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ON THE NON-ISOTHERMAL BEHAVIOUR OF ZrO_2 AND HfO_2–$Na_2/K_2/S_2O_8$ BINARY SYSTEMS

IBTISAM JAMEEL and FADHIL JASIM *

Department of Chemistry, College of Sciences, Baghdad University Jadiriya, Baghdad (Iraq)

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ABSTRACT

The non-isothermal solid-state derivatographic behaviour of HfO_2 and ZrO_2 and four systems of HfO_2 and ZrO_2–$Na_2/K_2/S_2O_8$ of various molar ratios have been investigated in a static air atmosphere from ambient temperature to 1050°C. HfO_2 gradually loses oxygen at higher temperatures yielding Hf(II)O which reoxidises to HfO_2 on cooling. No weight loss or change of valence state was observed in the case of ZrO_2. The 1 : 1 ::HfO_2-(ZrO_2):$Na_2/K_2/S_2O_8$ ratios were found to be stoichiometric. Accordingly, four different thermally stable basic double salts have been identified, namely, $Na_2HfO(SO_4)_2$, $K_2HfO(SO_4)_2$, $Na_2ZrO(SO_4)_2$ and $K_2ZrO(SO_4)_2$. Based on the DTA curves, a mechanism for the thermal degradation of these basic salts has been proposed which shows the liability of Hf(IV) to form unstable Hf(II) at higher temperatures. All systems tend to form melting eutectic mixtures. X-ray diffractometery has been employed to identify intermediate and final products.

INTRODUCTION

Because of the effects of the lanthanide contraction, the atomic radii, the ionic radii and therefore the chemical behaviour of hafnium and zirconium are extremely similar [1]. At high temperatures HfO_2 and ZrO_2 are good electrical and ionic conductors [2]. Both oxides form monoclinic structures at ambient temperatures [3]. Mixed metal oxides [1], halo-complexes, normal and basic double salts were prepared through reactions in aqueous solutions [4,5]. Hydrated normal and basic double salts (sulfates) with sodium or potassium were prepared similarly [6–8]. Jasim and co-workers [9–16] investigated the non-isothermal solid-state reactions between metallic oxides and peroxodisulfates (persulfates) of sodium and potassium. TiO_2, a congener to ZrO_2 and HfO_2, was found to form double salts with sodium or potassium persulfates on heating [9–11]; therefore it is expected that oxides of Zr(IV) and Hf(IV) react similarly at high temperatures with the two

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* To whom all correspondence should be addressed.

persulfates and form similar compounds through solid–solid state reactions which is the purpose of this research together with assigning their thermal stabilities, melting points, eutectics and valence states.

EXPERIMENTAL

All chemicals were commercially available; potassium and sodium persulfates were obtained from Hopkin and Williams, ZrO_2 and HfO_2 (puriss) from Fluka AG. Sample weights were 100 and 200 mg.

The apparatus and procedure employed were as described elsewhere [17].

RESULTS AND DISCUSSION

Pure HfO_2 was thermally stable up to 600°C (Fig. 1), after which it gradually lost O_2 (total of 8%), an amount equivalent to $\frac{1}{2}O_2$

