# Synthesis and Characterization of Zirconium and Hafnium Sulfates, Hydroxide Sulfates and Oxide Sulfates

M. A. K. Ahmed, H. Fjellvåg and A. Kjekshus*

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

Ahmed, M. A. K., Fjellvåg, H. and Kjekshus, A., 1999. Synthesis and Characterization of Zirconium and Hafnium Sulfates, Hydroxide Sulfates and Oxide Sulfates. Acta Chem. Scand. 53: 24–33. © Acta Chemica Scandinavica 1999.

Reactions between $ZrO_2$ or $HfO_2$ and 50–95 wt% $H_2SO_4$ have been studied at temperatures up to the boiling point of the acid. Eight different solid products, depending on the $H_2SO_4$ concentration, were obtained, including new polymorphs of $Zr(SO_4)_2 \cdot 7H_2O$, $Zr(SO_4)_2 \cdot 4H_2O$ and $Hf(SO_4)_2 \cdot 7H_2O$. In addition four solid intermediates were identified by thermal decomposition of $Zr(SO_4)_2 \cdot 4H_2O$ and $Hf(SO_4)_2 \cdot 4H_2O$. Zirconium and hafnium hydroxide sulfates were prepared by slow evaporation of diluted aqueous solutions of zirconium and hafnium sulfates, respectively. On partial thermal decomposition of these, the corresponding oxide sulfates were obtained as intermediates. A simple procedure for disengagement of zirconium and hafnium sulfates from the concentrated $H_2SO_4$ mother liquor is described. TG and DTA data are presented, unit-cell dimensions are derived from PXD data and formulae based on TG analyses are given for the synthesized products.

As a continuation of earlier investigations on the use of concentrated $H_2SO_4$ as a solvent for, and reactant with, oxides,[1–4] reactions between zirconium oxide or hafnium oxide and concentrated $H_2SO_4$ (in this context 50–95 wt% $H_2SO_4$) have been investigated.

$\alpha$-$Zr(SO_4)_2$ and $Zr(SO_4)_2 \cdot 4H_2O$ were first prepared by Berzelius in 1824.[5] Since then a large number of zirconium sulfates have been reported. Most of these compounds[6] have been obtained by partial thermal decomposion of other zirconium sulfates, or by rehydratization of the thus acquired products [notably $Zr(SO_4)_2 \cdot 4H_2O$]. The zirconium sulfates may be grouped in five categories according to composition: $Zr(SO_4)_2$, $Zr(SO_4)_2 \cdot H_2O$, $Zr(SO_4)_2 \cdot 4H_2O$, $Zr(SO_4)_2 \cdot 5H_2O$ and $Zr(SO_4)_2 \cdot 7H_2O$. Three of these five chemical entities exist in more than one structural modification, namely the anhydrate, monohydrate and pentahydrate.[6]

Structure determinations have been reported for a number of these compounds: $\alpha$-$Zr(SO_4)_2$,[7] $\alpha$-$Zr(SO_4)_2 \cdot H_2O$,[8] $\gamma$-$Zr(SO_4)_2 \cdot H_2O$,[9] $Zr(SO_4)_2 \cdot 4H_2O$,[10] $\alpha$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$,[11] $\beta$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$[12] and $Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$.[13] The crystal structures of $Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$, $\alpha$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$ and $\beta$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$ comprise isolated dimeric units of $Zr_2(SO_4)_4(H_2O)_8$ which are held

together by hydrogen bonds. The atomic arrangement in $Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$ and $\alpha$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$ are virtually the same except for two additional water molecules (not bonded to zirconium atoms) per monomeric unit in the former structure. $\alpha$- and $\beta$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$ differ in the relative disposition of the terminal groups and dimeric ring structure within the unit cell. $Zr(SO_4)_2 \cdot 4H_2O$ has a layer structure in which, presumably, hydrogen bonding provides the cohesion between the layers. The layers consist of intersecting Zr–S–Zr–S chains which form rings containing four zirconium atoms and four sulfate groups. Thus, unlike other structurally characterized zirconium sulfates, the structure of $Zr(SO_4)_2 \cdot 4H_2O$ does not contain dimeric ring units. $\alpha$- and $\gamma$-$Zr(SO_4)_2 \cdot H_2O$ also form layer structures (viz. comprising dimeric rings), of composition $[Zr(SO_4)_2 \cdot H_2O]_n$, which are held together by hydrogen bonds. In contrast to its hydrates, the structure of $\alpha$-$Zr(SO_4)_2$ consists of a three-dimensional network of sulfate-bridged zirconium atoms. The structure is built up of dimeric rings which are held together by Zr–O–S linkages.

Based on structural insights, some ideas have been presented concerning the nature of the species present in zirconium sulfate solutions. Clearfield[14] has pointed out that in order for one to dissolve $Zr(SO_4)_2 \cdot 4H_2O$ the infinite sheets must be broken into simpler units by

---

* To whom correspondence should be addressed.

scission of the bonds between the zirconium atoms and the sulfate groups and replacing the disconnected sulfate by hydroxide, thus producing monomeric, dimeric and trimeric anionic fragments such as $Zr(OH)_2(SO_4)_2^{2-}$, $Zr_2(OH)_3(SO_4)_4^{3-}$ and $Zr_3(OH)_4(SO_4)_6^{4-}$, respectively. Clearfield has described how it is possible to derive practically all known basic sulfates from these fragments. Bear and Mumme[6] have extended Clearfield's ideas to solutions which are more concentrated than that of a saturated solution of $Zr(SO_4)_2 \cdot 4H_2O$. Bear and Mumme point out that under these conditions the hydroxide replacement (olation) does not occur and the species react in solution only by formation of sulfate bridges so that the 1:2 ratio of $Zr:SO_4$ is maintained. When the concentration of $Zr(SO_4)_2$ in aqueous solutions becomes supersaturated, with respect to $Zr(SO_4)_2 \cdot 4H_2O$, the latter does not (at first sight paradoxically) crystallize from the solution. Instead, the more soluble $\alpha$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$ crystallizes initially at room temperature (r.t.), followed by $Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$ at ca. 0 °C. These solid products are accordingly derived from species in the solution and their formation indicates that the nature of the species in solution changes as the concentration of zirconium sulfate increases. The inference drawn from these findings is consequently that in such solutions the cyclic dimeric $Zr_2(SO_4)_4$ unit is the most prodominate species. This is precisely the basic structural fragment of $\alpha$-$Zr_2(SO_4)_4(H_2O)_8 \cdot 2H_2O$ and $Zr_2(SO_4)_4(H_2O)_8 \cdot 6H_2O$, but notably not of $Zr(SO_4)_2 \cdot 4H_2O$. The high acidity of zirconium sulfate solutions is thought to indicate that the dimeric units do not exist as neutral molecules in solution, but that hydrogen ions dissociate from some or all of the coordinated water molecules, leaving a negatively charged dimeric unit. A complex negative ion of this kind could also account for the anionic migration of zirconium observed in concentrated zirconium solutions (see Ref. 6 and references therein).

The literature concerning hafnium sulfates is much more limited. The preparation of $Hf(SO_4)_2$ from the reaction of $HfO_2$ with $H_2SO_4$ has been reported.[15] Bear and Mumme[16] have reported that hafnium sulfates can be prepared in different crystallographic modifications in close analogy with the zirconium sulfates already mentioned. From phase characterization by X-ray diffraction these compounds are shown to be isomorphous with corresponding zirconium sulfates.

Zirconium and hafnium hydroxide sulfates have been the subject of many publications. However, if one limits oneself to structurally well, or reasonably well, characterized compounds, the selection is limited to $Zr(OH)_2SO_4$,[17] $Zr(OH)_2SO_4 \cdot H_2O$,[18] $Zr_2(OH)_2(SO_4)_3 \cdot (H_2O)_4$,[19] $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$,[20] $Hf(OH)_2SO_4$,[21] $Hf(OH)_2SO_4 \cdot H_2O$[22] and $Hf_{18}O_{10}(OH)_{26}(SO_4)_{13} \cdot (H_2O)_{33}$.[23]

## Experimental

$ZrO_2$ [Aldrich; 99%, $a = 514.5(1)$, $b = 520.9(1)$, $c = 531.3(1)$ pm, $\beta = 99.26(2)°$], $HfO_2$ [Aldrich; >98%, $a =$

$511.91(7)$, $b = 517.15(8)$, $c = 529.4(1)$ pm, $\beta = 99.19(1)°$] and conc. $H_2SO_4$ (Merck; p.a.; 95–97 wt%, the former value being used throughout this paper) were applied as starting chemicals for the syntheses. Conc. $H_2SO_4$ in the range 50–95 wt% $H_2SO_4$ was made by diluting the as-purchased acid with distilled $H_2O$.

