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THERMAL DECOMPOSITION TEMPERATURES OF METAL SULFATES

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ABSTRACT

The thermal decomposition of sixteen metal sulfates was studied by thermogravimetry at heating rates of 2 and 5°C min^{-1} in flowing air and high-purity nitrogen. Their decomposition behaviors, especially the initial decomposition temperatures, were examined with relation to the thermodynamic functions for decomposition. Of the factors possibly influencing the decomposition temperature, the equilibrium SO_3 pressures over the sulfates were evaluated: the equilibrium pressures at the initial temperatures for sulfates of metals, of which the oxidation state was unchanged during decomposition, were nearly equal to 1×10^{-4} atm at 2°C min^{-1} in flowing nitrogen.

INTRODUCTION

The thermal decomposition of metal sulfates has long been used as an important reaction in chemical and metallurgical industries. The reaction has also been under recent investigation for a variety of potential applications, e.g., possible storage of solar energy or nuclear heat. One of the suggested applications is hydrogen production by a multi-thermochemical water-splitting process [1], using sulfur as a circulating material [2–4]. The hydrogen production is performed in a closed cycle composed of a number of reactions, using the decomposition of sulfates such as $MgSO_4$ [5], $NiSO_4$ [6] and $ZnSO_4$ [7] as an oxygen-generating reaction.

The thermal decomposition of metal sulfates is represented by the general formula

$$1/n\text{M}(n)_2(\text{SO}_4)_n \rightarrow 1/n\text{M}(n)_2\text{O}_n + \text{SO}_3 \tag{1}$$

where M is a metal of the oxidation state n. The sulfur trioxide evolved is autocatalytically decomposed on the oxide formed according to

$$\text{SO}_3 \rightarrow \text{SO}_2 + 1/2\text{O}_2 \tag{2}$$

Here the stability of sulfates can be evaluated by the Gibbs energy changes

TABLE 1

Thermodynamic functions for the decomposition of metal sulfates [a]

Reaction	ΔH^0_{298}(kJ)	ΔS^0_{298}(J K^{-1})	ΔG^0_T(J) = $a + bT$(K) log T(K) + cT(K)		
			a	b	c
$\frac{1}{3}$ $Al_2(SO_4)_3 \rightarrow \frac{1}{3}$ $\gamma - Al_2O_3 + SO_3$	198.93	196.83	203 635		−177.90 [10]
$BeSO_4 \rightarrow BeO + SO_3$	199.88	192.99	209 953	96.36	−477.56
$CdSO_4 \rightarrow CdO + SO_3$	279.36	188.52			
$\frac{1}{3}$ $Ce_2(SO_4)_3 \rightarrow \frac{2}{3}$ $CeO_2 + \frac{1}{3}$ $SO_2 + \frac{2}{3}$ SO_3	229.54				
$CoSO_4 \rightarrow CoO + SO_3$	254.64	191.73	289 658	115.60	−573.96
$CoSO_4 \rightarrow \frac{1}{3}$ $Co_3O_4 + \frac{1}{3}$ $SO_2 + \frac{2}{3}$ SO_3	228.54	169.97			
$\frac{1}{3}$ $Cr_2(SO_4)_3 \rightarrow \frac{1}{3}$ $Cr_2O_3 + SO_3$	197.95 [10]	196.90 [10]			
2 $CuSO_4 \rightarrow CuO \cdot CuSO_4 + SO_3$	216.61 [10]	195.48 [10]	216 648	21.59	−253.55
$CuO \cdot CuSO_4 \rightarrow 2\ CuO + SO_3$	220.12 [10]	184.51 [10]	217 694	21.59	−240.96
$\frac{1}{3}$ $Fe_2(SO_4)_3 \rightarrow \frac{1}{3}$ $Fe_2O_3 + SO_3$	190.05	191.63	203 300	34.104	−297.19
$\frac{1}{2}$ $La_2(SO_4)_3 \rightarrow \frac{1}{2}$ $(La_2O_3 \cdot SO_3) + SO_3$			253 048		−162.42
$MgSO_4 \rightarrow MgO + SO_3$	287.48	192.10			
$MnSO_4 \rightarrow \frac{1}{3}$ $Mn_3O_4 + \frac{1}{3}$ $SO_2 + \frac{2}{3}$ SO_3	239.89	193.68			
$NiSO_4 \rightarrow NiO + SO_3$	237.49	202.75	248 069		−198.82
3 $ZnSO_4 \rightarrow ZnO \cdot 2\ ZnSO_4 + SO_3$	246.04	205.17	224 806		−189.16
$\frac{1}{2}$ $(ZnO \cdot 2\ ZnSO_4) \rightarrow \frac{3}{2}$ $ZnO + SO_3$	235.18	182.27	239 283	31.80	−274.60
$\frac{1}{2}$ $Zr(SO_4)_2 \rightarrow \frac{1}{2}$ $ZrO_2 + SO_3$	162.55				
$SO_3 \rightarrow SO_2 + \frac{1}{2}$ O_2	98.89	94.03	98 920		−93.931 [9]

