Synthesis and Characterization of Tin Sulfates and Oxide Sulfate

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The reactions between metastannic acid, powdered or granulated tin and 50–95 wt% H_2SO_4 are studied at and above room temperature, and with or without passing oxygen through the reaction mixtures. At least six different solid products, in addition to minor amounts of sulfur as a by-product, are obtained depending on H_2SO_4 concentration, reaction temperature, reaction atmosphere and tin form. TG and DTA curves are interpreted, unit-cell dimensions are derived from PXD data, and formulae based on chemical and TG analyses are given for the synthesized products.

This report concerns the use of concentrated H_2SO_4 (in this context 50–95 wt% H_2SO_4) as a solvent for, and reactant with, tin or metastannic acid. The work represents a continuation of our investigations on iodine and titanium oxide sulfates.[1-3]

Various tin sulfates and oxide sulfates have been reported in the literature. However, if one limits oneself to structurally well or reasonably well characterized compounds the selection is limited to $SnSO_4$,[4,5] Sn_2OSO_4,[6] $Sn_3O(OH)_2SO_4$[7,8] and $Sn_7(OH)_{12}(SO_4)_2$.[9] In addition to structure, there is an extensive literature available concerning the preparation[10-13] and properties[11,14-16] of $SnSO_4$. $Sn(SO_4)_2$ has also been variously studied,[13,17-19] but its characteristics are not well documented and the structure is not determined. Tin (II or IV) oxide sulfates are considered in, e.g., Refs. 6 and 20. The reaction between tin and concentrated H_2SO_4 has been the subject of several papers. Mathers and Rothrock[13] have reported that $Sn(SO_4)_2$ can be prepared by the action of hot conc. H_2SO_4 on tin metal, and $H_2Sn(SO_4)_3 \cdot H_2O$[21] is claimed to be prepared by dissolution of tin metal in conc. H_2SO_4 at 190 °C. Milbauer and Mikolásek[22] have reported that tin oxidizes readily (in H_2SO_4) at 304 °C in the presence of SeO_2. Finely dispersed moist tin is oxidized by oxygen to SnO which readily dissolves in cold diluted H_2SO_4, and $SnSO_4$ is obtained[10] by subsequently heating the solution to 65–75 °C. $SnSO_4$ is also found[13] as product when tin foil is reacted with 75 wt% H_2SO_4 at 140 °C.

In view of the discrepancies in the literature concerning the reaction between conc. H_2SO_4 and tin or hydrous stannic oxide it seems highly appropriate to undertake a complete reinvestigation. The outcome of such a study is reported in this paper.

Experimental

Powdered (p-Sn; Fluka; 99.9%) and granulated (g-Sn; Fluka; 99.5%) tin, SnO_2 [Fluka; purum; tetragonal modification: $a=473.76(2)$, $c=318.63(3)$ pm], conc. HNO_3 (Merck; p.a.; 65 wt%) and conc. H_2SO_4 (Merck; p.a.; 95–97 wt%, the former value being used throughout this paper) were used 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. Owing to the lack of reactivity of the as-purchased anhydrous SnO_2 with conc. H_2SO_4, a parallel series of syntheses made use of metastannic acid ($SnO_2 \cdot xH_2O$) as the tin source. This intermediate was obtained according to the procedure in Ref. 23. First g-Sn was reacted with conc. HNO_3 at 100 °C under constant stirring for some 2 h, until no brown gas (NO_2) was seen in the reaction flask fitted with a reflux cooler. The product was cooled to room temperature (r.t.), whereupon the liquid phase (mainly acid) was removed by decantation. The white precipitate thus obtained was washed with distilled H_2O (successive decantations) until pH of the washing water became 6–7. The resulting deposite was then filtered off, washed with distilled H_2O, acetone and diethylether, and dried in air for about 1 h. The thus obtained metastannic acid was virtually X-ray amorphous (am).

Eleven parallel series of syntheses were performed using as tin source either $SnO_2 \cdot xH_2O$-am, g-Sn or p-Sn, with or without passing $O_2(g)$ through the reaction mixtures. Four grams of metastannic acid were added to

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12 ml conc. H_2SO_4 (50–95 wt%) in a round bottom flask equipped with a reflux cooler and a thermometer. The mixtures were stirred, with a magnet stirrer, and heated to ca. 95 °C until all metastannic acid had dissolved and a clear yellowish solution obtained (15–60 min). The stirring was then stopped, but the heating was continued. After some time (5–48 h) with clear solution, the liquid turned cloudy and a precipitate began to deposite. The heating was still maintained for 1 wk and then stopped. After cooling to r.t., the yellowish to brownish clear liquid phase was removed by decantation. The precipitate was transferred to a beaker containing ca. 100 ml of glacial acetic acid, stirred for 15 min, filtered off, 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 vacuum.