1.8 g of well ground $ZrO_2$ (2.1 g $HfO_2$) was added to 20 ml of $H_2SO_4$ (50–95 wt%) in a round-bottomed flask with a reflux cooler. In some cases '$Zr(OH)_4$' or '$Hf(OH)_4$' was used as starting material to increase the reaction rate. The mixtures were stirred with a magnetic stirrer, and heated at the boiling point (b.p.; in some cases 170 °C or r.t. was used) for ca. 20 h. The stirring and heating were then stopped. After cooling to r.t. (with frequent stirring in order to avoid mass solidification and sticking of the product to the glass of the reaction vessel) white precipitates were obtained, for concentrations in the ranges 85–95 and 50–65 wt% $H_2SO_4$. For 70–80 wt% $H_2SO_4$ either a white precipitate, a suspension or a colourless solution was the outcome. When the whole reaction mixtures of the latter syntheses were poured into a beaker containing ca. 150 ml of glacial acetic acid and stirred for ca. 1 day a white precipitate separated out and settled when the stirring was discontinued. The remaining acid mixtures (after separation of the precipitate by decantation or filteration through a sintered glass funnel) were also clear and colourless (except for some cases with 85 wt% $H_2SO_4$, where the final solutions were brown). All obtained precipitates were ultimately transferred to beakers containing ca. 100 ml of glacial acetic acid, stirred for 15 min, filtered off, and washed with glacial acetic acid, acetone and diethylether. The entire washing procedure was repeated twice. The products were then transferred to a desicator, dried and kept under a $CO_2$ atmosphere.

A separate series of syntheses followed a slightly modified recipe. $ZrO_2$ or $HfO_2$ were treated in 95 wt% $H_2SO_4$ as described above, but before the solid product and the mother liquor were separated an appropriate amount of distilled $H_2O$ was added. The mixture thus obtained was heated at b.p. for ca. 20 h, then cooled to r.t., and at this stage separated and subjected to the washing procedure.

Treatment of the as-synthesized solid reaction products with $H_2O$ resulted usually in new products. Three different routes were followed: (i) slow evaporation from concentrated aqueous solutions of zirconium or hafnium sulfates, (ii) slow evaporation from diluted aqueous solutions of zirconium or hafnium sulfates and (iii) slow degradation of anhydrous or hydrous zirconium or hafnium sulfates in moist air at r.t.

'$Zr(OH)_4$' or '$Hf(OH)_4$' was prepared by adding conc. $NH_3$ to an aqueous zirconium or hafnium sulfate solution under stirring. The mixture was left to settle down and the colourless upper layer was removed by decantation. The colloid layer was washed with distilled $H_2O$ several times until $SO_4^{2-}$ could not be detected in the washing liquid. Then the colloid layer was left to dry by slow

evaporation at r.t. After ca. 4 days a white (virtually X-ray amorphous) precipitate was obtained.

All samples were characterized by powder X-ray diffraction (PXD) using Guinier–Hägg cameras (Cu $K\alpha_1$ radiation, Si as internal standard and a $CO_2$ atmosphere to protect the samples from moisture during the examination). The positions of the Bragg reflections were obtained from the films by means of a Nicolet L18 scanner using the SCANPI program system.[24] The diffraction patterns of structurally unknown phases were attempted indexed with the help of the TREOR program.[25] Unit-cell parameters were obtained by least-squares refinements using the CELLKANT program.[26]

Thermogravimetric (TG) and differential thermal (DTA) analyses were performed (in separate experiments) between 20 and 900 °C with a Perkin Elmer TGA 7 and DTA 7 system, respectively. The 15–40 mg samples were placed in $Al_2O_3$ crucibles, flowing nitrogen was used as atmosphere and the heating rate was 10 °C min$^{-1}$.

## Results and discussion

*Zirconium(IV) oxide as reactant.* As seen from Table 1 the only solid compounds obtained by reaction between $ZrO_2$ and 95–50 wt% $H_2SO_4$ are $\alpha$-$Zr(SO_4)_2$, $Zr(SO_4)_2 \cdot 7H_2O(B)$, $Zr(SO_4)_2 \cdot 4H_2O(B)$ and $Zr(SO_4)_2 \cdot$

*Table 1.* Solid (crystalline) products (sulfates) prepared from $ZrO_2$ or $HfO_2$ and $H_2SO_4$ in different concentrations at b.p.

| Reaction product | wt% $H_2SO_4$ | wt% unreacted $ZrO_2$ or $HfO_2$ |
|---|---|---|
| $\alpha$-$Zr(SO_4)_2$ | 95–85 | 0 |
| $Zr(SO_4)_2 \cdot 7H_2O(B)$ | 80 | 0 |
| $Zr(SO_4)_2 \cdot 4H_2O(B)$ | 77.5 | 0 |
| $Zr(SO_4)_2 \cdot 4H_2O(A)$ | 75–70 | 0 |
| $Zr(SO_4)_2 \cdot 4H_2O(A)$ | 65–50 | 5–81 |
| $\alpha$-$Hf(SO_4)_2$ | 95–90 | 0 |
| $Hf(SO_4)_2 \cdot 7H_2O(B)^a$ | 85–72.5 | 1–7 |
| $Hf(SO_4)_2 \cdot 4H_2O(A)$ | 70–60 | 23–98 |

$^a$$Hf(SO_4)_2 \cdot 2H_2O$ plus some $HfO_2$ has been obtained in one case with 80 wt% $H_2SO_4$.

$4H_2O(A)$, arranged according to decreasing concentration of $H_2SO_4$. (The notations A and B are used to distinguish new modifications synthesized in this study.) For syntheses performed at b.p. the yields are generally very good. The same reaction products were found at 170 °C, but their phase purities were poorer and the yields were lower. No reaction appears to take place at r.t. [With '$Zr(OH)_4$' as reactant a slow reaction is seen at r.t.]

Characterization by PXD (cf. the unit-cell dimensions in Table 2) show that $\alpha$-$Zr(SO_4)_2$ and $Zr(SO_4)_2 \cdot 4H_2O(A)$ are identical with the corresponding phases described in Ref. 6. $Zr(SO_4)_2 \cdot 7H_2O(B)$ and $Zr(SO_4)_2 \cdot 4H_2O(B)$ are obtained directly as solid products in syntheses with ca. 80 and 77.5 wt% $H_2SO_4$, respectively. However, both compounds can also be extracted from the decanted mother liquor over wider ranges of $H_2SO_4$ concentrations: 90–80 wt% for $Zr(SO_4)_2 \cdot 7H_2O(B)$ and 77.5–75 wt% for $Zr(SO_4)_2 \cdot 4H_2O(B)$. As seen from Table 1 $\alpha$-$Zr(SO_4)_2$ and $Zr(SO_4)_2 \cdot 4H_2O(A)$ rule comparatively wide concentration ranges alone and are accordingly easy to prepare phase pure. Syntheses of phase-pure $Zr(SO_4)_2 \cdot 7H_2O(B)$ and $Zr(SO_4)_2 \cdot 4H_2O(B)$, on the other hand, require more careful attention to the $H_2SO_4$ concentration. Even rather slight deviations from the concentrations specified in Table 1 result in phase mixtures with $\alpha$-$Zr(SO_4)_2$ or $Zr(SO_4)_2 \cdot 4H_2O(A)$ or phase-pure products of the latter compounds.
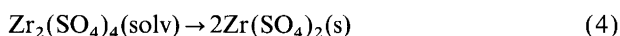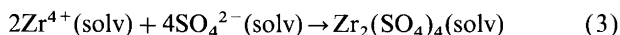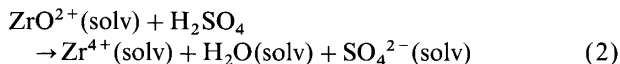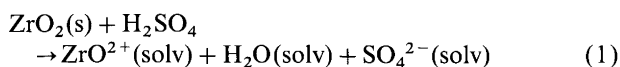
The progressing reaction between $ZrO_2$ and 95–77.5 wt% $H_2SO_4$ is evidenced by the dissolution of $ZrO_2$ and the subsequent appearance of either a white-to-yellow, milky (colloid-like) or colourless solution, and ultimately either the deposition of a white precipitate or a persistent colourless solution. In order to gain insight into the progress of this reaction, it was noted from experiments with reduced amounts of $ZrO_2$ (using, say, half the amount of $ZrO_2$, see Experimental), 90 wt% $H_2SO_4$ and heating at b.p., that when $ZrO_2$ dissolves a clear colourless solution is obtained first, which in turn gradually becomes yellow, and finally after a few minutes a white precipitate slowly separates out (the whole pro-