[a] ΔH^0_{298} and ΔS^0_{298}, and ΔG^0 were taken from refs. 8 and 11, respectively, unless otherwise specified.

of decomposition, $\Delta G_\mathrm{d}^0(T)$. When not directly given or exactly calculated from data sources, $\Delta G_\mathrm{d}^0(T)$ can be approximately obtained using the enthalpy changes at 298.15 K, $\Delta H_{\mathrm{d}298.15}^0$, and the entropy changes at 298.15 K, $\Delta S_{\mathrm{d}298.15}^0$, instead of $\Delta H_\mathrm{d}^0(T)$ and $\Delta S_\mathrm{d}^0(T)$ as

$$\Delta G_\mathrm{d}^0(T) = \Delta H_{\mathrm{d}298.15}^0 - T\Delta S_{\mathrm{d}298.15}^0 \tag{3}$$

The thermodynamic properties of common metal sulfates have been compiled in the NBS Thermodynamic Table [8] and other tables [9,10], and the Gibbs energy changes for thermal decomposition of metal sulfates have been reviewed by Kellogg [11]. The thermodynamic functions for the decomposition of the sulfates used in the present study, per mole of SO_3, are summarized in Table 1. When the table is overviewed, it is easily found that $\Delta H_{\mathrm{d}298.15}^0 \approx 240$ kJ $\mathrm{mol}(SO_3)^{-1}$ for divalent metal sulfates, and ≈ 195 kJ $\mathrm{mol}(SO_3)^{-1}$ for trivalent metal sulfates; $\Delta S_{\mathrm{d}298.15}^0 \approx 195$ J K^{-1} $\mathrm{mol}(SO_3)^{-1}$ for the sulfates regardless of the oxidation state of the metal. From these facts, it is deduced that the equilibrium SO_3 pressures over trivalent metal sulfates are higher than those over divalent metal sulfates at a fixed temperature, therefore, if the thermal decomposition begins at the same SO_3 pressure, trivalent metal sulfates will decompose at lower temperatures than divalent metal sulfates.

The thermal decomposition of metal sulfates have been studied by many investigators, but, unfortunately, widely discrepant values are reported for the same compound. We measured anew the initial decomposition temperatures and examined whether the decomposition temperature is related to thermodynamic properties. Here the decomposition temperature was defined as the temperature at which the thermogravimetry curve first breaks detectably from constancy. The thermal stability of metal sulfates was discussed by Ostroff and Sanderson [12] from the standpoint of the effects of the metal's electronegativity and polarizing power on the condition of the sulfate ion.