$$HfO_2 \xrightarrow{\Delta} HfO + \tfrac{1}{2}O_2$$

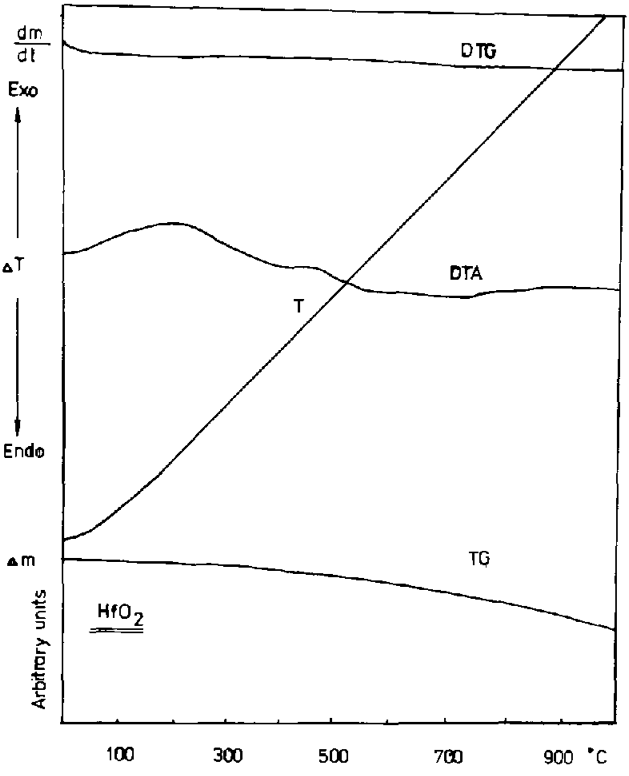

Fig. 1. Thermogram of HfO_2.

Samples of HfO_2, sintered at 1000°C and examined by X-ray analysis showed the following *d*-lines: 3.15, 2.82, 2.59, 2.52, 2.196, 1.838, 1.807 and 1.684 Å, which belong to HfO_2 [18]. This indicates that Hf(II) exists at high temperatures only [1] and oxidises on cooling to ambient conditions.

ZrO_2 was stable up to the ceiling of the heating program (1050°C).

HfO_2–$K_2S_2O_8$ system

Figure 2 depicts TG and DTA curves (DTG curves are not shown for the sake of saving space) obtained for the various molar ratios (Table 1). The oxide could catalytically lower the T_i of the decomposition of $K_2S_2O_8$ by 20°C. The endotherm obtained at 310°C belongs to the crystalline phase change (β–α) of $K_2S_2O_7$. The melting endotherm of the latter disappears because of thermal neutrality and instead an exotherm appears which refers to the occurrence of a solid-state reaction between HfO_2 and $K_2S_2O_7$

$$HfO_2 + K_2S_2O_7 \xrightarrow{\Delta} K_2HfO(SO_4)_2 + \text{heat}$$

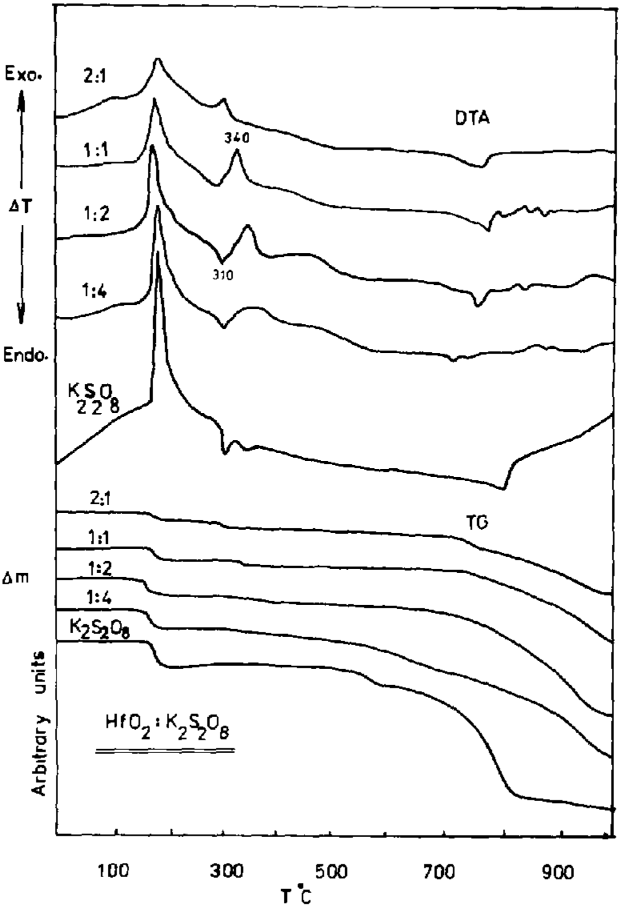

Fig. 2. TG and DTA curves of HfO_2–$K_2S_2O_8$ mixtures.