*Table 2.* Unit-cell dimensions at r.t. with calculated standard deviations in parentheses for hafnium and zirconium sulfates.

| Compound | Symmetry | $a$/pm | $b$/pm | $c$/pm | $\alpha$/° | $\beta$/° | $\gamma$/° | $V$/$10^6$ pm$^3$ | $M(20)^a$ | Ref.$^b$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha$-$Zr(SO_4)_2$ | Orthorhombic | 861.4(1) | 544.85(3) | 1089.1(1) | 90 | 90 | 90 | 511.15(5) | 170.2 | 6, 7 |
| $\beta$-$Zr(SO_4)_2$ | Unindexed | | | | | | | | | |
| $\gamma$-$Zr(SO_4)_2 \cdot H_2O$ | Triclinic | 789.1(2) | 521.4(2) | 898.1(3) | 95.13(3) | 99.84(2) | 109.21(2) | 339.6(2) | 35.8 | 6, 9 |
| $Zr(SO_4)_2 \cdot 4H_2O(A)$ | Orthorhombic | 2591.9(4) | 1161.7(1) | 553.4(4) | 90 | 90 | 90 | 1666.4(4) | 189.8 | 6, 10 |
| $Zr(SO_4)_2 \cdot 4H_2O(B)^c$ | Monoclinic | 1115.6(2) | 1097.2(2) | 769.3(3) | 90 | 113.27(2) | 90 | 865.1(4) | 161.1 | |
| $Zr(SO_4)_2 \cdot 7H_2O^c$ | Monoclinic | 1935.6(3) | 746.4(1) | 946.5(1) | 90 | 110.35(1) | 90 | 1282.1(3) | 140.5 | |
| $\alpha$-$Hf(SO_4)_2$ | Orthorhombic | 1085.5(1) | 543.17(3) | 858.85(4) | 90 | 90 | 90 | 506.39(4) | 234.1 | 6, 16 |
| $\gamma$-$Hf(SO_4)_2$ | Orthorhombic | 590.5(1) | 593.1(1) | 724.2(1) | 90 | 90 | 90 | 253.62(8) | 225.0 | 6, 16 |
| $\gamma$-$Hf(SO_4)_2 \cdot H_2O$ | Triclinic | 788.9(3) | 520.0(3) | 896.8(5) | 95.04(4) | 99.73(4) | 109.07(4) | 338.6(3) | 40.2 | 6, 16 |
| $Hf(SO_4)_2 \cdot 2H_2O^d$ | Monoclinic | 1201.8(2) | 850.3(2) | 732.1(2) | 90 | 109.60(2) | 90 | 704.71(3) | 89.5 | |
| $Hf(SO_4)_2 \cdot 4H_2O(A)$ | Orthorhombic | 2586.1(2) | 1159.2(1) | 552.9(1) | 90 | 90 | 90 | 1657.4(3) | 130.2 | 6, 16 |
| $Hf(SO_4)_2 \cdot 7H_2O(B)^c$ | Monoclinic | 1934.8(3) | 745.9(1) | 946.8(2) | 90 | 110.35(1) | 90 | 1281.2(4) | 47.0 | |

$^a$Figure of merit. $^b$Reference to earlier data for same material. $^c$New modification. $^d$Indexing according to the unit-cell dimensions reported by Bear and Mumme[16] gave: $a = 731.9(2)$, $b = 850.3(2)$, $c = 1179.0(2)$ pm, $\beta = 106.29(1)°$ and $M(20) = 85.1$.

cedure takes some 45 min). These observations, together with the insight provided in Ref. 6, lead us to propose the following simplified scheme for the most concentrated reaction media (viz. 95–85 wt% $H_2SO_4$):

$$ZrO_2(s) + H_2SO_4$$
$$\rightarrow ZrO^{2+}(solv) + H_2O(solv) + SO_4^{2-}(solv) \qquad (1)$$

$$ZrO^{2+}(solv) + H_2SO_4$$
$$\rightarrow Zr^{4+}(solv) + H_2O(solv) + SO_4^{2-}(solv) \qquad (2)$$

$$2Zr^{4+}(solv) + 4SO_4^{2-}(solv) \rightarrow Zr_2(SO_4)_4(solv) \qquad (3)$$

$$Zr_2(SO_4)_4(solv) \rightarrow 2Zr(SO_4)_2(s) \qquad (4)$$

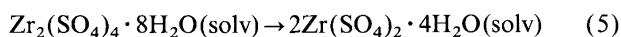neglecting the concentration-dependent equilibria assosiated with $H_2O$ in $H_2SO_4$.

The reality of eqn. (1) should be regarded as more uncertain than the occurrence of eqns. (2)–(4). However, the main purpose of eqns. (1)–(4) is to focus attention on the existence of significant amounts of the dimeric species $Zr_2(SO_4)_4(solv)$ in the most concentrated $H_2SO_4$ solutions. This approach is in accord with the concepts of Bear and Mumme.[6]

When the concentration of $H_2SO_4$ is decreased to ca. 80 wt% the visible difference in the reaction pattern is that the initial clear colourless solution (*vide supra*) turns only faintly yellow (or remains colourless) as the reaction progresses. A likely inference of this is that the anhydrous dimeric species $Zr_2(SO_4)_4(solv)$ becomes hydrated $[Zr_2(SO_4)_4 \cdot 8H_2O(solv)]$ in the less concentrated $H_2SO_4$ solutions. A $Zr_2(SO_4)_4 \cdot 8H_2O$ fragment is precisely a basic unit of the crystal structures of $Zr(SO_4)_2 \cdot 7H_2O$ and $Zr(SO_4)_2 \cdot 5H_2O$.[11–13]

The fact that $Zr(SO_4)_2 \cdot 7H_2O(B)$ can also be extracted by treatment of the mother liquors (over a wide range of $H_2SO_4$ concentrations, *vide supra*) with glacial acetic acid raises three important points: (i) $Zr(SO_4)_2 \cdot 7H_2O(B)$ is much more soluble than $\alpha$-$Zr(SO_4)_2$ and $Zr(SO_4)_2 \cdot 4H_2O(A)$ in the reaction media $[Zr(SO_4)_2 \cdot 7H_2O(B)$ is also more soluble in water than the other zirconium sulfates synthesized in this study]. (ii) Species like $Zr_2(SO_4)_4(solv)$ and $Zr_2(SO_4)_4 \cdot 8H_2O(solv)$ really occur in these conc. $H_2SO_4$ solutions, and there exist concentration-dependent equilibria between the anhydrous and hydrous variants. (iii) The recovery of dissolved species from the mother liquors by treatment with glacial acetic acid is a general means to improve the yields of such syntheses. The present authors have previously observed[1] that glacial acetic acid is an efficient chemical to remove adhered $H_2SO_4$ on the surfaces of solid sulfates.

It is, moreover, worth noting that $Zr(SO_4)_2 \cdot 7H_2O(B)$ is metastable with respect to $Zr(SO_4)_2 \cdot 4H_2O(A)$.

When the concentration of $H_2SO_4$ is decreased below ca. 80 wt% (viz. ca. 77.5–50 wt%), a significant proportion of the hydrated dimeric ring species $Zr_2(SO_4)_4 \cdot 8H_2O(solv)$ becomes a monomeric species:

$$Zr_2(SO_4)_4 \cdot 8H_2O(solv) \rightarrow 2Zr(SO_4)_2 \cdot 4H_2O(solv) \qquad (5)$$

From these solutions $Zr(SO_4)_2 \cdot 4H_2O(A)$ or $Zr(SO_4)_2 \cdot$

$4H_2O(B)$ in turn precipitate. The appearance of the two modifications shows that different polymerization mechanisms are involved in the concentration ranges concerned.