EXPERIMENTAL

Materials

Metal sulfates used were as follows: $BeSO_4 \cdot 4\ H_2O$, $MgSO_4 \cdot 7\ H_2O$, $CdSO_4 \cdot 2.4\ H_2O$, $MnSO_4 \cdot 5\ H_2O$, $FeSO_4 \cdot 7\ H_2O$, $CoSO_4 \cdot 7\ H_2O$, $NiSO_4 \cdot 6\ H_2O$, $CuSO_4 \cdot 5\ H_2O$ and $ZnSO_4 \cdot 7\ H_2O$ for divalent metal sulfates; $Al_2(SO_4)_3 \cdot 14\ H_2O$, $Cr_2(SO_4)_3 \cdot 3\ H_2O$, $Fe_2(SO_4)_3 \cdot 13\ H_2O$, $La_2(SO_4)_3 \cdot 9\ H_2O$ and $Ce_2(SO_4)_3 \cdot 8\ H_2O$ for trivalent metal sulfates; and $Zr(SO_4)_2 \cdot 4\ H_2O$ and $Ce(SO_4)_2 \cdot 4\ H_2O$ for tetravalent metal sulfates. These sulfates were provided by Kanto Chemical Co. as guaranteed reagent grade, except for the lanthanum sulfate (99.999%), which was obtained from Aldrich Chemical Co.

Apparatus and procedures

The apparatus consisted of an electrobalance (Cahn model 2000) used as a thermobalance, a Kanthal resistance furnace, 35 mm ID and 200 mm in length, a gas supply system and vacuum pumps. A thin platinum bucket, 10 mm in diameter and 5 mm in height, was suspended in the heating zone by means of a platinum wire extending from one end of the balance arm. A quartz reaction tube, 20 mm ID and 350 mm in length, was connected to the vacuum bottle containing the balance. An SO_3 absorber was followed to the bottom end of the reaction tube.

All experiments were run on samples ground in an agate mortar to 200 mesh. After the ~ 120-mg sample was loaded, air or high purity nitrogen ($P_{O_2} < 10^{-6}$ atm) was allowed to flow at a rate of 100 cm^3 min^{-1}. The linear flow rate at the bucket side was 42 cm min^{-1} at room temperature. The temperature of the sample was measured by means of a Pt/Pt–13%Rh thermocouple placed in the middle space between the bucket and the inner wall of the reaction tube, and it was automatically controlled and recorded to be raised at a constant heating rate.

X-ray diffraction for all the products and the intermediates was performed by a diffractometer (Rigaku Denki Co., type Rad-1A) with CuK_α radiation monochromatized with a bent graphite crystal.

RESULTS AND DISCUSSION

The thermal decomposition of sixteen metal sulfate hydrates was examined by thermogravimetry (TG) at heating rates of 2 and 5 °C min^{-1} in flowing air and high-purity nitrogen. Figure 1 shows the results for sulfates of magnesium, iron(II), nickel, copper, iron(III) and cerium(IV) at 2 °C min^{-1} in flowing nitrogen. In the figure weight losses are shown in moles of crystalline water per SO_4 ion for dehydration and in percentage loss of SO_3 for decomposition of sulfates.

When divalent metal sulfate hydrates were heated at a constant rate, weight loss due to dehydration occurred in a stepwise manner, and the hydrates, except iron(II) sulfate, were changed to the anhydrous form by 400 °C after they became monohydrates. The decomposition of $FeSO_4 \cdot H_2O$ did not give the anhydrate, but gave iron(III) oxide directly. As found by Kubo et al. [13], the oxidation of iron(II) and the decomposition of the newly-formed $Fe_2(SO_4)_3$ occurred successively as the dehydration proceeded. The reaction may be represented as $FeSO_4 \cdot H_2O \rightarrow 1/6\ Fe_2(SO_4)_3 + 1/3\ Fe_2O_3 + 1/2\ SO_2 + H_2O$, and then $1/6\ Fe_2(SO_4)_3 \rightarrow 1/6\ Fe_2O_3 + 1/2\ SO_3$.

