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Note

DECOMPOSITION OF $ZnSO_4$ IN A SELF-GENERATED ATMOSPHERE

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Zinc sulphate currently receives an increased interest as a component in fused-salt electrolytes. Also of importance is its use in making ZnO (zinc-blende roasting) for the production of zinc metal.

The reported thermoanalytical studies of $ZnSO_4$ in air [1,2] have shown the decomposition to start at 610—646°C. The final decomposition product is ZnO but a basic sulphate is reported to form as an intermediate product. It can also be prepared by reacting mixtures of ZnO and $ZnSO_4$. The composition of this basic sulphate is claimed to correspond to either 2 ZnO · 3 $ZnSO_4$ [3,4] or ZnO · 2 $ZnSO_4$ [2,5,6]. A reversible phase transition of $ZnSO_4$ ($\alpha \leftrightarrow \beta$) has been observed by many authors during the initial stage of decomposition of $ZnSO_4$ to the basic sulphate. Ingraham and Kellogg [6], using the tabulated thermodynamic data and their own equilibrium pressure values, determined the transition temperature to be 1007.5 K (734.3°C). They also estimated the molar transition enthalpy using both the thermodynamic data (4820 cal) and quantitative DTA (4575 cal, K_2SO_4 as a calibration standard).

In the present work, a modified technique of self-generated atmosphere [7] was used in a combined TG—DTG—DTA analysis of $ZnSO_4$. The purpose has been to resolve the decomposition steps leading to the formation of the basic sulphate and to ZnO and, to study the phase transition of $ZnSO_4$.

The runs were made using a micro-thermobalance (Mettler TA1) with the recording capability for simultaneous TG—DTG—DTA analysis. In the experiments in self-generated atmosphere, samples (30—50 mg) of $ZnSO_4$ in Pt crucibles were covered with a compacted layer of alumina powder. The enthalpy of the phase transition for $ZnSO_4$ was estimated using K_2SO_4 for calibration of the DTA peak area.

RESULTS AND DISCUSSION

In a preliminary run, $ZnSO_4$ powder was heated at 8°C min^{-1}. Decomposition started at ca. 630°C. A DTA peak indicating the $\alpha \rightarrow \beta$-$ZnSO_4$ transition appeared at ca. 740°C. The DTA and DTG curves displayed two consecutive peaks during this decomposition in the temperature regions 630—815 and 815—945°C. The X-ray pattern of the specimen cooled from 815°C showed

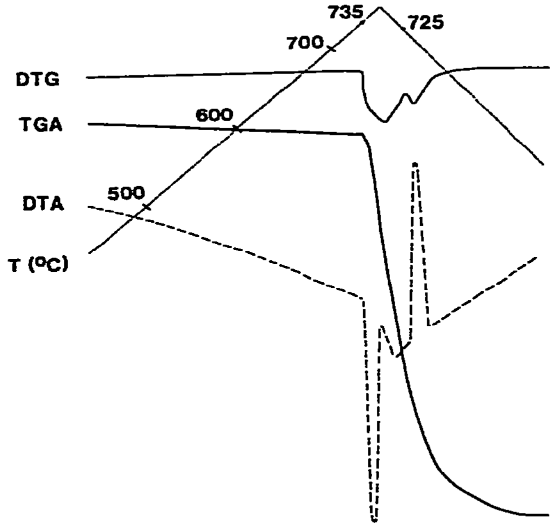

Fig. 1. Thermogram showing the decomposition of $ZnSO_4$ in self-generated atmosphere in the temperature region of $ZnSO_4$ ($\alpha \rightarrow \beta$) phase transition. (The total weight loss, TG curve, corresponds to about 6% conversion of $ZnSO_4$ to $ZnO \cdot 2\,ZnSO_4$.)

the presence of $ZnSO_4$ and of the basic sulphate according to the ASTM index [3,6].

Figure 1 shows part of the thermogram [heating (cooling) rate: 6°C min^{-1}] obtained for a run in the self-generating atmosphere. The salt is seen to be stabilized (TG) up to 735°C (cf. above) where the decomposition sets in rapidly, coinciding with the start of the $\alpha \rightarrow \beta$ transition. On decreasing the temperature, the β-$ZnSO_4$ supercools slightly and the transition occurs at 723—725°C. The DTG curve shows an increased decomposition rate during these phase transitions. This is a typical indication of the so-called Hedvall effect [8] (decreased activation energy for decomposition during a phase transition). The concurrent start of the abruptly initiated decomposition and phase transition gives an unusually sharp indication of the transition temperature (735°C) which is very close to the thermodynamically determined equilibrium temperature [6] of 734.3°C.

The evaluation of the $\alpha \rightarrow \beta$ transition enthalpy was carried out in two independent runs. Correction was made for the partial decomposition of $ZnSO_4$ but not for the peak area variation with temperature for the K_2SO_4 calibration peak. The mean deviations for the K_2SO_4 and $ZnSO_4$ peak areas were about 8% and 3%, respectively. The peak-to-peak area ratio per mole was 1.26 (2.138 in ref. 6) giving, finally, the transition enthalpy of 2.7 ± 0.3 kcal $mole^{-1}$ $ZnSO_4$. This value is, of course, significantly lower than that of Ingraham and Kellogg [6]. The numerical precision of their reported DTA enthalpy (4575 cal) may suggest that the estimation may lack a sufficient statistical foundation. On the other hand, to determine this transition enthalpy from the enthalpies of formation is possible only when these enthalpies (being typically one or two orders of magnitude larger than those of solid state transition) are known very accurately.

The $ZnSO_4$ specimen (covered by a compacted alumina layer) was heated at 765°C for about 2 h. The TG curve then essentially stabilized. The weight loss was 16.6 wt. % and corresponded closely to the calculated value (16.5 wt. %) for the formation of the intermediate basic sulphate of the formula $ZnO \cdot 2\ ZnSO_4$. Thus, the technique of self-generated atmosphere could be successfully applied to resolving the two dissociation steps of $ZnSO_4$ and to confirming the stoichiometry of the basic sulphate ($ZnO \cdot 2\ ZnSO_4$). This resolution is possible probably because the dissociation pressure (SO_3) of this basic sulphate is one order of magnitude lower than that of $ZnSO_4$ [6].

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