Additional support for the above considerations are provided by the following experiments: (i) $\alpha$-$Zr(SO_4)_2$ was prepared from 95 wt% $H_2SO_4$ according to usual procedure. After the reaction mixture had been cooled to r.t., the calculated amount of distilled water for dilution to 80 wt% $H_2SO_4$ was added. The reaction mixture thus obtained was then reheated at b.p. (under stirring) for another 20 h and the resulting product was treated as described above. The product proved to be $Zr(SO_4)_2 \cdot 7H_2O(B)$. (ii) When similar experiments with dilution to 77.5–75 wt% $H_2SO_4$ were performed, the products proved to be $Zr(SO_4)_2 \cdot 4H_2O(B)$.

*Hafnium(IV) oxide as reactant.* The syntheses with $HfO_2$ generally follow the same evolution patterns as those with $ZrO_2$, but as seen from Table 1 the products differ; in particular with regard to the $H_2SO_4$ concentrations at which they are found. $\alpha$-$Hf(SO_4)_2$, $Hf(SO_4)_2 \cdot 2H_2O$ (obtained in just one case), $Hf(SO_4)_2 \cdot 7H_2O(B)$ and $Hf(SO_4)_2 \cdot 4H_2O(A)$ are the only solid compounds prepared from $HfO_2$ and 95–50 wt% $H_2SO_4$. As for the zirconium sulfates, the yields of the syntheses are very good.

The solid products were characterized by PXD, and according to the unit-cell dimensions (Table 2) $\alpha$-$Hf(SO_4)_2$ and $Hf(SO_4)_2 \cdot 4H_2O(A)$ are identical with the corresponding compounds considered in Ref. 6 (and moreover isostructural with the corresponding zirconium sulfates). $Hf(SO_4)_2 \cdot 7H_2O(B)$ is a new compound, almost certainly isostructural with the corresponding zirconium sulfate (Table 2). Indexing of the PXD pattern of $Hf(SO_4)_2 \cdot 2H_2O$ by the TREOR program[25] gave unit-cell dimensions (Table 2) which are only slightly different from those recorded for $\alpha$-$Hf(SO_4)_2 \cdot H_2O$ in Ref. 6. This leads us to suggest that both formulae refer to the same phase, and that $Hf(SO_4)_2 \cdot 2H_2O$ is the correct composition. [Despite numerous attempts we have been unable to reproduce our once successful synthesis of $Hf(SO_4)_2 \cdot 2H_2O$.]

On comparing the results for the zirconium and hafnium sulfates in Table 1, it is seen that, although the pattern is largely the same, there are also remarkable distinctive features. $Hf(SO_4)_2 \cdot 7H_2O(B)$, e.g., can be prepared over a much wider range of $H_2SO_4$ concentrations than the corresponding zirconium sulfate. [Note that $Hf(SO_4)_2 \cdot 7H_2O(B)$ can also be obtained (phase pure) from mother liquors and diluted reaction mixtures which contain $\alpha$-$Hf(SO_4)_2(s)$, as described for $Zr(SO_4)_2 \cdot 7H_2O(B)$.] However, the most remarkable features are the phases which appear for only one of the oxides, viz. $Zr(SO_4)_2 \cdot 4H_2O(B)$ among the zirconium sulfates and $Hf(SO_4)_2 \cdot 2H_2O$ among the hafnium sulfates. The exposed distinctions were in fact somewhat unexpected in view of the close correspondence between

27

zirconium and hafnium in ionic size and chemical behaviour.

The corresponding syntheses with $TiO_2$ as reactant gave[3] only oxide sulfates in reaction with conc. $H_4SO_4$. This feature is clearly correlated with the smaller ionic size of titanium which prefers octahedral coordination as compared with the more space demanding coordinations adopted by the larger zirconium and hafnium ions.

*Solubility in water and solid products recovered from aqueous solutions.* All the zirconium and hafnium sulfates listed in Table 1 are easily soluble in $H_2O$, and the resulting solutions react acidic. When a concentrated aqueous solution of any of the zirconium (hafnium) sulfates in Table 1 is subjected to slow evaporation at r.t., the solid product which is ultimately deposited is invariably $Zr(SO_4)_2 \cdot 4H_2O(A)$ $[Hf(SO_4)_2 \cdot 4H_2O(A)]$. The same final products are obtained when zirconium (hafnium) sulfates degrade in moist air at r.t. A few weeks are, e.g., required for complete conversion of $\alpha$-$Zr(SO_4)_2$ $[\alpha$-$Hf(SO_4)_2]$ into $Zr(SO_4)_2 \cdot 4H_2O(A)$ $[Hf(SO_4)_2 \cdot 4H_2O(A)]$.

On the other hand, slow evaporation from diluted aqueous solutions of the same sulfates gives an entirely different product: $M_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$, $M = Zr$ or Hf. Tentatively we suggest that a condensation type polymerization takes place between, say, $Zr_2(SO_4)_4 \cdot 8H_2O$ $[Hf_2(SO_4)_4 \cdot 8H_2O]$ species in the aqueous solutions. Using $\alpha$-$Zr(SO_4)_2$ as an example to illustrate the point, the overall reaction is as follows:

$$18Zr(SO_4)_2(s) + 79H_2O$$
$$\rightarrow Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O(s) + 46H^+(aq)$$
$$+ 23SO_4^{2-}(aq) \tag{6}$$
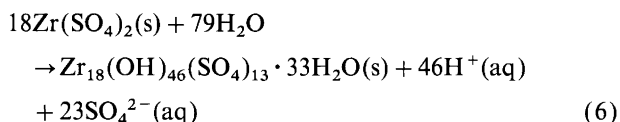
On heating $Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$ at ca. 480 °C for ca. 2 days (a shorter time is possible) in an open crucible (and cooling the product in a vacuum desicator) the corresponding oxide sulfate, $Zr_{18}O_{23}(SO_4)_{13}$, is obtained. Similar results are obtained for the hafnium case. Support for the rather complex formulae for these zirconium and hafnium hydroxide sulfates comes from the single-crystal X-ray diffraction structure determinations of $Zr_{18}O_4(OH)_{38.8}(SO_4)_{12.6} \cdot 33H_2O$[20] and $Hf_{18}O_{10}(OH)_{26}$-$(SO_4)_{13} \cdot 33H_2O$.[23] Even though the latter compounds have been obtained under quite different preparative conditions (which easily explain the rather minor variations in oxide vs. hydroxide content), together with TG analytical data (*vide infra*) the structurally confirmed compositions give confidence in the formulae $Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$ and $Hf_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$. Unfortunately our PXD data for these compounds are very poor (only a few rather diffuse, low-angle reflections are measurable with reasonable accuracy), and unambiguous phase identification on diffraction basis could accordingly not be obtained.

$Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$, $Zr_{18}O_{23}(SO_4)_{13}$ and the

analogously composed hafnium sulfates are rather poorly soluble in $H_2O$ at r.t.

*Effect of heat treatment on the reaction products.* The results of the TG and DTA examinations of the reaction products are presented in Figs. 1a–1r, and temperature regions and relative mass losses for the decomposition reactions that occur are summarized in Table 3. The agreement between observed and calculated $\Delta m/\Delta m_0$ values is generally good, and the TG data accordingly serve to confirm the composition of the synthesized compounds.