TABLE 1

Mode of preparation and results of thermal behaviour of the HfO_2–$K_2S_2O_8$ system

$HfO_2:K_2S_2O_8$ mole ratio	HfO_2 in sample (mg)	$K_2S_2O_8$ in sample (mg)	Total wt. of mix. (mg)	O_2 lost in $K_2S_2O_8$ decomp. step. (mg)		SO_3 lost (mg)		Decomp. Temp. (°C)	
				Theor.	Prac.	Theor.	Prac.	T_i	T_f
0:1	0	100	100	5.92	5.7	29.59	29	160	180
1:4	16.29	83.71	100	4.95	4	24.77	8	140	200
1:2	28.02	71.98	100	4.26	3.7	21.3	2	130	200
1:1	56.22	43.78	100	3.33	2.4	16.64	1	140	200
2:1	39.11	60.89	100	2.31	1.7	11.57	1.3	150	200

The unreacted $K_2S_2O_7$ decomposes between 530 and 740°C forming K_2SO_4 and SO_3. Calculations from the TG curves of the various molar ratios indicate that 67.69, 90.6, 93.99 and 88.74% of $K_2S_2O_7$ reacts with the oxide of the molar ratios 1 : 4, 1 : 2, 1 : 1 and 2 : 1 respectively. Since the 1 : 1 ratios involve the highest percentages of reacting $K_2S_2O_7$ and their exo-peaks have the largest and sharpest areas, therefore they are considered the stoichiometric ones and the above reaction fulfills stoichiometry as well. Moreover, samples sintered at 500°C gave white powders whose XRD patterns are as follows: 3.127, 2.81, 3.34, 7.4 and 3.899 Å. Normal and basic hafnium sulfates, HfO_2, mixed oxides of Hf, $K_2S_2O_8$ and K_2SO_4 have no such *d*-lines; therefore these lines are ascribed to the basic hafnium sulfate, $K_2HfO,(SO_4)_2$, which is thermally stable up to 700°C, then decomposes where the DTA curve shows small consecutive degradation endotherms. X-ray analysis for samples sintered afterwards indicate the gradual decomposition of $K_2HfO(SO_4)_2$ and the reappearance of the off-white HfO_2 powder and K_2SO_4 [19]. The overall degradation reaction is as follows

$$K_2HfO(SO_4)_2 \xrightarrow{\Delta} HfO_2 + K_2SO_4 + SO_3$$

A stepwise mechanistic degradation may be proposed as follows

$$K_2HfO(SO_4)_2 \xrightarrow{\Delta} HfOSO_4 + K_2SO_4$$

$$HfOSO_4 \xrightarrow{\Delta} HfSO_4 + \tfrac{1}{2}O_2$$

$$HfSO_4 \xrightarrow{\Delta} HfO + SO_3$$

$$HfO + \tfrac{1}{2}O_2 \xrightarrow{\Delta} HfO_2$$

The mechanism explains why the small endotherms appear on the DTA curves above 700°C. At higher temperatures $HfOSO_4$ is reduced to $HfSO_4$ through the liberation of $\frac{1}{2}O_2$ then HfO and SO_3 are formed. The former Hf(II)O is reoxidised to Hf(IV)O_2 on cooling.

HfO_2–$Na_2S_2O_8$ system

The thermograms for the various molar ratios (Table 2) of this system are shown in Fig. 3. HfO_2 could catalytically depress the T_i of $Na_2S_2O_8$ decomposition by 10°C (Table 2). However, it was shown that as HfO_2 concentration increases, T_i lowers due to the dilution effect. A large sharp exotherm is shown (T_i = 370°C) on the DTA curve of the 1 : 1 ratio where 93.24 wt% of the thermally produced $Na_2S_2O_7$ reacts with the available HfO_2. For the ratios 1 : 4, 1 : 2 and 2 : 1, 76.39, 87.12, and 85.12 wt% of the available $Na_2S_2O_7$ reacted with HfO_2. The reactions occurred before the end

TABLE 2

Mode of preparation and results of thermal behaviour of the HfO_2–$Na_2S_2O_8$ system

