Thermochimica Acta, 158 (1990) 293–300
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF CADMIUM SULPHATE *

HIROAKI TAGAWA and KATSUYA KAWABE

Institute of Environmental Science and Technology, Yokohama National University, 156 Tokiwadai, Hodogaya-ku, Yokohama 240 (Japan)

(Received 25 July 1989)

ABSTRACT

The thermal decomposition of $CdSO_4$ in the form of a disk-shaped pellet was studied in flowing high-purity nitrogen by use of an electrobalance. As the product oxide was vaporised at temperatures as high as 1000 ° C, the decomposition rate constant was determined below 840 ° C. The reaction proceeded from the surface of a pellet yielding an oxide layer. The growing rate of the layer fitted an equation derived from a model in which the rate-determining step is the decomposition reaction, $dx/dt = k$, where k is a rate constant, x is the oxide layer thickness and t is time. The activation energy for the decomposition of $CdSO_4$ was 289 kJ mol^{-1}, which was close to the enthalpy of the decomposition of $CdSO_4$.

INTRODUCTION

There have been many investigations into the thermal decomposition of metal sulphates; however, discrepant values have been reported for the same compound and there has been no systematic research into their decomposition. The present authors have studied the thermal decomposition behaviour of 16 metal sulphates using thermogravimetry (TG) [1] and the kinetics of the decomposition of the sulphates of iron(III), cobalt, nickel, copper and zinc, which belong to the first row of the transition elements [2]. The results can be summarised as follows.

(i) The thermal decomposition of the metal sulphates occurs at around the temperature at which the decomposition SO_3-pressures have a certain value, namely approximately 1×10^{-4} atm.

(ii) The initial decomposition temperatures for trivalent metal sulphates are lower than those for divalent metal sulphates. This leads to the fact that the decomposition temperatures for divalent metal sulphates are lower than those for the monovalent metal sulphates under thermodynamic considera-

---

* Paper originally presented at the Fall 1987 meeting of the Electrochemical Society, held in Honolulu, Hawaii.

0040-6031/90/$03.50

tion. Thus, it can generally be deduced that the higher the oxidation state of the metal in the metal sulphate, the less stable the sulphate.

For the kinetics of the isothermal decomposition of pelletised specimens, the following results were obtained [2]:

(i) The decomposition occurs on the surface of the pellet, not on a particle, and the newly formed product layer on the sulphate proceeds towards the interior.

(ii) The thickness of the product layer is proportional to the heating time, for sulphates of transition elements.

(iii) The activation energies for the thermal decomposition are closely related to the standard enthalpies for the decomposition.

In the present work, the thermal decomposition of cadmium sulphate, cadmium being a second-row transition element, was examined by TG and differential thermal analysis (DTA) and the rate constants were determined isothermally using an electrobalance.

EXPERIMENTAL

Hydrated cadmium sulphate, $CdSO_4 \cdot 2.4H_2O$, was used as a starting material. The sulphate was provided by Kanto Chemical Co. in guaranteed reagent grade. The hydrate was ground and used for TG and DTA. For the kinetic study, the hydrate was converted to the anhydrate by heating at 300 °C in air, then it was compacted into disk-shaped pellets, 7 mm in diameter and 1.5 mm in thickness, at 3000 kg cm^{-2}. The bulk density was 77% of the theoretical.

The non-isothermal decomposition was examined using a TG–DTA apparatus (Shinku-Riko Co., type TGD-5000). The details of the apparatus were described in ref. 3, where a powder specimen of 100 mg was placed in a Pt sample holder, 8 mm in diameter and 10 mm in height, and heated at a rate of 5 °C min^{-1} in a 100 cm^3 min^{-1} air flow.

The apparatus used for examining the isothermal decomposition consisted of an electrobalance (Cahn, model 2000), an electric resistance furnace, 35 mm inner diameter and 200 mm in length, a gas supply system and vacuum pumps. An approximately 200-mg pellet sample, loaded onto a Pt hook, was suspended by means of a platinum wire from one end of the balance arm in the heating zone. Experiments were carried out in flowing high-purity nitrogen at 200 cm^3 min^{-1}.

As was found in the decomposition of sulphates of transition elements [2], in the case of $CdSO_4$ the product oxide was formed on the surface of the sulphate pellet, and the phase boundary between the sulphate and the oxide moved towards the interior with nearly the same product thickness. The decomposition rate, k, is defined as the ratio of oxide layer thickness to time. The thickness is calculated geometrically from the fraction decomposed, α

$$1 - \alpha = (1 - x'/R)^2(1 - x'/H) \qquad (1)$$

where x' is the apparent thickness, H is half the height and R the radius of a pellet. In order to evaluate the decomposition rate constant of metal sulphates with different bulk densities, the real thickness of the product layer with theoretical density, x, was calculated using the equation $x = \gamma_L x'$. The factor γ_L is defined as the cubic root of the ratio of filling density, which is the ratio of the bulk density to the theoretical. The value was 0.908 for $CdSO_4$.