For trivalent and tetravalent metal sulfates, weight loss due to dehydration did not occur in a stepwise manner, but rather almost continuously. The decomposition behavior of salts of iron(III) and cerium(IV) are also shown in Fig. 1. The TG curve of $Fe_2(SO_4)_3$ is seen to be similar to that of $FeSO_4 \cdot H_2O$. For $Cr_2(SO_4)_3 \cdot 3\ H_2O$, the TG curve of which is not shown in the figure, the weight loss at any heating rate in flowing air or nitrogen proceeded almost linearly with rising temperature to about 15% as the decomposition ratio of the anhydrate, then the loss became sharper and finished at about 680 °C. The anhydrate was not obtained under these conditions. The initial temperature was not precisely determined because of losing both H_2O and SO_3. The temperatures at the bend of the curves can be read as 496 and 500 °C at 2 °C min^{-1} in flowing nitrogen and air, respectively. Dehydration behaviors of all the sulfates in air, regardless of the

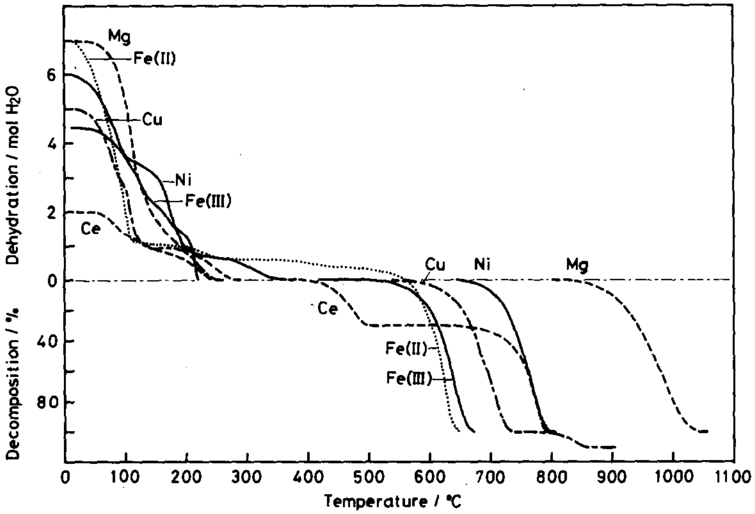

Fig. 1. TG curves for metal sulfate hydrates in flowing high-purity nitrogen at a heating rate of 2 °C min^{-1}.

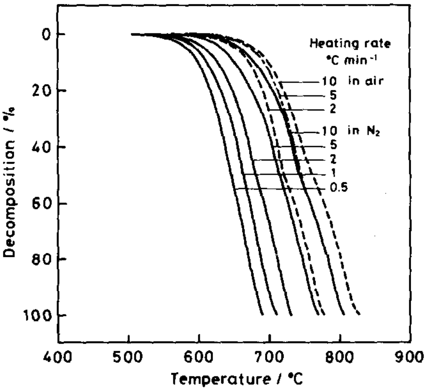

Fig. 2. TG curves for $CuSO_4$ in flowing air and high-purity nitrogen at various heating rates.

oxidation state of the metals, were not found to be different to those in nitrogen.

Figure 2 shows the TG curves of copper sulfate at various heating rates in flowing air and high-purity nitrogen. It is seen in the figure that the curves, and also initial temperatures, shift towards a high temperature with rising heating rate, and those obtained in flowing air locate at higher temperatures than those in nitrogen at the same heating rate. The initial temperatures in nitrogen were 582, 561, 538, 526 and 505 °C at heating rates of 10, 5, 2, 1 and 0.5 °C min^{-1}, respectively, and they can almost be expressed with respect to heating rate by the equation: $t\ (^\circ\text{C}) = 56 \log v\ (^\circ\text{C min}^{-1}) + 522$, where v is the heating rate. The temperatures in flowing air were about 40 °C higher than those in a nitrogen stream at any heating rate: they were 610, 605, 586, 568 and 557 °C at the same rates as in nitrogen, respectively. The relationship between initial temperature and heating rate was given by $t\ (^\circ\text{C}) = 48 \log v\ (^\circ\text{C min}^{-1}) + 571$.