$HfO_2:Na_2S_2O_8$ mole ratio	HfO_2 in sample (mg)	$Na_2S_2O_8$ in sample (mg)	Total wt. of mix. (mg)	O_2 lost in $Na_2S_2O_8$ decomp. step. (mg)		SO_3 lost (mg)		Decomp. temp. (°C)	
				Theor.	Prac.	Theor.	Prac.	T_i	T_f
0:1	0	100	100	6.72	6.7	33.60	33.5	160	260
1:4	18.1	81.9	100	5.5	5.5	27.52	11.5	150 210	210 320
1:2	69.35	30.65	100	4.66	4.5	23.3	3	150 220	220 280
1:1	53.08	46.92	100	3.56	3.5	17.83	1.2	150 190	190 290
2:1	36.13	63.87	100	2.43	2.4	12.14	1.8	150 200	200 250

of melting of $Na_2S_2O_7$. The small melting endotherms at 360°C belong to the latter. Samples sintered at 500°C that is, after the reaction, were found to be white crystalline powders whose bright *d*-lines are: 3.87, 3.276, 3.125 and 2.8 Å. According to ASTM cards [20] these lines are those of basic sodium hafnium sulfate, $Na_2HfO(SO_4)_2$. The solid-state stoichiometric reaction can be written as follows

$$HfO_2 + Na_2S_2O_7 \xrightarrow{370^\circ C} Na_2HfO(SO_4)_2$$

The compound decomposes in two steps: 600–770°C and 770–1050°C. A small melting eutectic endotherm ($Na_2HfO(SO_4)_2 + Na_2SO_4$) appears at 650°C whose area depends upon the mole ratio. On cooling, the melt solidifies forming a white mass. The ripple-like endotherms represent, as in the case of the previous system, the stepwise thermal degradation of $Na_2HfO(SO_4)_2$ into HfO_2, Na_2SO_4 and SO_3 gas.

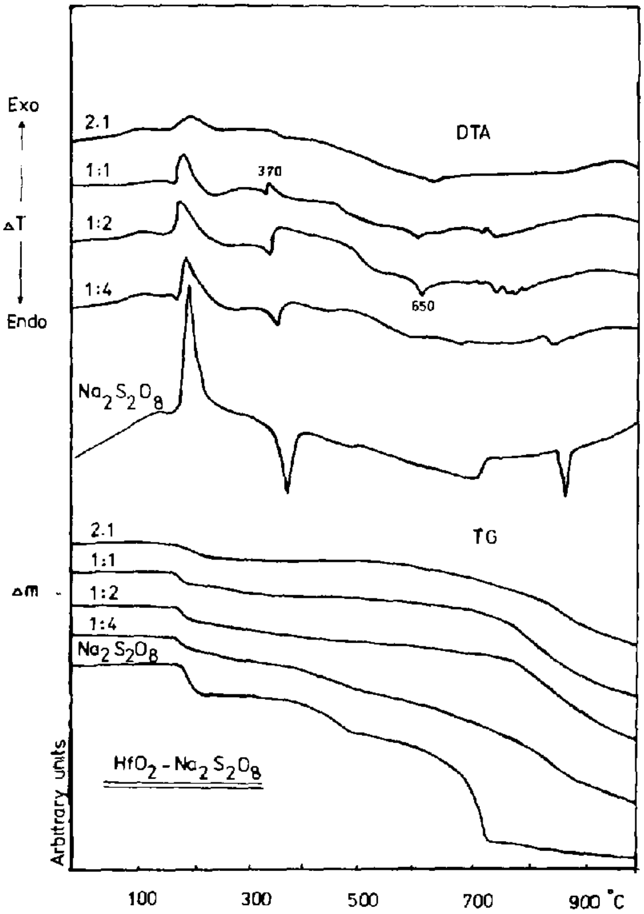

Fig. 3. TG and DTA curves of HfO_2–$Na_2S_2O_8$ mixtures.