RESULTS AND DISCUSSION

TG and DTA curves for the thermal decomposition of cadmium sulphate hydrate are shown in Fig. 1. In the figure, weight loss is shown in moles of crystalline water per mole of SO_4 ion for dehydration, and in percentage loss of SO_3 for the decomposition of the anhydrous sulphate, instead of the overall fraction decomposed. The number of moles of crystalline water for $CdSO_4$ changes step-wise from 2.4 to zero. The initial decomposition temperature, i.e. the temperature at which a TG curve begins to deviate from the base line, was 842 °C. Two endothermic peaks which appear at 786 and 826 °C on the DTA curve, correspond to the phase transitions. After completion of the decomposition, the weight loss due to vaporisation of the product CdO was clearly seen above 1030 °C.

When experiments were carried out at temperatures as high as 1000 °C,

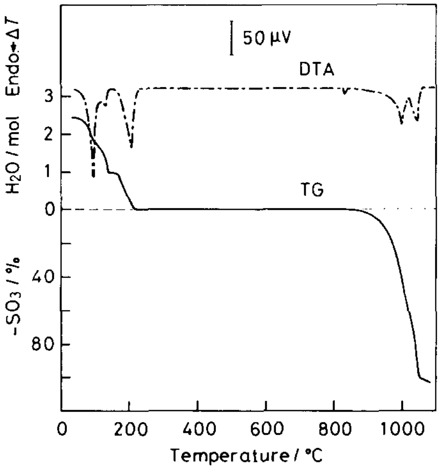

Fig. 1. TG and DTA curves of $CdSO_4 \cdot 2.4H_2O$ at 5 °C min^{-1} in a 100 cm^3 min^{-1} air flow.

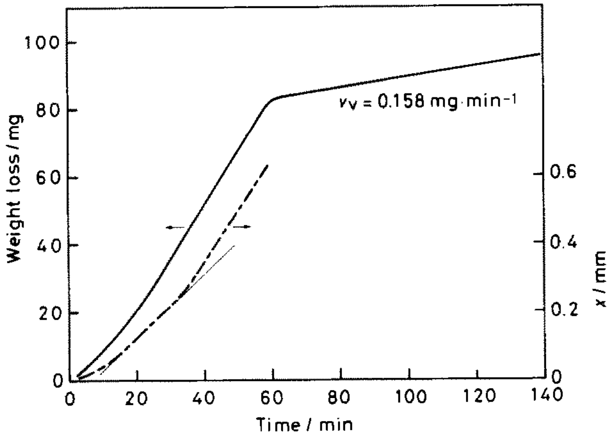

Fig. 2. Weight loss for $CdSO_4$ at 1000 °C in a 200 cm^3 min^{-1} high-purity nitrogen flow. The thickness, x, of the product layer calculated from the weight loss is also shown.

weight loss due to the vaporisation of the product was observed to occur during and after the decomposition. The run at 1000 °C is shown in Fig. 2. Here, during the sulphate decomposition, the maximum gradient of weight loss against time is 1.23 mg min^{-1} for a sample weight of 202.91 mg $CdSO_4$. The vaporisation, seen in the figure after 60 min, occurs at the rate of 0.158 mg min^{-1}. To evaluate vaporisation rates of CdO, the weight loss of CdO was examined above 800 °C in a 200 cm^3 min^{-1} nitrogen flow using a disk-shaped pellet with the same dimensions as the sulphate sample. The weight loss of CdO was actually observed to occur above 850 °C, and the weight loss was approximately proportional to time at any temperature. At six temperatures between 850 and 1000 °C, the relationship between vaporisation rate and temperature can be written v_v (mg s^{-1}) $= 3.50 \times 10^{12} \exp(-324200/RT)$, where the heat of vaporisation is 324 kJ mol^{-1} and R is the gas constant.

The vapour pressures in an inert gas flow at steady state are calculated from the following equation [4]

$$p = (k/v)(RT/M) \qquad (2)$$

where p is the equilibrium pressure, k the weight loss, v the flow rate of an inert gas and M the gram molecular weight. It is reported that the vaporisation of CdO takes place predominantly by dissociation into gaseous Cd and O_2 below 1150 K [5–7]

$$CdO(s) = Cd(g) + O_2(g) \qquad (3)$$

When calculated using eqn. (2), the vapour pressures of Cd(g) over the oxide are 1.2×10^{-4} and 6.4×10^{-4} atm at 925 and 1000 °C, respectively. The vapour pressures of Cd(g) at temperatures between 880 and 1110 °C have been determined using the transpiration method by Gilbert and Kitchener

