Thermochimica Acta, 11 (1975) 65–72

THERMAL DECOMPOSITION OF SOME METAL SULPHATES

G. A. KOLTA AND M. H. ASKAR
National Research Centre, Dokki, Cairo (Egypt)
(Received 21 July 1974)

ABSTRACT

The thermal decomposition temperatures of some metal sulphates (iron, copper, cobalt, nickel, zinc and lead sulphates) have been investigated by TG and DTA. The mechanism of decomposition of these sulphates is discussed, making use of additional information obtained from isothermal studies and X-ray diffraction measurements. The activation energies of these reactions were calculated and found to increase, with almost the same increments, in the order $Zn < Fe < Co < Ni < Cu$.

INTRODUCTION

The thermal decomposition of metal sulphates plays an important role during metallurgical dead-roasting processes. The stability of the sulphates in high-temperature reactions and during sulphatation roasting has also been paid attention to in this study. The thermal decomposition of $Fe_2(SO_4)_3$, $CuSO_4$, $ZnSO_4$, $CoSO_4$, $NiSO_4$ and $PbSO_4$ has been studied in previous papers [1–19]. However, the values reported for the same sulphate varied widely, making any dependable correlation impossible.

It is therefore of interest to investigate the thermal decomposition of these sulphates by TG and DTA. Little attention[20–23] has been given to study the mechanism of decomposition of these sulphates. To investigate this mechanism, isothermal experiments were performed in the range of the decomposition temperatures, from which the activation energies were accurately derived. The TG and isothermal studies were performed in a flow of air and not in equilibrium systems with the decomposition products.

The final stage of decomposition and the formation of intermediate products have been observed from the DTA and TG curves. The formation of these compounds has also been detected from the X-ray analysis of the final and intermediate products.

EXPERIMENTAL

The chemicals used were B.D.H. analytical grade. The anhydrous sulphates were prepared by heating the hydrated sulphates up to 400 °C, applying the recommendations of Ostroff and Sanderson[3]. The chemical analysis of the anhydrous sulphates indicated that these compounds contain the theoretical values of metal and sulphate (±0.5%).

The TG was conducted with an automatically recording thermobalance provided by Gebrüder Netzch-Selb, G.F.R. The weight change was recorded (on a 6-in. chart over a range of 240 mg) simultaneously with temperature up to 1100°C at a rate of 5°C min^{-1}.

The isothermal study at a series of fixed temperatures was also followed with the thermobalance, which was equipped with a device to keep the temperature constant arbitrarily during the whole experiment. The temperature of the furnace was first raised to the required value and the specimen was then shock-heated by lowering the furnace to surround it.

The DTA was carried out using an automatically recording Linseis apparatus, Type L 160 KS (G.F.R.): the heating rate was 5°C min^{-1}. For TG and DTA, the technique used was according to the recommendations of McAdie[24].

X-ray diffraction patterns were obtained with the aid of a Philips unit, Type PW 1010. The diffraction patterns of the different products were compared with the corresponding ASTM cards.

RESULTS

TG

The results shown in Fig. 1 for six anhydrous metal sulphates are represented as relative weight changes in g g^{-1} vs. temperature. The TG curves show certain characteristics which can be summarised as follows:

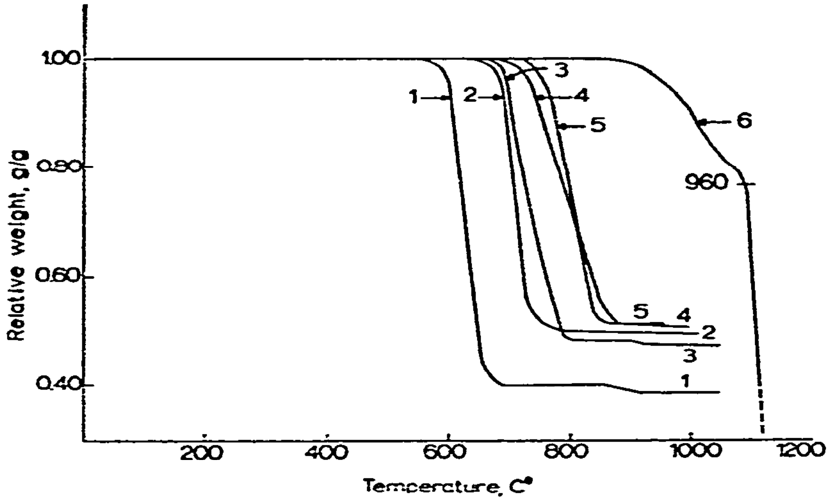

Fig. 1. Thermogravimetric analysis of: (1) $Fe_2(SO_4)_3$; (2) $CuSO_4$; (3) $NiSO_4$; (4) $ZnSO_4$; (5) $CoSO_4$; and (6) $PbSO_4$. Heating rate: 5°C min^{-1}.

(i) The decomposition temperature of these sulphates in air differs greatly from that mentioned in the literature. Table 1 illustrates the different data in detail.

TABLE 1

DECOMPOSITION TEMPERATURES OF SOME METAL SULPHATES

Metal sulphates	*Decomposition temperature*			
	By TG		*By DTA*	
	Published work	*Present investigation*	*Published work*	*Present investigation*
$Fe_2(SO_4)_3$	600[1]	575	—	580
$CuSO_4$	598[3,7,8], 600[25], 620[17], 624[1,4,5]	625	598[3], 750[26]	655
$NiSO_4$	675[3], 730[9], 750[10], 848[18]	675	675[3], 840[25]	678
$CoSO_4$	550[15], 708[3], 730[9], 820[16], 904[18]	720	708[3], 400[26]	722
$ZnSO_4$	610[17], 646[3], 675[11], 846[18]	675	646[3], 740[26]	682
$PbSO_4$	637[20], 803[3], 860[19], 971[1]	870	803[3]	880

(ii) The rates of weight loss show slight variations. The slopes of the TG curves increase in the order Zn>Fe>Co>Ni>Cu. This phenomenon will be compared with the results of isothermal studies (vide infra).

(iii) Other processes, rather than decomposition of sulphates, are displayed at temperatures higher than that of sulphate decomposition, viz., partial transformation to other oxides ($Fe_2O_3 \rightarrow Fe_3O_4$) and sublimation of metal oxides (e.g., PbO). These processes are accompanied by decrease in weight as can be seen in the TG curves. For other oxides, there is a tendency for each curve to flatten out towards a limiting value at different temperatures which is characteristic of the metal sulphates.

DTA

The DTA curves illustrated in Fig. 2 show several interesting features, of which the most important are the initial temperature of decomposition and the different subsequent endothermic peaks displayed by the metal sulphates. There is a slight difference between the results of TG and DTA as depicted from Table 1. This can be attributed to the differences in pressure of the gaseous products in both techniques. There are also wide discrepancies between the values reported in the previous investigations and those given in this work. This is ascribed mainly to differences in the method of investigation and the method of preparation of the sulphates.

The small endothermic peaks which can be observed close to the end of the decomposition, may be attributed to crystallization or to a rearrangement process, such as from amorphous to crystalline[25]. It is probable that removal of SO_3 causes disruption of the crystal and, at higher temperatures, the oxide crystallizes releasing some heat of crystallization. In addition the DTA curve of $CuSO_4$ manifests a second well-defined endothermic peak in the temperature range 800 to 880°C. This may correspond to decomposition of basic sulphate ($2CuO \cdot SO_3$) to the oxide (CuO). This relatively high decomposition temperature, in comparison with the value of the TG