ZrO_2–$Na_2S_2O_8$ system

Figure 4 and Table 3 show the thermal curves and the mode of preparation of the various ratios of the ZrO_2–$Na_2S_2O_8$ system. The large exotherm belongs to (175–215°C) the decomposition of $Na_2S_2O_8$. The T_i of the decomposition of $Na_2S_2O_8$ was lowered by 10°C due to the catalytic effect of ZrO_2. The reaction between thermally produced $Na_2S_2O_7$ and ZrO_2 starts before the melting of the former, then continues during melting and finishes immediately after it. Calculations obtained from TG curves indicate that 26, 80 and 88% of $Na_2S_2O_7$ reacts with the available ZrO_2 of the ratios 1 : 4, 1 : 2 and 1 : 1. Since the 1 : 1 involves the highest percent of $Na_2S_2O_7$, therefore it is considered the stoichiometric ratio and the reaction can be written as

$$ZrO_2 + Na_2S_2O_7 \xrightarrow{380-422^\circ C} Na_2ZrO(SO_4)_2 + \text{heat}$$

The heat energy liberated is due to crystallisation of the basic sodium zirconium sulfate. The unreacted $Na_2S_2O_7$ finally decomposes into Na_2SO_4 and SO_3. Samples sintered at 420°C for the 1 : 1 ratio gave the bright *d*-lines: 2.40, 2.72, 3.21, 3.38 and 3.51 Å which do not exactly match those belonging to either $Zr(SO_4)_2$, $ZrOSO_4$ [21] or $Na_2Zr(SO_4)_3$ [7]. The stoichiometry of the latter lends support to its existence. The basic salt is thermally stable between 380 and 578°C. Melting eutectics were formed at 450°C. Another clue to the existence of the double salt is the disappearance of the melting endotherm of Na_2SO_4 in all molar ratios because of its formation. The basic double salt, above 570°C, undergoes a stepwise decomposition, as was observed from the many consecutive small endotherms

$$Na_2ZrO(SO_4)_2 \xrightarrow{570^\circ C} ZrOSO_4 + NaSO_4$$

$$2ZrOSO_4 \xrightarrow{750^\circ C} ZrO(SO_4)_2 + 2ZrO_2$$

TABLE 3

Mode of preparation and results of thermal behaviour of the ZrO_2–$Na_2S_2O_8$ system

ZrO_2 : $Na_2S_2O_8$ mole ratio	Wt. of sample (mg)	$Na_2S_2O_8$ in sample (mg)	O_2 lost (mg)		SO_3 lost (mg)		Decomp. temp. (°C)	
			Theor.	Prac.	Theor.	Prac.	T_i	T_f
0:1	200.0	200.000	13.439	13.00	67.195	67.0	180	220
1:4	200.0	177.089	11.899	11.60	59.498	24.0	180	220
1:2	200.0	158.888	10.676	10.00	53.383	10.5	170	220
1:1	200.0	131.796	8.856	8.25	44.280	5.0	175	230
2:1	199.5	98.035	6.580	6.20	32.937	5.0	178	232
4:1	200.0	65.147	4.377	4.00	21.888	6.0	180	233
1:0	200.0	–	–	–	–	–	–	–

$$Zr(SO_4)_2 \xrightarrow{750°C} ZrO_2 + 2SO_3$$

ZrO_2 did not exhibit any catalysis towards $Na_2S_2O_8$ in the 2 : 1 and 4 : 1 ratios.

ZrO_2–$K_2S_2O_8$ system

Figure 5 and Table 4 show the thermal curves and the mode of preparation of the different ratios of the ZrO_2–$K_2S_2O_8$ system. The catalytic effect of ZrO_2 on the decomposition of $K_2S_2O_8$ is shown in Table 4. The first large exotherm represents the decomposition of $K_2S_2O_8$ into $K_2S_2O_7$ and O_2, next to it comes β–α phase change of $K_2S_2O_7$. The exotherm adjacent to it indicates to the reaction between ZrO_2 and $K_2S_2O_7$. Calculations have shown that 55, 81 and 90% of $K_2S_2O_7$ react with the available ZrO_2 of the 1 : 4, 1 : 2 and 1 : 1 ratios, respectively. As to the 1 : 1, 2 : 1 and 4 : 1 ratios, reactions take place within the melting endotherm of $K_2S_2O_7$ in addition to