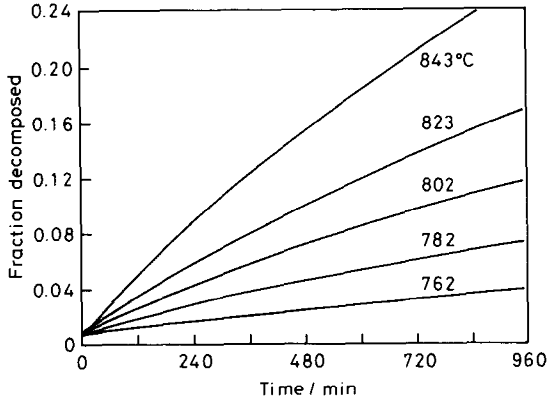

Fig. 3. Relation between fraction decomposed and time for $CdSO_4$ in a 200 cm^3 min^{-1} high-purity nitrogen flow.

[8]. Their results, which are in agreement with Cd vapour pressures calculated using thermodynamic functions [9], are given by the equation: log P_{Cd}(atm) = 7.1272 − 12548/T. Our results are about a third of their values. This discrepancy may be due to the conditions in the transpiration method. According to thermodynamic calculations, cadmium vapour pressures over the oxide are not affected by the partial pressure of the impurity oxygen contained in a flow of 'high-purity' nitrogen.

The heat of vaporisation of CdO obtained in the present work is 324.2 kJ mol^{-1}. The heat of vaporisation reported by some investigators are 360.3 [8], 359 kJ mol^{-1}, at the average temperature of 965 K, and 365 kJ mol^{-1} as the 2nd law heat [6]. The standard enthalpy of vaporisation of CdO(s) into Cd(g) and O_2(g), H_{v1100}, was calculated as 359 kJ mol^{-1} using a database in ref. 9.

Because of the vaporisation of CdO, the thermal decomposition runs for $CdSO_4$ were performed below 840 ° C, although the reaction rate constant was not so large. Figure 3 shows the relation between the fraction decomposed and time, at various temperatures.

The mechanism of the thermal decomposition was determined by the fitting equations deduced from theoretical models. Two models were considered: eqn. (4) is derived from the model that considers that the rate is controlled by chemical reaction, i.e. the thermal decomposition which occurs at the phase boundary between sulphate and oxide

$$x = k_C t \tag{4}$$

and eqn. (5) is obtained from the model based on the rate being controlled by diffusion of the product gases through the oxide layer

$$x^2 = k_D t \tag{5}$$

Figure 4 shows the relation between the thickness of the product layer and time. It can be seen that the curves are nearly linear. The linear curves

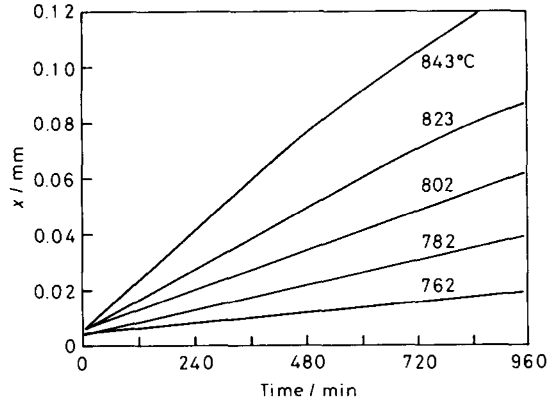

Fig. 4. Relation between thickness of the oxide layer and time for $CdSO_4$. The curves were calculated from the data in Fig. 3.

indicate that the decomposition of $CdSO_4$ proceeds according to eqn. (4).

When metal sulphate decomposes, the oxide formed has a volume different from the volume of the original sulphate. The volume change of the product may affect the reaction mechanism. Pilling and Bedworth's rule [10] is known to apply to the oxidation of metals. The formation of a protective layer can be evaluated from the criterion whether the ratio of the molar volume of the product oxide to that of the metal is larger or smaller than 1. If the ratio is smaller than 1, the protective layer will not be formed, and the rate-determining step will probably be due to the chemical reaction. This concept could be applied to the decomposition of metal sulphates. The ratio of the molar volume of oxide to that of sulphate is in the range 0.2–0.4 for all metal sulphates, e.g. 0.36 for $CdSO_4$. From Pilling and Bedworth's rule, it can be deduced that the rate-controlling mechanism of the decomposition of transition metal sulphates is chemical reaction at the phase boundary.

Figure 5 shows the relation between the logarithm of the decomposition rate constant and the reciprocal of the absolute temperature for $CdSO_4$. In the figure, the $\ln k_C$ versus $1/T$ curves for the sulphates of iron(III), cobalt, nickel, copper and zinc are also shown. The relation between $\ln k_C$ and $1/T$ for $CdSO_4$ is linear. In the figure, the calibrated result obtained at 1000 °C is also shown. From Fig. 5, the order of the curves from lower toward higher temperatures is as follows: $Fe_2(SO_4)_3$, $CuSO_4$, $CoSO_4$, $NiSO_4$, $ZnSO_4$ and $CdSO_4$. The order is similar to the order of the standard enthalpy per mole of SO_3 for the decomposition of the sulphates at 298.15 K.