The thermal decomposition of the anhydrous zirconium (hafnium) sulfates, $\alpha$-$Zr(SO_4)_2$, and $\beta$-$Zr(SO_4)_2$ $[\alpha$-$Hf(SO_4)_2$, and $\gamma$-$Hf(SO_4)_2]$ into $ZrO_2$ $(HfO_2)$ and $SO_3$ takes place in one step (Figs. 1a, 1b, 1i and 1j). Different modifications differ in the onset and end temperatures for the decompositions. In general the $\alpha$-forms have a higher decomposition temperature than the assumed metastable $\beta$- and $\gamma$-forms. The TG curves for the other sulfates show more than one feature (Figs. 1c–1f and 1k–1n; Table 3). $\gamma$-$Zr(SO_4)_2 \cdot H_2O$ and $\gamma$-$Hf(SO_4)_2 \cdot H_2O$ decompose in two steps (Figs. 1c and 1k); first one $H_2O$ is lost and then $Zr(SO_4)_2$ $[Hf(SO_4)_2]$ decomposes into $ZrO_2$ $(HfO_2)$ and $SO_3$. The DTA curves for these compounds show an extra endothermic feature which probably reflects a phase transition in $Zr(SO_4)_2$ and $Hf(SO_4)_2$, soon after they have been formed. However, such features were not observed in the decomposition products of the tetra- and heptahydrates (Figs. 1c–1f and 1k–1n). The thermal decomposition of $Zr(SO_4)_2 \cdot 4H_2O(A)$ and $Hf(SO_4)_2 \cdot 4H_2O(A)$ takes place in three steps (Figs. 1d and 1m). The first three $H_2O$ are lost, then one $H_2O$ and finally the decomposition into $ZrO_2$ $(HfO_2)$ and $SO_3$ takes place. $Zr(SO_4)_2 \cdot 4H_2O(B)$, on the other hand, gradually looses the water before $Zr(SO_4)_2$ finally decomposes into $ZrO_2$ and $SO_3$ (Fig. 1e).

Thermoanalytical data for some zirconium sulfates have been previously reported (Ref. 27 and references therein), and the present data are in agreement except for the earlier claim that $\alpha$-, $\beta$- and $\gamma$-$Zr(SO_4)_2$ initially decompose into cubic $ZrO_2$, which in turn is transformed into the monoclinic form. The present PXD data unequivocally show that monoclinic $ZrO_2$ is the reaction product, and DTA did not give any indication of a phase transition at the temperatures concerned. Neither could the claim by Vinarov *et al.*[28] that $Hf(SO_4)_2$ obtained by thermal decomposition of $Hf(SO_4)_2 \cdot 4H_2O(A)$ undergoes stepwise thermal decomposition into $HfO_2$ be confirmed here (Figs. 1i, 1j and 1m and Table 3).

Dehydratization of $Zr(SO_4)_2 \cdot 4H_2O(A)$ at ca. 150 and 400 °C in open crucibles resulted in $\gamma$-$Zr(SO_4)_2 \cdot H_2O$ and $\beta$-$Zr(SO_4)_2$, respectively, whereas a corresponding treatment of $Hf(SO_4)_2 \cdot 4H_2O(A)$ resulted in $\gamma$-$Hf(SO_4)_2 \cdot H_2O$ and $\gamma$-$Hf(SO_4)_2$, respectively, plus some $\beta$-$Hf(SO_4)_2$. Bear[27] points out that three factors determine whether $\gamma$- or $\beta$-$Zr(SO_4)_2$ will predominate in

*Table 3.* Summary of TG results for phase-pure reaction products.

| Compound | Ilustration no. | Decomposition reaction | Eqn. | $t_{start}/°C$ | $t_{end}/°C$ | $(\Delta m/m_0)^a$ obs. | $(\Delta m/m_0)$ calc. |
|---|---|---|---|---|---|---|---|
| $\alpha$-$Zr(SO_4)_2$ | 1a | $Zr(SO_4)_2(s) \rightarrow ZrO_2(s) + 2SO_3(g)$ | (7) | 655 | 835 | 0.558 | 0.565 |
| $\beta$-$Zr(SO_4)_2$ | 1b | $Zr(SO_4)_2(s) \rightarrow ZrO_2(s) + 2SO_3(g)$ | (7) | 600 | 765 | 0.555 | 0.565 |
| $\gamma$-$Zr(SO_4)_2 \cdot H_2O$ | 1c | $Zr(SO_4)_2 \cdot H_2O(s) \rightarrow Zr(SO_4)_2(s) + H_2O(g)$ | (8) | 215 | 290 | 0.059 | 0.060 |
| | | $Zr(SO_4)_2(s) \rightarrow ZrO_2(s) + 2SO_3(g)$ | (7) | 600 | 770 | 0.563 | 0.565 |
| | | $Zr(SO_4)_2 \cdot H_2O(s) \rightarrow$ $ZrO_2(s) + 2SO_3(g) + H_2O(g)$ | (8+7) | 215 | 770 | 0.599 | 0.591 |
| $Zr(SO_4)_2 \cdot 4H_2O(A)$ | 1d | $Zr(SO_4)_2 \cdot 4H_2O(s) \rightarrow$ $Zr(SO_4)_2 \cdot H_2O(s) + 3H_2O(g)$ | (9) | 125 | 205 | 0.152 | 0.152 |
| | | $Zr(SO_4)_2 \cdot H_2O(s) \rightarrow Zr(SO_4)_2(s) + H_2O(g)$ | (8) | 205 | 290 | 0.056 | 0.060 |
| | | $Zr(SO_4)_2(s) \rightarrow ZrO_2(s) + 3SO_3(g)$ | (7) | 635 | 780 | 0.565 | 0.565 |
| | | $Zr(SO_4)_2 \cdot 4H_2O(s) \rightarrow$ $ZrO_2(s) + 4H_2O(g) + 3SO_3(g)$ | (9+8+7) | 125 | 780 | 0.652 | 0.653 |
| $Zr(SO_4)_2 \cdot 4H_2O(B)$ | 1e | $Zr(SO_4)_2 \cdot 4H_2O(s) \rightarrow Zr(SO_4)_2(s) + 4H_2O(g)$ | (9) | 115 | 205 | 0.195 | 0.203 |
| | | $Zr(SO_4)_2(s) \rightarrow ZrO_2(s) + 3SO_3(g)$ | (7) | 680 | 735 | 0.558 | 0.565 |
| | | $Zr(SO_4)_2 \cdot 4H_2O(s) \rightarrow$ $ZrO_2(s) + 4H_2O(g) + 2SO_3(g)$ | (9+7) | 115 | 735 | 0.646 | 0.653 |
| $Zr(SO_4)_2 \cdot 7H_2O$ | 1f | $Zr(SO_4)_2 \cdot 7H_2O(s) \rightarrow$ $Zr(SO_4)_2 \cdot H_2O(s) + 6H_2O(g)$ | (10) | 120 | 175 | 0.257 | 0.264 |
| | | $Zr(SO_4)_2 \cdot H_2O(s) \rightarrow Zr(SO_4)_2(s) + H_2O(g)$ | (8) | 215 | 280 | 0.057 | 0.060 |
| | | $Zr(SO_4)_2(s) \rightarrow ZrO_2(s) + 2SO_3(g)$ | (7) | 630 | 750 | 0.566 | 0.565 |
| | | $Zr(SO_4)_2 \cdot 7H_2O(s) \rightarrow$ $ZrO_2(s) + 2SO_3(g) + 7H_2O(g)$ | (10+8+7) | 120 | 750 | 0.695 | 0.699 |
| $Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$ | 1g | $Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O(s) \rightarrow$ $Zr_{18}O_{23}(SO_4)_{13}(s) + 56H_2O(g)$ | (11) | 40 | 550 | 0.236 | 0.236 |
| | | $Zr_{18}O_{23}(SO_4)_{13}(s) \rightarrow 18ZrO_2(s) + 13SO_3(g)$ | (12) | 665 | 780 | 0.320 | 0.320 |
| | | $Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O(s) \rightarrow$ $18ZrO_2(s) + 13SO_3(g) + 56H_2O(g)$ | (11+12) | 40 | 780 | 0.480 | 0.480 |
| $Zr_{18}O_{23}(SO_4)_{13}$ | 1h | $Zr_{18}O_{23}(SO_4)_{13}(s) \rightarrow 18ZrO_2(s) + 13SO_3(g)$ | (12) | 665 | 780 | 0.316 | 0.320 |
| $\alpha$-$Hf(SO_4)_2$ | 1i | $Hf(SO_4)_2(s) \rightarrow HfO_2(s) + 2SO_3(g)$ | (13) | 660 | 835 | 0.429 | 0.432 |
| $\gamma$-$Hf(SO_4)_2$ | 1j | $Hf(SO_4)_2(s) \rightarrow HfO_2(s) + 2SO_3(g)$ | (13) | 550 | 810 | 0.423 | 0.432 |
| $\gamma$-$Hf(SO_4)_2 \cdot H_2O$ | 1k | $Hf(SO_4)_2 \cdot H_2O(s) \rightarrow Hf(SO_4)_2(s) + H_2O(g)$ | (14) | 205 | 305 | 0.046 | 0.046 |
| | | $Hf(SO_4)_2(s) \rightarrow HfO_2(s) + 2SO_3(g)$ | (13) | 635 | 825 | 0.429 | 0.432 |
| | | $Hf(SO_4)_2 \cdot H_2O(s) \rightarrow$ $HfO_2(s) + 2SO_3(g) + H_2O(g)$ | (14+13) | 205 | 825 | 0.455 | 0.458 |
| $Hf(SO_4)_2 \cdot 2H_2O$ | 1l | $Hf(SO_4)_2 \cdot 2H_2O(s) \rightarrow$ $Hf(SO_4)_2 \cdot H_2O(s) + H_2O(g)$ | (15) | 100 | 160 | 0.038 | 0.044 |
| | | $Hf(SO_4)_2 \cdot H_2O(s) \rightarrow Hf(SO_4)_2(s) + H_2O(g)$ | (14) | 275 | 355 | 0.050 | 0.046 |
| | | $Hf(SO_4)_2(s) \rightarrow HfO_2(s) + 2SO_3(g)$ | (13) | 645 | 825 | 0.431 | 0.432 |
| | | $Hf(SO_4)_2 \cdot 2H_2O(s) \rightarrow$ $HfO_2(s) + 2SO_3(g) + 2H_2O(g)$ | (15+14+13) | 100 | 825 | 0.482 | 0.482 |
| $Hf(SO_4)_2 \cdot 4H_2O(A)$ | 1m | $Hf(SO_4)_2 \cdot 4H_2O(s) \rightarrow$ $Hf(SO_4)_2 \cdot H_2O(s) + 3H_2O(g)$ | (16) | 125 | 185 | 0.126 | 0.122 |
| | | $Hf(SO_4)_2 \cdot H_2O(s) \rightarrow Hf(SO_4)_2(s) + H_2O(g)$ | (14) | 185 | 225 | 0.054 | 0.046 |
| | | $Hf(SO_4)_2(s) \rightarrow HfO_2(s) + 2SO_3(g)$ | (13) | 700 | 835 | 0.437 | 0.432 |
| | | $Hf(SO_4)_2 \cdot 4H_2O(s) \rightarrow$ $HfO_2(s) + 2SO_3(g) + 4H_2O(g)$ | (16+14+13) | 125 | 835 | 0.530 | 0.524 |
| $Hf(SO_4)_2 \cdot 7H_2O(B)$ | 1n | $Hf(SO_4)_2 \cdot 7H_2O(s) \rightarrow$ $Hf(SO_4)_2 \cdot H_2O(s) + 6H_2O(g)$ | (17) | 115 | 155 | 0.217 | 0.217 |
| | | $Hf(SO_4)_2 \cdot H_2O(s) \rightarrow Hf(SO_4)_2(s) + H_2O(g)$ | (14) | 225 | 290 | 0.051 | 0.046 |
| | | $Hf(SO_4)_2(s) \rightarrow HfO_2(s) + 2SO_3(g)$ | (13) | 635 | 770 | 0.422 | 0.432 |
| | | $Hf(SO_4)_2 \cdot 7H_2O(s) \rightarrow$ $HfO_2(s) + 2SO_3(g) + 7H_2O(g)$ | (17+14+13) | 115 | 770 | 0.572 | 0.576 |
| $Hf_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$ | 1o | $Hf_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O(s) \rightarrow$ $Hf_{18}O_{23}(SO_4)_{13}(s) + 56H_2O(g)$ | (18) | 40 | 650 | 0.170 | 0.172 |
| | | $Hf_{18}O_{23}(SO_4)_{13}(s) \rightarrow 18HfO_2(s) + 13SO_3(g)$ | (19) | 735 | 875 | 0.213 | 0.215 |
| | | $Hf_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O(s) \rightarrow$ $18HfO_2(s) + 13SO_3(g) + 56H_2O(g)$ | (18+19) | 40 | 875 | 0.347 | 0.351 |
| $Hf_{18}O_{23}(SO_4)_{13}$ | 1p | $Hf_{18}O_{23}(SO_4)_{13}(s) \rightarrow 18HfO_2(s) + 13SO_3(g)$ | (19) | 735 | 875 | 0.213 | 0.215 |
| '$Zr(OH)_4$' | 1q | $Zr(OH)_4(s) \rightarrow ZrO_2(s) + 2H_2O(g)$ | (20) | 40 | 275 | 0.231 | 0.226 |
| '$Hf(OH)_4$' | 1r | $Hf(OH)_4(s) \rightarrow HfO_2(s) + 2H_2O(g)$ | (21) | 40 | 300 | 0.154 | 0.146 |