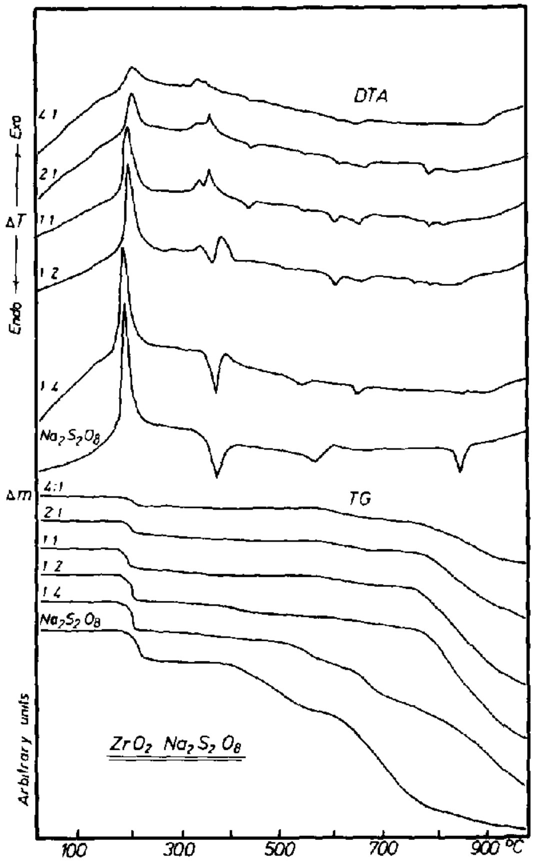

Fig. 4. TG and DTA curves of zirconium(IV) oxide–sodium persulfate mixtures.

TABLE 4

Mode of preparation and results of thermal behaviour of the ZrO_2-$K_2S_2O_8$ system

ZrO_2 : $K_2S_2O_8$ mole ratio	Wt. of sample (mg)	$K_2S_2O_8$ in sample (mg)	O_2 lost (mg)		SO_3 lost (mg)		Decomp. temp. (°C)	
			Theor.	Prac.	Theor.	Prac.	T_i	T_f
0:1	200.0	200.00	11.84	11.50	59.18	59.00	165	200
1:4	200.0	179.54	10.63	9.00	53.13	24.00	165	196
1:2	200.0	162.89	9.64	9.00	48.20	9.00	158	182
1:1	200.0	137.38	8.13	7.25	40.65	4.00	162	196
2:1	200.0	104.62	6.17	4.00	30.96	4.00	163	193
4:1	200.0	70.83	4.19	2.00	20.96	4.00	166	190
1:0	200.0	–	–	–	–	–	–	–

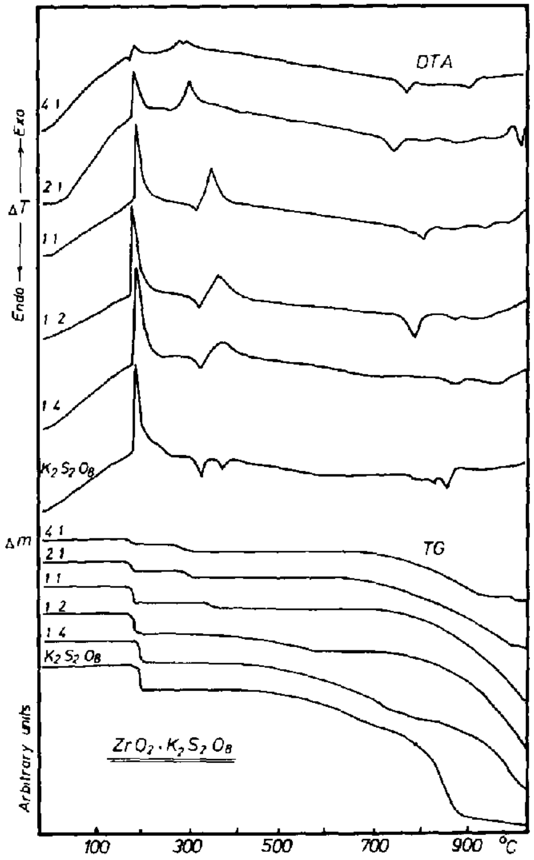

Fig. 5. TG and DTA curves of zirconium(IV) oxide-potassium persulfate mixtures.