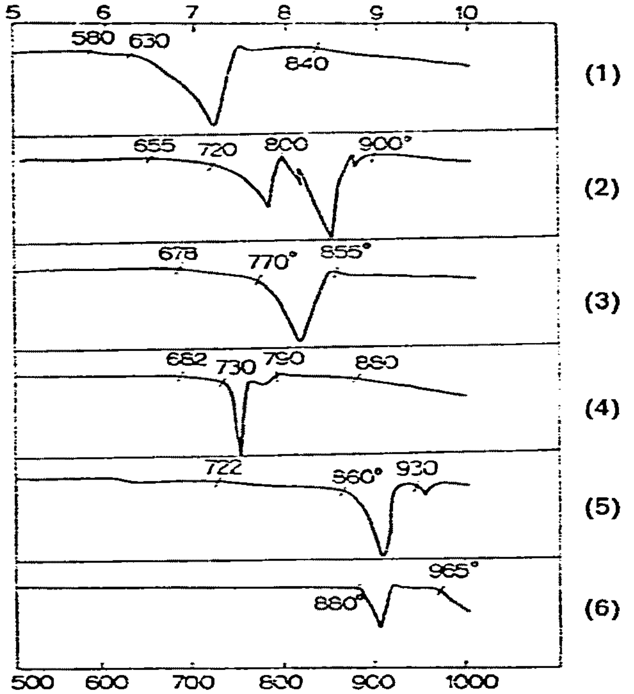

Fig. 2. Differential thermal analysis of: (1) $Fe_2(SO_4)_3$; (2) $CuSO_4$; (3) $ZnSO_4$; (4) $ZnSO_4$; (5) $CoSO_4$; and (6) $PbSO_4$. Heating rate: 5 °C min^{-1}.

curve, can be correlated with the variation in the partial pressure of SO_3 in the vicinity of the basic sulphate. In the literature there is very little recognition of this aspect[25,26].

The deflection of the DTA curves after complete decomposition of the metal sulphate corresponds either to decomposition or volatilization of the metal oxide. It is probable that Fe_2O_3 is decomposed to Fe_3O_4 at temperatures higher than 840 °C. A similar trend is noticed in the DTA curve of $CuO \rightarrow Cu_2O$. However, the sloping trend of the DTA decomposition curves of $ZnSO_4$ and $PbSO_4$ at temperatures higher than 880 and 965 °C, respectively, can be related to the process of sublimation of their oxides. In addition, deoxygenation may also take place at these relatively high temperatures for both ZnO and NiO. One may also expect to obtain more information on the influence of temperature on the final decomposition products by X-ray analysis.

X-ray analysis

The X-ray analysis of the final products obtained at different extents of decomposition and at 1000 °C revealed that the intermediate products which were investigated elsewhere[1,4,5,12], could not be identified in this investigation. The patterns obtained are mixtures of the starting material and the respective oxide. However, at 1000 °C, the final products show marked variable patterns, especially for iron ($Fe_2O_3 + Fe_3O_4$) and copper ($CuO + Cu_2O$). ZnO and NiO patterns show a slight variation from those given by ASTM cards. PbO is detected in the temperature range 900 to 1000 °C, without any other patterns corresponding to metallic lead, as was considered before[1]. Co_3O_4 is the final product of decomposition of $CoSO_4$, owing to instantaneous oxidation of the oxide CoO to Co_3O_4 when the reaction proceeds in air. The oxidation process could not be detected from the results of DTA or TG.

The intermediate products which could not be observed by X-ray diffraction analysis may be present in amorphous forms. It is difficult to exclude their formation during the decomposition processes. The same conclusion was reached by Kamel et al.[27], during decomposition of ferrous sulphate.

Isothermal decomposition

The kinetics of isothermal decomposition in air were studied in the respective ranges of decomposition. A typical set of isotherms, obtained for five sulphates, is shown in Fig. 3 for $Fe_2(SO_4)_3$. On the basis of several theories put forward to account for the kinetics of such reactions, the results of the present investigation do agree with the law achieved by Mampel[28], applied to the decomposition of solids in the form of a powder. Assuming that the powder is composed of a large number of isotropic spheres of uniform radii, Mampel applied a fractional order reaction which is a close approximation to the one-third power law of contracting spheres, possessing a constant velocity of propagation of the interface. A plot of $(W/W_0)^{1/3}$ vs. time gave a linear relationship, where W_0 is the initial mass of reactant and W is the mass at time t. The process of decomposition is thus influenced by the formation of a progressively thickening layer of oxide which results in producing an impendence effect due to the restriction of diffusion imposed by the oxide formed and to the possibility of its recombination with SO_3 at the interface. The same conclusion was reached by Fahim and Kolta[29] in the decomposition of hydroxides and generally given by Sharp et al.[30] in solid-state decomposition reactions.