It is known that the initial decomposition temperature generally depends on the quantity, particle size, shape, and surface area-to-volume ratio of a sample, the shape and size of the sample holder, the heating rate of the sample, and the flow rate of the environmental gas, which decides the virtual partial pressure if the gaseous product is evolved. Thermogravimetry, however, has often been carried out without specifying these factors. For example, the reported initial temperatures for the decomposition of metal sulfates differ widely, as tabulated by Ostroff and Sanderson [12], Kolta and Askar [14] and Mu and Perlmutter [15].Of these several factors possibly influencing the decomposition temperatures, the partial pressure of the gaseous product over the samples is thought to be the most important for the endothermic decomposition in reversible systems such as metal sulfate–metal oxide–SO_3 and metal carbonate–metal oxide–CO_2. The virtual equilibrium pressure over the sample is varied by the heating rate, which governs the reaction rate, or by flow rate of the ambient atmosphere. The equilibrium SO_3 pressures over $CuSO_4$, if SO_3 was not dissociated, at the initial temperatures under the rates of 5 and 2 °C min^{-1}, which were calculated using Kellogg's $\Delta G_\text{d}^0(T)$ [11], were 1.09×10^{-3} and 5.77×10^{-4} atm in flowing air, and 2.58×10^{-4} and 1.02×10^{-4} atm in flowing nitrogen, respectively. From this, it is known that the initial temperature for sulfate decomposition is related to the oxygen partial pressure, because SO_3 is dissociated to SO_2 and O_2 on the formed oxide following eqn. (2).

Figure 3 shows the TG curves for the thermal decomposition of the anhydrate parts in the sulfate hydrates of divalent metals and lanthanum at 2 °C min^{-1} in a flow of nitrogen. In the figure, sulfate of manganese(II), which was oxidized during decomposition, was changed to Mn_3O_4 in nitrogen and to Mn_2O_3 in air. For $CuSO_4$, the product was CuO at the final temperature, but CuO was changed to Cu_2O by further heating in nitrogen. For $CoSO_4$ it was observed that Co_3O_4 coexisted with CoO during decomposition in nitrogen, and disappeared at the final temperature. In air the product was Co_3O_4. Thermodynamically the formation of Co_3O_4 by the decomposition of $CoSO_4$ is about 8 kJ mol$(SO_3)^{-1}$ more stable than the formation of CoO at the initial decomposition temperature in an oxygen-free atmosphere.

Figure 4 shows the TG curves for the thermal decomposition of the anhydrate parts in the sulfate hydrates of trivalent and tetravalent metals. The decomposition of these sulfates generally occurred at lower temperatures than those divalent metal sulfates, except $La_2(SO_4)_3$. Lanthanum sulfate was decomposed to $La_2O_2SO_4$ below 1200 °C. The decomposition temperature of $La_2O_2SO_4$ was 1270 °C at 10 °C min^{-1} in air flow. The decomposition of zirconium sulfate was followed by its dehydration, so that if the anhydrate was used, the initial temperature might be slightly lowered. The shapes of

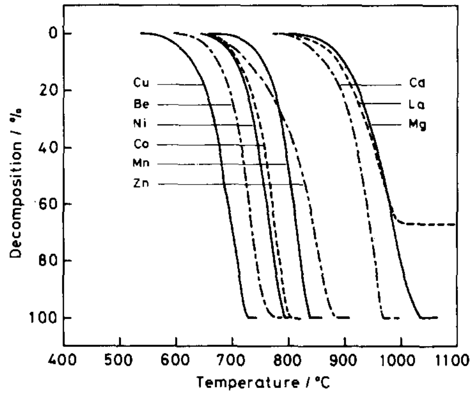

Fig. 3. TG curves for sulfates of divalent metals and lanthanum in flowing high-purity nitrogen at a heating rate of 2 °C min^{-1}.