The activation energy for the chemical reaction was calculated according to the equation

$$k = C \exp(-Q/RT) \tag{6}$$

where k is the reaction rate constant, C is a constant and Q is the activation energy. The slope of each line in Fig. 5 gives the activation energy for the

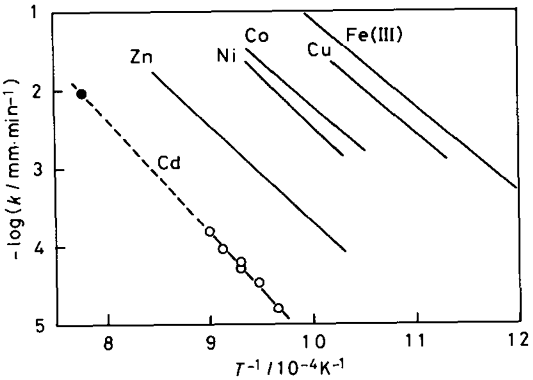

Fig. 5. Relation between decomposition rate constant and temperature for $CdSO_4$. The plotted data are for $CdSO_4$: o, experimental values directly obtained from weight loss; ●, values corrected for weight loss due to vaporisation; and ———, results previously reported [2] for sulphates of iron(III), cobalt, nickel, copper and zinc.

decomposition. The activation energy for $CdSO_4$ was 289.3 ± 2.9 kJ mol^{-1} of SO_3.

When an endothermic reaction such as the decomposition of sulphates or carbonates occurs, the energy required for the reaction is supplied from the surroundings to the reaction interface through the product layer. The heat flow is important for the reaction to proceed. If the reaction is controlled by the heat flow, it is thought that the activation energy of the endothermic reaction should be related in some way to the enthalpy change of the reaction. Figure 6 shows the relation between the activation energy for the decomposition of $CdSO_4$ and its standard enthalpy change at 298.15 K, $\Delta H^{\ominus}_{d298}$. In the figure, data for the decomposition of sulphates of first-row

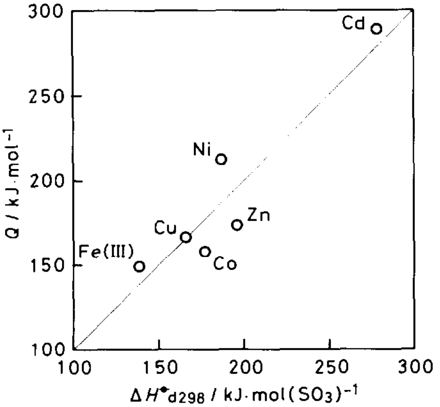

Fig. 6. Relation between activation energy, Q, and standard enthalpy change at 298.15 K, $\Delta H^{\ominus}_{d298.15}$, for the decomposition of metal sulphates, where the activation energy for $CdSO_4$ was obtained in the present work and the others were taken from ref. 2.

transition elements are also shown. It can be seen that the activation energy for the decomposition of any of the sulphates is close to its standard enthalpy of decomposition. For $CdSO_4$, the activation energy is nearly the same as the enthalpy of decomposition, 279.4 kJ mol^{-1}. This is in agreement with the results obtained for sulphates of first-row transition elements [2].

REFERENCES

1 H. Tagawa, Thermochim. Acta, 80 (1984) 23.
2 H. Tagawa and H. Saijo, Thermochim. Acta, 91 (1985) 67.
3 H. Tagawa and K. Igarashi, Thermochim. Acta, 119 (1987) 347.
4 U. Merten and W.E. Bell, in J.L. Margrave (Ed.), The Characterization of High Temperature Vapors, John Wiley, New York, 1967, p. 91.
5 R.G. Behrens and C.F.V. Mason, J. Less-Common Met., 77 (1981) 169.
6 M. Grade and W. Hirschwald, Ber. Bunsenges. Phys. Chem., 86 (1982) 899.
7 R.H. Lamoreaux, D.L. Hildenbrand and L. Brewer, J. Phys. Chem. Ref. Data, 16 (1987) 419.
8 I. Gilbert and J. Kitchener, J. Chem. Soc., Part VI, (1956) 3919.
9 The Society of Calorimetry and Thermal Analysis of Japan, Thermodynamic Data Base for Personal Computers, "MALT", Kagaku-Gijutsu-sha, Tokyo, 1985.
10 N.B. Pilling and R.E. Bedworth, J. Inst. Metals, 29 (1923) 529.