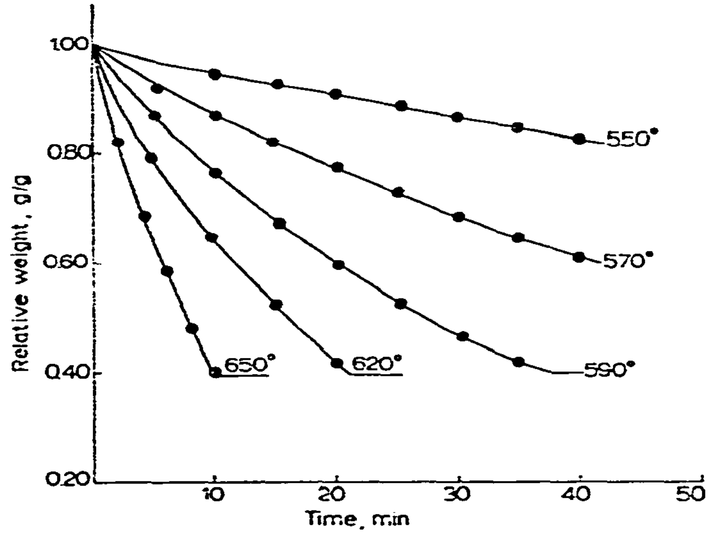

Fig. 3. Relative weight changes of isothermal decomposition of $Fe_2(SO_4)_3$.

Copper sulphate shows a marked difference from other sulphates as it is characterized by a break in the linear relationship (Fig. 4). The significance of this break can be interpreted on the assumption of the presence of two-step processes during decomposition of $CuSO_4$ to CuO via basic copper sulphate according to the following equations:

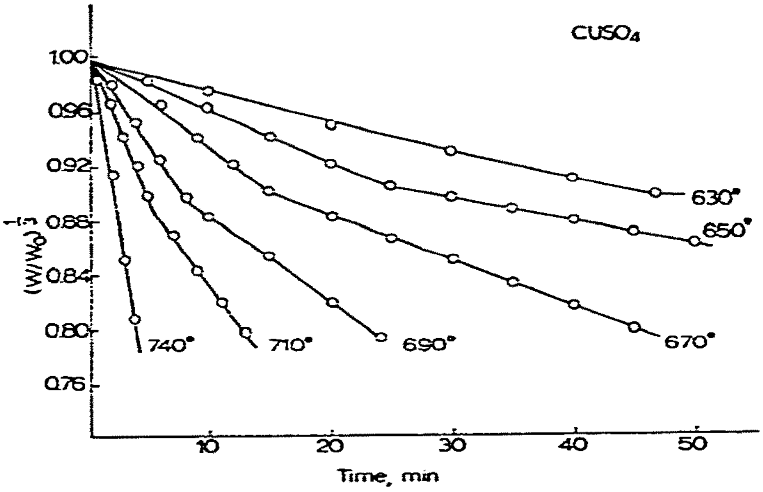

Fig. 4. Application of Mample's equation on the isothermal decomposition curves of $CuSO_4$.

$$2CuSO_4 \rightarrow 2CuO \cdot SO_3 + SO_3$$

$$2CuO \cdot SO_3 \rightarrow 2CuO + SO_3$$

The velocity constant, K, is obtained from the linear relationship of $(W/W_0)^{1/3}$ vs. t, at different temperatures for all sulphates. A plot of log K against the reciprocal of the absolute temperature, gives satisfactory straight lines, from which it is possible to evaluate the energy of activation from the Arrhenius equation:

$$\frac{d \ln K}{d(1/T)} = -E/R$$

The activation energies of the decomposition of metal sulphates, evaluated from Fig. 5, are given in Table 2.