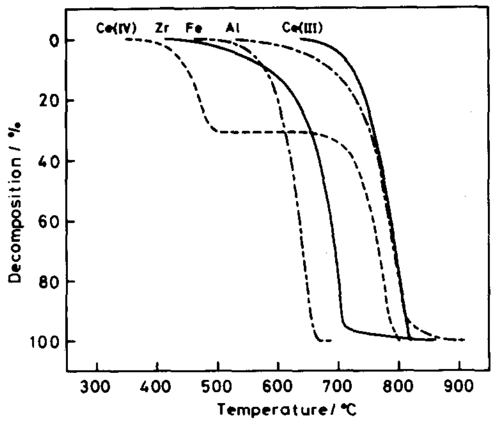

Fig. 4. TG curves for trivalent and tetravalent metal sulfates in flowing high-purity nitrogen at a heating rate of 2 °C min^{-1}.

TG curves of $Al_2(SO_4)_3$ and $Zr(SO_4)_2$ differ from those of other sulfates. This is thought to be due to the different mechanism of decomposition from sulfates of transition elements such as copper and iron(III) [16].

For the decomposition of the sulfates at 5 °C min^{-1}, as seen in the decomposition of $CuSO_4$, the TG curves and also the initial temperatures were shifted towards slightly higher temperatures than those at 2 °C min^{-1}, but the shapes of the curves were not changed. The initial temperatures in air were higher than those in high-purity nitrogen. The initial temperatures of the sulfates at 2 and 5 °C min^{-1} in flowing air and high-purity nitrogen are shown in Table 2. As already mentioned for $CuSO_4$ decomposition, the difference between the initial temperatures obtained at 2 and 5 °C min^{-1} was 23 °C. In this table, it can be seen that this difference for the other sulfates was also around 20 °C, though they were scattered.

The equilibrium SO_3 pressure over $CuSO_4$ at the initial temperature at 2 °C min^{-1} in flowing nitrogen was 1.0×10^{-4} atm. In order to examine whether the initial temperature is actually related to the thermodynamic properties, the temperatures, at which the equilibrium SO_3 pressures of the other sulfates used in the present work are 1.0×10^{-4} atm, were calculated using the thermodynamic functions of Table 1, where the pressures were obtained from $\Delta G_d^0(T)$, or from ΔH_{d298}^0 and ΔS_{d298}^0 using eqn. (3) when $\Delta G_d^0(T)$ was not found in the table. The calculated temperatures are plotted against the observed initial decomposition temperatures in Fig. 5. Here, sulfates of metals, of which the oxidation state was not varied during

TABLE 2

Initial decomposition temperatures of metal sulfates at heating rates of 2 and 5 °C min^{-1} in flowing air and high-purity nitrogen

Metal sulfates	Nitrogen (°C min^{-1})		Air (°C min^{-1})	
	2	5	2	5
$Al_2(SO_4)_3$	493	500	516	524
$BeSO_4$	578	586	583	592
$CdSO_4$	759	778	783	783
$Ce_2(SO_4)_3$	630	650	632	666
$Ce(SO_4)_2$	340	379	377	383
$CoSO_4$	644	658	690	690
$CuSO_4$	538	561	586	605
$Fe_2(SO_4)_3$	464	485	507	545
$La_2(SO_4)_3$	772	782	790	817
$MgSO_4$	800	803	843	849
$MnSO_4$	650	693	687	717
$NiSO_4$	640	660	642	676
$ZnSO_4$	615	620	620	630
$Zr(SO_4)_2$	382	435	386	438

decomposition, were employed. The equilibrium pressure over $CoSO_4$ was conventionally calculated from the equation: $CoSO_4 \rightarrow CoO + SO_3$ instead of $CoSO_4 \rightarrow 1/3\ Co_3O_4 + 1/3\ SO_2 + 2/3\ SO_3$. It is seen in the figure that any sulfate is located on or near the diagonal line. For a heating rate of 5 °C min^{-1}, it is also shown that the pressure becomes $\sim 3 \times 10^{-4}$ atm. An initial temperature is not a thermodynamic property. However, if the same apparatus is used and if the reaction system considered is mobile, the figure shows that the initial temperature becomes a measure of the thermodynamic property.