$^a$Note that $m_0$ refers to the mass at the start of the appropriate decomposition reaction.

the dehydratization product of $Zr(SO_4)_2 \cdot 4H_2O(A)$: particle size, sample size and dehydratization procedure (in particular the temperature program). On this basis the different results described above are not surprising.

The thermal decomposition of $Zr(SO_4)_2 \cdot 7H_2O(B)$ [$Hf(SO_4)_2 \cdot 7H_2O(B)$] takes place in three steps (Figs. 1f and 1n and Table 3); first decomposition into $Zr(SO_4)_2 \cdot H_2O$ [$Hf(SO_4)_2 \cdot H_2O$], then loss of one $H_2O$ and finally decomposition into $ZrO_2$ ($HfO_2$) and $SO_3$. The weak endothermic features in DTA at around 250 °C
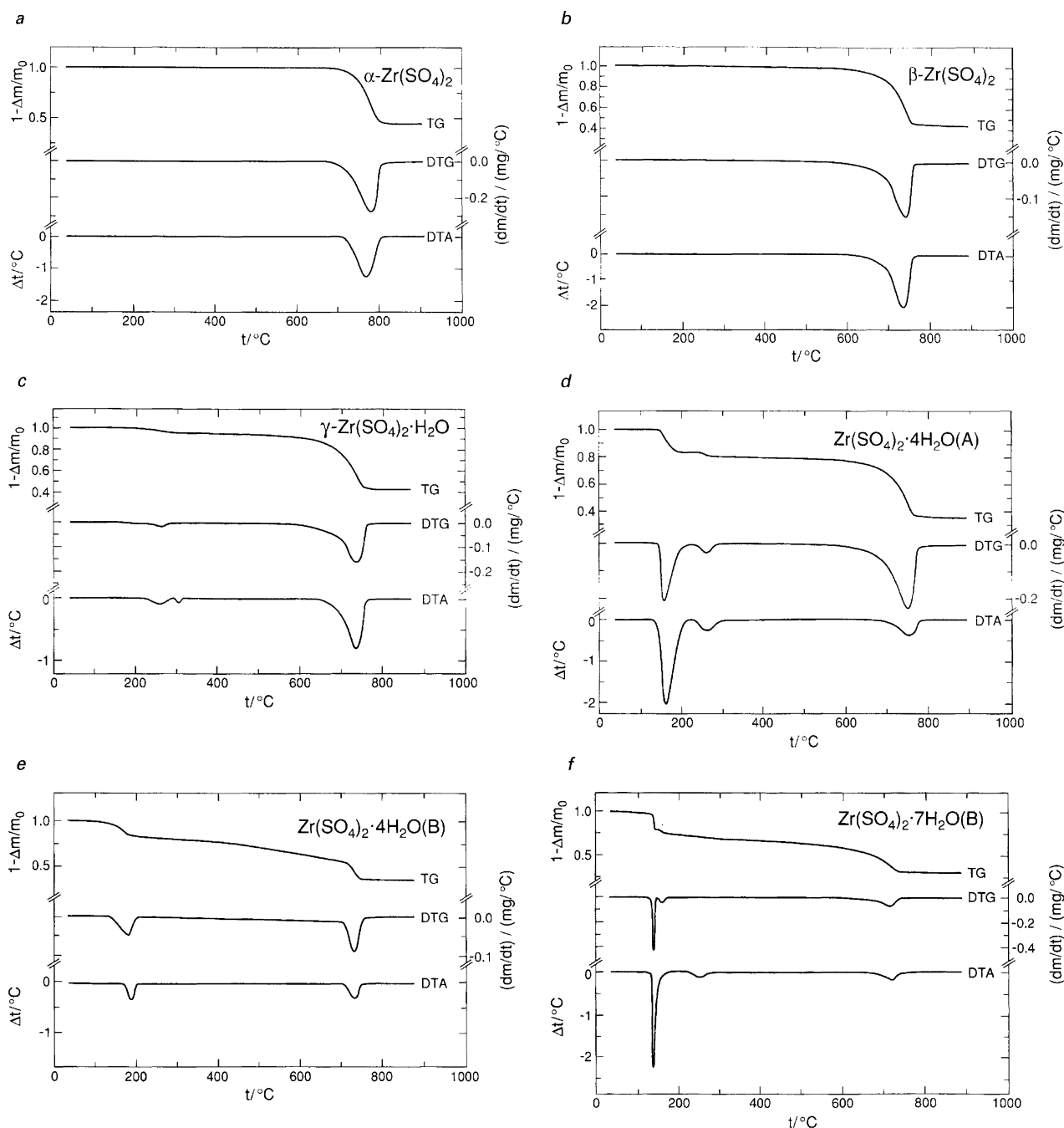
*Fig. 1.* TG, DTG and DTA data for (a) $\alpha$-Zr(SO$_4$)$_2$, (b) $\beta$-Zr(SO$_4$)$_2$, (c) $\gamma$-Zr(SO$_4$)$_2 \cdot$H$_2$O, (d) Zr(SO$_4$)$_2 \cdot$4H$_2$O(A), (e) Zr(SO$_4$)$_2 \cdot$4H$_2$O(B), (f) Zr(SO$_4$)$_2 \cdot$7H$_2$O(B), (g) Zr$_{18}$(OH)$_{46}$(SO)$_{13} \cdot$33H$_2$O, (h) Zr$_{18}$O$_{23}$(SO$_4$)$_{13}$, (i) $\alpha$-Hf(SO$_4$)$_2$, (j) $\gamma$-Hf(SO$_4$)$_2$, (k) $\gamma$-Hf(SO$_4$)$_2 \cdot$H$_2$O, (l) Hf(SO$_4$)$_2 \cdot$2H$_2$O (insufficient amount for DTA), (m) Hf(SO$_4$)$_2 \cdot$4H$_2$O(A), (n) Hf(SO$_4$)$_2 \cdot$7H$_2$O(B), (o) Hf$_{18}$(OH)$_{46}$(SO$_4$)$_{13} \cdot$33H$_2$O, (p) Hf$_{18}$O$_{23}$(SO$_4$)$_{13}$, (q) 'Zr(OH)$_4$' and (r) 'Hf(OH)$_4$'. The DTA scans are adjusted to a constant background signal.