It can be noticed that despite the fact that the isothermal decomposition of these sulphates can be considered in the same order of magnitude, the slight variation in the activation energies increases in the order $Zn < Fe < Co < Ni < Cu$. The same conclusion was deduced from the slopes of the curves given in Fig. 1 for the TG results. The activation energy calculated from the slopes of the TG curves was found to be nearly the same as that deduced from the isothermal results. The same result was also mentioned by Satava and coworker[31,32].

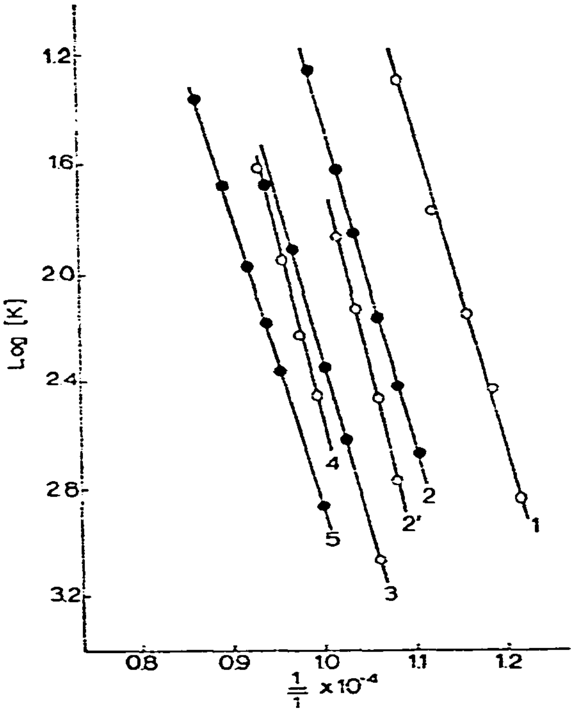

Fig. 5. Application of Arrhenius equation to the rate constants for the reactions: (1) $Fe_2(SO_4)_3 \rightarrow Fe_2O_3$; (2) $CuSO_4 \rightarrow \frac{1}{2}CuO \cdot CuSO_4$; (2') $CuO \cdot CuSO_4 \rightarrow 2CuO$; (3) $NiSO_4 \rightarrow NiO$; (4) $CoSO_4 \rightarrow CoO \rightarrow \frac{1}{3}Co_3O_4$; (5) $ZnSO_4 \rightarrow ZnO$.

TABLE 2

ACTIVATION ENERGIES OF THERMAL DECOMPOSITION OF SOME METAL SULPHATES

Reaction	*Activation energy (kcal mol^{-1})*
$ZnSO_4 \rightarrow ZnO$	22.9
$Fe_2(SO_4)_3 \rightarrow Fe_2O_3$	25.5
$Co(SO_4)_2 \rightarrow CoO \rightarrow 1/3Co_3O_4$	26.5
$NiSO_4 \rightarrow NiO$	27.6
$2\,CuSO_4 \rightarrow (CuO \cdot CuSO_4)$	25.5
$(CuO \cdot CuSO_4) \rightarrow 2CuO$	29.5

The thermal decomposition of metal sulphates can be considered as a complex process. The temperature at which the decomposition rate becomes perceptable depends mainly on the mechanism of decomposition and the diffusion of SO_3 through the crystals which have different structures. One must not ignore the fact that the decomposition temperature is also dependent on the electronegativity radius and polarizing power of the metal cations. In the present investigation, it was difficult to support these assumptions by expressing accurate relationships between these possible factors affecting decomposition and the temperatures of decomposition of sulphates. For example, while decomposition of ferric sulphate starts at 700°C, cobalt sulphate is decomposed at 720°C, in spite of the fact that both metals have nearly the same atomic radius (0.83 Å for Fe and 0.82 Å for Co).