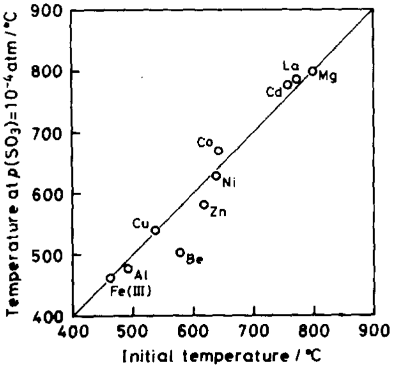

Fig. 5. Relationship between the initial decomposition temperatures observed in high-purity nitrogen at 2 °C min^{-1} and the calculated temperatures at 10^{-4} atm of the equilibrium SO_3 pressures over the metal sulfates.

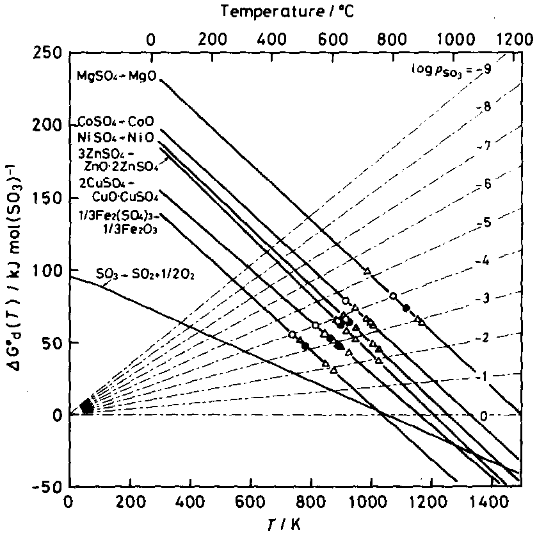

Fig. 6. The reported initial decomposition temperatures plotted on the curves of the Gibbs energy changes for decomposition of metal sulfates vs. temperature. Temperatures in flowing high-purity nitrogen (○) and air (●) at 2 °C min^{-1}, obtained in the present work, and the reported temperatures (△) for sulfates of Mg [12,15,17,18], Fe(III) [14,15,19,20], Co [12,14,15,21], Ni [12,14,15,17,21,22], Cu [12,14,15,21,23–25] and Zn [12,14,19,24].

Figure 6 shows the reported initial temperatures [12,14,15,17–25] plotted on the curves of $\Delta G_d^0(T)$ of metal sulfates vs. temperature. In the figure the reported values are seen to be between 10^{-4} and 10^{-2} atm of the equilibrium SO_3 pressure. This equilibrium pressure at the initial decomposition temperature will become the so-called characteristic pressure, if the apparatus used and experimental conditions are fixed. In the present work it was 1.0×10^{-4} atm. For the results in nitrogen flow obtained by Ostroff and Sanderson [12], the equilibrium pressures calculated were $MgSO_4$, 15.1; $CoSO_4$, 3.1; $NiSO_4$, 5.5; $CuSO_4$, 8.6; $ZnSO_4$, 12.7; and $CdSO_4$, 2.8×10^{-4} atm, and the average was $(8.0 \pm 3.6) \times 10^{-4}$ atm. The average pressure calculated from the results of Mu and Perlmutter [15] was $(2.8 \pm 2.1) \times 10^{-4}$ atm, where the equilibrium pressures at the initial temperatures for sulfates of Mg, Al, Fe(III), Co, Ni and Cu in flowing nitrogen were 0.6, 6.6, 3.5, 0.9, 1.4 and 3.6×10^{-4} atm, respectively.

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