in Figs. 1f and 1n suggest that the monohydrate phases formed on decomposition of the heptahydrates undergo phase transitions. However, such features do not occur in any of the other DTA curves where Zr(SO$_4$)$_2 \cdot$ H$_2$O and Hf(SO$_4$)$_2 \cdot$ H$_2$O appear.

In some cases thermal decomposition curves may differ somewhat (especially for the compounds with crystal

water), although PXD show that the products are the same. Bear[27] suggests that factors such as the conditions during precipitation, the washing chemical and washing procedure may affect the decomposition process to some extent.

The thermal decomposition of Zr$_{18}$(OH)$_{46}$(SO$_4$)$_{13} \cdot$ 33H$_2$O [Hf$_{18}$(OH)$_{46}$(SO$_4$)$_{13} \cdot$33H$_2$O] takes place in two

*g* $Zr_{18}(OH)_{46}(SO_4)_{13} \cdot 33H_2O$

*h* $Zr_{18}O_{23}(SO_4)_{13}$

*i* $\alpha\text{-}Hf(SO_4)_2$

*j* $\gamma\text{-}Hf(SO_4)_2$

*k* $\gamma\text{-}Hf(SO_4)_2 \cdot H_2O$
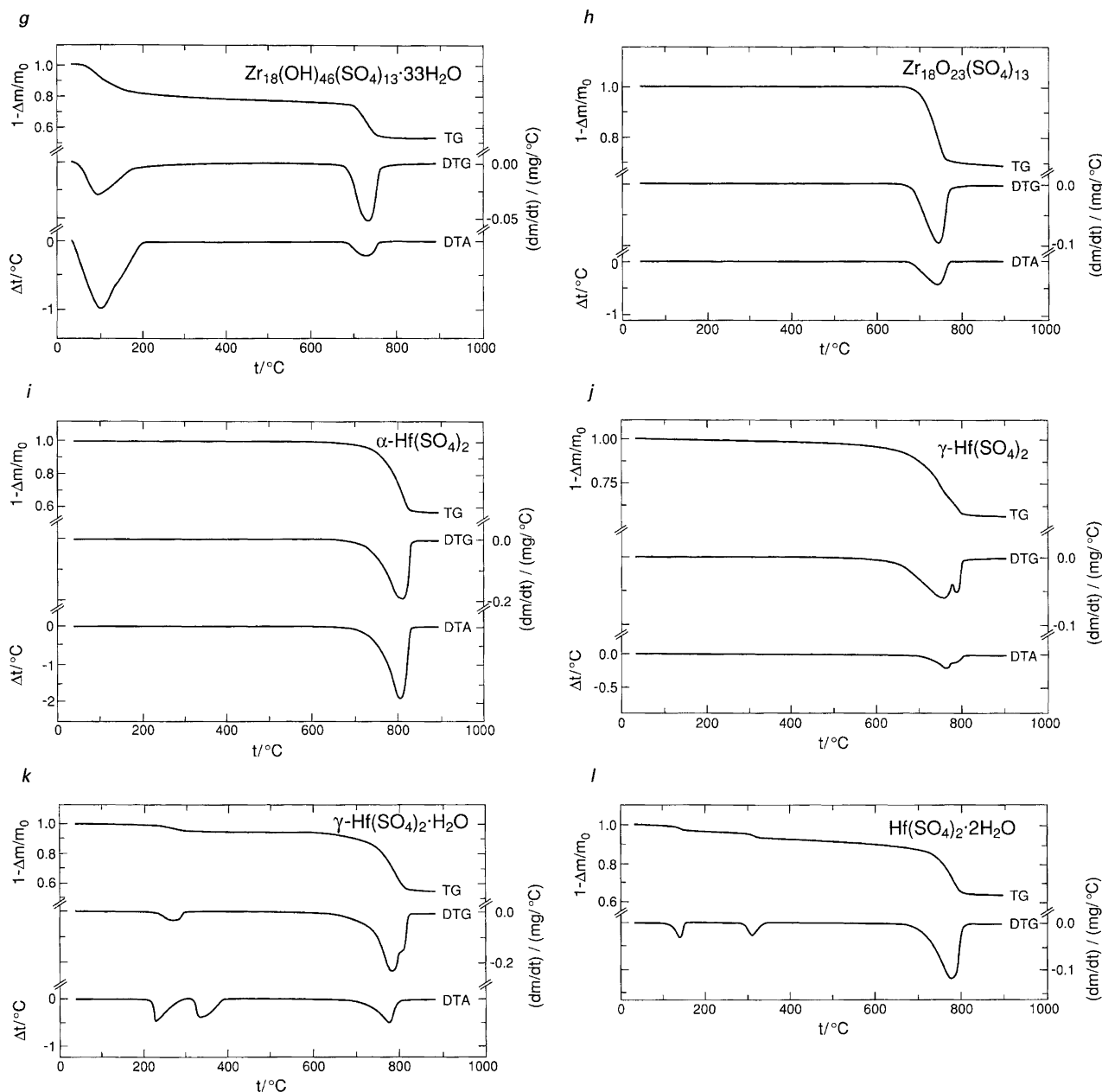
*l* $Hf(SO_4)_2 \cdot 2H_2O$

*Fig. 1. (Continued.)*

steps. First there is decomposition into $Zr_{18}O_{23}(SO_4)_{13}$ [$Hf_{18}O_{23}(SO_4)_{13}$] between ca. 40 and 550 (650) °C. This shows that some of the water is loosely bound whereas other water is more difficult to remove (probably water molecules eliminated from the the OH groups in the structure). $Zr_{18}O_{23}(SO_4)_{13}$ [$Hf_{18}O_{23}(SO_4)_{13}$] decomposes into $ZrO_2$ ($HfO_2$) and $SO_3$ in one step at 780 (875) °C (Figs. 1g, 1h, 1o and 1p and Table 3).