REFERENCES

1 C. Duval, *Inorganic thermogravimetric analysis*, 2nd ed. Elsevier, 1963, for iron sulphates p. 327, for $CuSO_4$ p. 382, for $NiSO_4$ p. 358, for $ZnSO_4$ p. 407, for $PbSO_4$ p. 625, for $CoSO_4$ p. 339.
2 C. Duval, *Anal. Chim. Acta*, 20 (1959) 23.
3 A. G. Ostroff and R. T. Sanderson, *J. Inorg. Nucl. Chem.*, 9 (1959) 45.
4 Y. Marin and C. Duval, *Anal. Chim. Acta*, 6 (1952) 47.
5 C. Duval, *Anal. Chim. Acta*, 16 (1957) 223.
6 T. R. Ingraham and P. Marier, *Trans. Met. Soc. AIME*, 233 (1965) 363.
7 C. Rigault, *Atti Accad. Sci. (Torino)*, 93 (1958) 489.
8 B. E. Gordon and A. M. Denisov, *Ukrain. Khim. Zhur.*, 19 (1953) 368; *C.A.*, (1955) 5062.
9 R. Fruchart and A. Michel, *R. H. Acad. Sci.*, 246 (1958) 1222.
10 N. Demassieux and C. Malard, *C. R. H. Acad. Sci.*, 245 (1957) 1544.
11 T. R. Ingraham and P. Marier, *Trans. Met. Soc. AIME*, 242 (1968) 20.39.
12 Bui-Nam, *C. R. H. Acad. Sci.*, 249 (1959) 1108.
13 T. R. Ingraham and P. Marier, *Thermochim. Acta*, 1 (1970) 39.
14 F. Paulik and L. Erdey, *Acta Chim. Acad. Sci, Hung.*, 13 (1957) 117.
15 T. R. Ingraham and P. Marier, *Can. J. Chem. Eng.*, 41 (1963) 170.
16 R. Duval and C. Duval, *Anal. Chim. Acta*, 5 (1951) 71.
17 A. J. Hegiis and K. Fukker, *Z. Anorg. Allg. Chem.*, 284 (1956) 20.
18 C. Malard, *Bull. Soc. Chim. Fr.*, 7 (1961) 2296.
19 H. N. Terem and S. Akalan, *C. R. Acad. Sci. (Paris)*, 232 (1951) 973.
20 P. W. Jacobs and F. C. Tompkins, in W. E. Garner (Ed.), *Chemistry of the Solid State*, Butterworths, London, 1955, Ch. 7.
21 T. R. Ingraham, *Can. Met. Quart.*, 3 (1964) 221; and 5 (1966) 109.
22 J. M. Thomas and G. D. Renshow, *J. Chem. Soc. (A)*, (1969) 2749.
23 T. Palanisamy, J. Gopalakrishnan, B. Viswanathan, V. Srinivasan and M. V. C. Sastri, *Thermochim. Acta*, 2 (1971) 265.
24 H. G. McAdie, *Anal. Chem.*, 37 (1967) 543.
25 R. C. Mackenzie, *Differential Thermal Analysis*, Vol. 1, Academic Press, London, 1970.
26 H. J. Borchardt and F. Daniels, *J. Phys. Chem., Ithaca*, 61 (1957) 917.
27 A. H. Kamel, Z. Sawires, H. Khalifa, S. A. Saleh and A. M. Abdallah, *J. Appl. Chem. Biotechnol.*, 22 (1972) 591.
28 K. L. Mampel, *Z. Phys. Chem., Abt. A*, 187 (1940) 43 and 257.
29 R. B. Fahim and G. A. Kolta, *J. Phys. Chem.*, 74 (1970) 2502.
30 K. H. Sharp, G. W. Brindley and B. N. N. Achar, *Numerical Data for some Commonly Used Solid State Reaction Equations*, Brindley and Ray, Scientific Report, No. AFCRL-65-606-(1965) 94-104.
31 V. Satava and F. Skvara, *J. Amer. Ceram. Soc.*, 52 (1969) 591.
32 V. Satava, *Thermochim. Acta*, 2 (1971) 423.