulphate is thermodynamically stable up to >850°C. The consequent extension of the temperature range in which the β form is stable allows for a systematic study of the reverse transformation.

EXPERIMENTAL

Sample preparation

Fisons analytical grade $ZnSO_4 \cdot 7\,H_2O$ was dehydrated at 380°C for 48 h, desiccated under vacuum for a further 48 h, and ground to a fine powder. $MgSO_4$, prepared from Fisons analytical grade $MgSO_4 \cdot 7\,H_2O$, was chosen as the reference material because it is thermally inert in the temperature range and atmosphere involved.

Apparatus

Two calibrated Pt13%Rh—Pt thermocouples dipped into the sample and reference salts (60 mg), which were contained in silica melting tubes, 2 mm in diameter and 15 mm high. These tubes fitted closely into a ceramic heating block, 19 mm in diameter and 17 mm high, and the whole arrangement was situated in the 20 mm diameter ceramic tube of a vertically-mounted furnace. Heating and cooling were controlled by a Stanton-Redcroft temperature programmer, and the sample and difference temperatures were recorded from a digital millivoltmeter with a resolution equivalent to

0.08° C. British Oxygen Company research grade SO_2 and O_2 were dried by passage through an activated molecular sieve, and metered by needle valves to give flow rates of 24 ml min^{-1}, and 47 ml min^{-1}, respectively. A 10 cm^2 strip of Pt foil catalysed the formation of SO_3 in the vicinity of the salts; the absence of a catalyst resulted in little suppression of the decomposition. The materials used in the construction showed no sign of attack by the salts or atmosphere.

RESULTS

The DTA curves obtained at four heating and cooling rates are collected in Fig. 1. Table 1 gives T_{onset}, the sample temperature associated with deviation from a constant heating/cooling rate, and T_{peak}, the sample temperature at a peak in temperature difference. The choice of the feature of a DTA curve used to locate a transformation temperature is a disputed point [7]. A plateau in sample temperature indicates the coexistence of polymorphs at a constant temperature for a finite time and is a necessary if not a sufficient criterion of reversibility. The plateaux in the cooling curves are the most conspicuous feature of the data, and on this evidence we give the $\alpha \rightleftharpoons \beta$ transformation temperature as 730.5 ± 1.0° C.

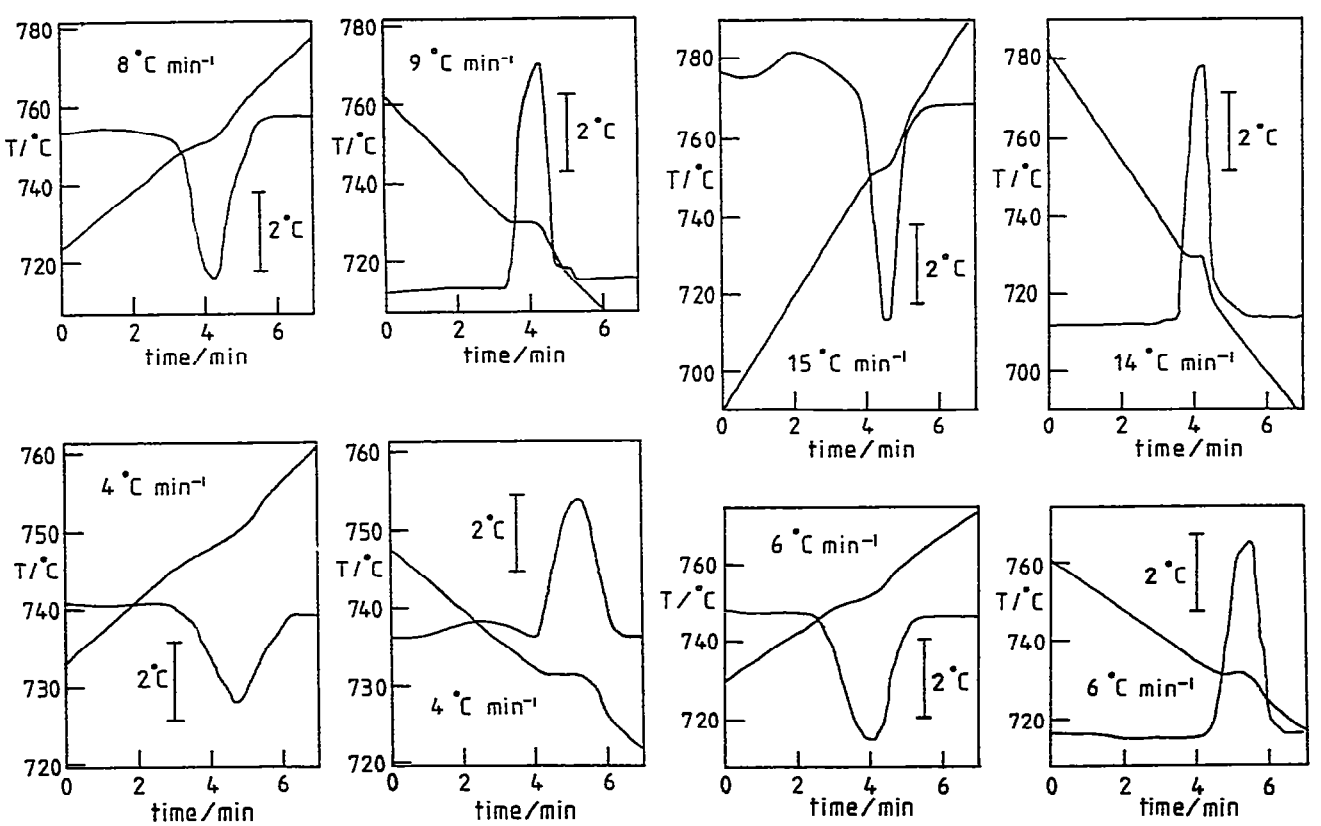

Fig. 1. Plots of sample and difference temperatures against time at four heating/cooling rates for the $\alpha \rightleftharpoons \beta$ transformation of $ZnSO_4$.

TABLE 1

DTA results for the transformation of $ZnSO_4$

Heating rate (°C min^{-1})	Cooling rate (°C min^{-1})	T_{onset} (°C)	T_{peak} (°C)
4		747.0	750.0
	4	731.5[p]	731.5
6		749.0	751.5
	6	731.5[p]	730.5
8		748.0	751.5
	9	729.5[p]	728.5
15		749.0	752.0
	14	730.0[p]	728.5

[p] Plateau in sample temperature.

The small disparity with Ingraham's value may result from the difference in purity between our analytical grade and Ingraham's reagent grade salt, an effect investigated by Rao and Mehrota [8] for the transformation of K_2SO_4. The brevity of Nam's paper makes comparison difficult, and the values of Friedrich and Blicke [1] (740°C) and Shargorodsk'i [2] (735°C) were obtained for heating only.

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REFERENCES

1 K. Friedrich and A. Blicke, Metallurgie (Halle, Ger.), 7 (1910) 323.
2 S.D. Shargorodskii, Ukr. Khim. Zh., 15 (1949) 332.
3 B. Nam, C. R., 249 (1959) 1108.
4 T.R. Ingraham and H.H. Kellogg, Trans. Metall. Soc. AIME, 227 (1963) 1419.
5 G.A. Kolta and M.H. Askar, Thermochim. Acta, 11 (1975) 65.
6 G. Hoschek, Monatsh. Chem., 93 (1962) 826.
7 W. Gutt and A.J. Majumdar, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Academic Press, London, 1972.
8 C.R.M. Rao and P.N. Mehrota, Thermochim. Acta, 29 (1979) 180.