partial decomposition of the latter. This infers that excess ZrO_2 lowers the T_i of $K_2S_2O_7$ decomposition by its catalytic activity, and consequently the horizontal plateaus of the latter become shorter. In accordance with calculation obtained above, 1 : 1 is to be taken as the stoichiometric ratio and therefore the reaction is as follows

$$ZrO_2 + K_2S_2O_7 \xrightarrow{330-380°C} K_2ZrO(SO_4)_2 + \text{heat}$$

The basic potassium zirconium sulfate is stable up to 875°C. Samples of 1 : 1 ratios sintered at 650°C gave the *d*-lines: 2.82, 2.96, 3.14 and 3.33 Å [22]. These bright lines do not belong to any basic or normal sulfates or double salts of zirconium.

The endotherm at $T_{max} = 770°C$ represents the melting decomposition of the basic salts

$$K_2ZrO(SO_4)_2 \xrightarrow{770°C} ZrOSO_4 + K_2SO_4$$

The small endotherm beyond 800°C infers the reactions

$$2ZrOSO_4 \xrightarrow{800-900°C} Zr(SO_4)_2 + ZrO_2$$

$$Zr(SO_4)_2 \xrightarrow{900°C} ZrO_2 + 2SO_3$$

Indeed X-ray analysis of the final residues confirm the presence of K_2SO_4 and ZrO_2 only.

REFERENCES

1 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, New York, 1972.
2 R.J.H. Clark, D.C. Bradley and P. Thornton, The Chemistry of Titanium, Zirconium and Hafnium, University of London Press, London, 1973, p. 426.
3 M.M. Godneva, R.A. Papova, D.L. Motov, R.F. Okhrimenko and D.L. Ragachev, Russ. J. Inorg. Chem., 19 (1974) 9.
4 D.L. Motov and Y.A. Sozinova, Russ. J. Inorg. Chem., 21 (1976) 54.
5 L.I. Fedoryako, I.A. Sheka and F.G. Kramarenko, Russ. J. Inorg. Chem., 16 (1971) 690.
6 H.A. Papazian, P.J. Pizolato and R.R. Orrell, Thermochim. Acta, 4 (1972) 97.
7 I.J. Bear and W.J. Mumme, Acta Crystallogr., Sect. B, 27 (1971) 494.
8 V.I. Sokol, I.G. Antanov and K.M. Zaitsev, Russ. J. Inorg. Chem., 12 (1967) 899.
9 M.M. Barbooti, F. Jasim and S.K. Tobia, Thermochim. Acta, 11 (1975) 79.
10 M.M. Barbooti, F. Jasim and S.K. Tobia, Thermochim. Acta, 21 (1977) 399.
11 M.M. Barbooti and F. Jasim, J. Therm. Anal., 13 (1978) 563.
12 R.M. Al-Shukry and F. Jasim, J. Therm. Anal., 19 (1980) 25.
13 R.M. Al-Shukry and F. Jasim, J. Therm. Anal., 37 (1980) 97.
14 R.M. Al-Shukry and F. Jasim, J. Therm. Anal., 41 (1980) 281.
15 K.R. Idan and F. Jasim, Thermochim. Acta, 39 (1980) 227.
16 H.J. Jaffer and F. Jasim, Thermochim. Acta, 45 (1981) 39.

17 K.R. Idan and F. Jasim, J. Therm. Anal., 21 (1981) 249.
18 ASTM Card 6-1318.
19 ASTM Card 24-703.
20 Y.P. Sozinova, D.L. Motov, R.A. Popova and S.D. Nikitina, Izv. Akad. Nauk SSSR, Neorg. Mater., 18 (8) (1982) 1363.
21 ASTM Card 24-1492.
22 Chem. Abstr., 61 (1974) 14158c.