The TG and DTA data for 'Zr(OH)$_4$' ('Hf(OH)$_4$') show (Figs. 1q and 1r and Table 3) that the initially amorphous $ZrO_2$ ($HfO_2$) formed on thermal dehydratization crystallizes at ca. 430 (555) °C.

*Hygroscopic behaviour.* All the present sulfates except $Zr(SO_4)_2 \cdot 4H_2O(A)$ [$Hf(SO_4)_2 \cdot 4H_2O(A)$] are hygroscopic when exposed to moist air under ambient conditions. $Zr(SO_4)_2 \cdot 4H_2O(A)$ [$Hf(SO_4)_2 \cdot 4H_2O(A)$] is the product obtained by such treatment (samples may be stored for an indefinite period under an inert atmosphere in a sealed glass tube, for example).
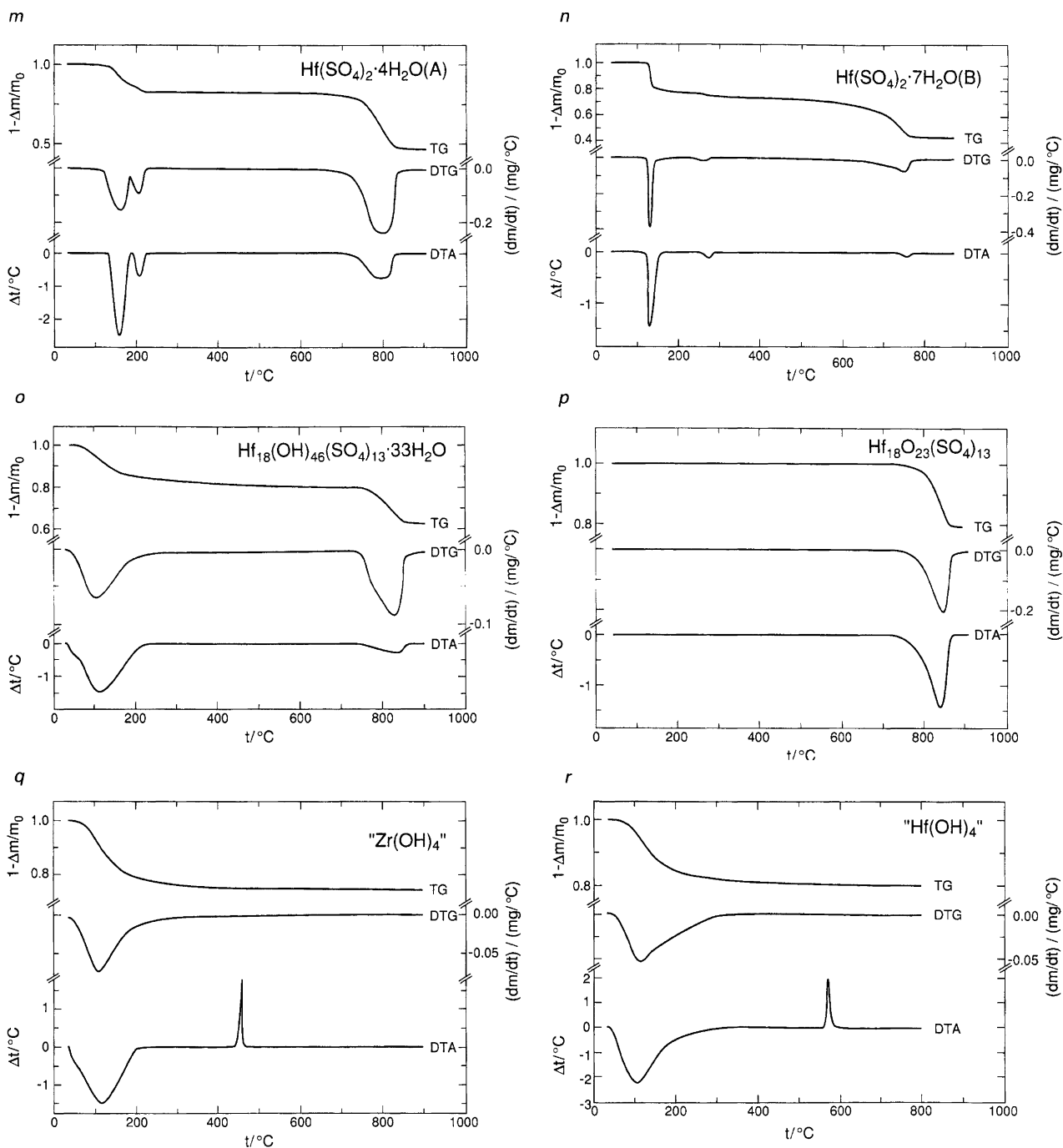
31

m



n

o

p

q

r

*Fig. 1. (Continued.)*

## References

1. Ahmed, M. A. K., Fjellvåg, H. and Kjekshus, A. *Acta Chem. Scand. 48* (1994) 537.
2. Ahmed, M. A. K., Fjellvåg, H. and Kjekshus, A. *Acta Chem. Scand. 49* (1995) 457.
3. Ahmed, M. A. K., Fjellvåg, H. and Kjekshus, A. *Acta Chem. Scand. 50* (1996) 275.
4. Ahmed, M. A. K., Fjellvåg, H. and Kjekshus, A. *Acta Chem. Scand. 52* (1998) 305.

5. Berzelius, J. J. *Kongl. Vetensk. Akad. Handl. Sth.* (1824) 295.
6. Bear, I. J. and Mumme, W. G. *Rev. Pure Appl. Chem. 21* (1971) 189.
7. Bear, I. J. and Mumme, W. G. *Acta Crystallogr., Sect. B 26* (1970) 1140.
8. Bear, I. J. and Mumme, W. G. *Acta Crystallogr., Sect. B 26* (1970) 1131.
9. Bear, I. J. and Mumme, W. G. *Acta Crystallogr., Sect. B 26* (1970) 1125.

10. Singer, J. and Cromer, D. T. *Acta Crystallogr. 12* (1959) 719.
11. Bear, I. J. and Mumme, W. G. *Acta Crystallogr., Sect. B 25* (1969) 1566.
12. Bear, I. J. and Mumme, W. G. *Acta Crystallogr., Sect. B 25* (1969) 1572.
13. Bear, I. J. and Mumme, W. G. *Acta Crystallogr., Sect. B 25* (1969) 1558.
14. Clearfield, A. *Rev. Pure Appl. Chem. 14* (1964) 91.
15. Hevesy, G. V. and Cremer, E. *Z. Anorg. Allg. Chem. 195* (1931) 339.
16. Bear, I. J. and Mumme, W. G. *J. Inorg. Nucl. Chem. 32* (1970) 1159.
17. McWhan, D. B. and Lundgren, G. *Acta Crystallogr. 16* (1963) A36.
18. Hansson, M. *Acta Chem. Scand. 27* (1973) 2614.
19. McWhan, D. B. and Lundgren, G. *Inorg. Chem. 5* (1966) 284.
20. Squattrito, P. J., Rudolf, P. R. and Clearfield, A. *Inorg. Chem. 26* (1987) 4240.
21. Hansson, M. *Acta Chem. Scand. 27* (1973) 2455.
22. Hansson, M. *Acta Chem. Scand. 23* (1969) 3541.
23. Mark, W. and Hansson, M. *Acta Crystallogr., Sect. B 31* (1975) 1101.
24. Werner, P.-E. *Program SCANPI-6*, Institute of Inorganic Chemistry, Stockholm University, Sweden 1988.
25. Werner, P.-E. *Program TREOR-5*, Institute of Inorganic Chemistry, Stockholm University, Sweden 1988 [see also *Z. Kristallogr. 120* (1964) 375].
26. Ersson, N. O. *Program CELLKANT*, Chemical Institute, Uppsala University, Sweden 1981.
27. Bear, I. J. *Aust. J. Chem. 20* (1967) 415.
28. Vinarov, I.V., Kovaleva, E. I. and Gertsenshtein, E. S. *Russ. J. Inorg. Chem. 13* (1968) 152.