With tin as starting chemical, 3.57 g of g- or p-Sn, was added to 38 ml of H_2SO_4, using the same set-up. The mixtures were stirred at r.t. or heated at ca. 95 °C (with or without passing oxygen through the reaction mixture) until complete precipitation had occurred (5–30 d, depending on the H_2SO_4 concentration, temperature, tin form and reaction atmosphere; at r.t. only some 35% of g-Sn had reacted in 95 wt% H_2SO_4). The reactions were then stopped, and in the heated cases, cooled to r.t. The liquid phase (mainly acid) was removed by decantation and the precipitates were washed, dried and stored as described above.

$Sn(SO_4)_2$ was prepared by reacting g- or p-Sn with 95 wt% H_2SO_4 at ca. 150 °C until a clear yellow solution was obtained. Then the temperature was increased (to ca. 230–300 °C) until a quantitative amount of a white precipitate deposited, during which time the colour of the solution changed to colourless. The mixture was cooled to r.t. in a vacuum desicator, and the precipitate was treated as described above. Also all other products can be converted to $Sn(SO_4)_2$ either by increasing the reaction temperature or by dissolving the solid products in 95 wt% H_2SO_4 at ca. 230 °C and fuming the solution.

Pure $SnSO_4$ was obtained in quantitative yield by dissolving tin at ca. 90 °C in conc. HCl (12 M) under stirring until a conc. $SnCl_2$ solution was obtained. The solution was cooled to r.t., filtered off and the filterate was added to 95 wt% H_2SO_4. A white precipitate deposited which in turn was washed, dried and stored as described above.

All samples were characterized by powder X-ray diffraction (PXD) using Guinier–Hägg cameras ($CuK\alpha_1$ radiation, Si as internal standard and a CO_2 atmosphere to protect the samples from moisture during the examination). High-temperature PXD data were collected with a Guinier–Simon camera (Enraf–Nonius) between 20–900 °C at a heating rate of 50 °C h^{-1}. The samples were contained in open silica-glass capillaries. The positions of the Bragg reflections were obtained from the films by means of a Nicolet L18 scanner using the SCANPI program system.[24] Indexing the diffraction pat-

terns of structurally unknown phases was attempted with the help of the TREOR program.[25] Unit-cell parameters were obtained by least-squares refinements using the CELLKANT program.[26]
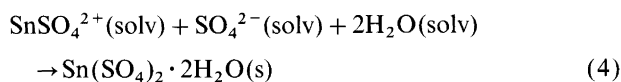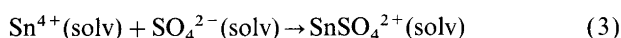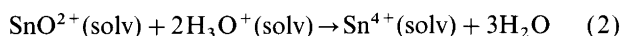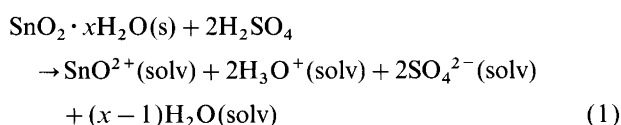
Thermogravimetric (TG) and differential thermal (DTA) analyses were performed between 20 and 900 °C with a Perkin–Elmer TGA 7 and DTA 7 system, respectively. The 15–40 mg samples were placed in Al_2O_3 crucibles, nitrogen was used as atmosphere and the heating rate was 10 °C min^{-1}.

Results and discussion

The outcome of the syntheses is summarized in Tables 1 and 2, where it is seen that, as expected, the resulting product depends on the tin source, the concentration of the sulfuric acid, the reaction temperature and whether or not oxygen is present. In the following considerations of the results there is conveniently made a distinction between metastannic acid and elementary tin as reactant.

Metastannic acid as reactant. The progressing reaction between $SnO_2 \cdot xH_2O$ and 75–95 wt% H_2SO_4 is evidenced by the dissolution of the metastannic acid and a subseqently resulting yellowish solution. This treatment gave two different solid reaction products, $Sn(SO_4)_2 \cdot 2H_2O$ in modifications A and B. Below 75 wt% H_2SO_4 yet unidentified hydrolysis products were obtained.

The course of the reaction between $SnO_2 \cdot xH_2O$ and H_2SO_4 has certain notable features: After the dissolution is completed there is a period with a clear yellowish coloured solution which in turn is succeeded by a slow precipitation of $Sn(SO_4)_2 \cdot 2H_2O$. This leads us to suggest the following simplified scheme:

$$SnO_2 \cdot xH_2O(s) + 2H_2SO_4$$
$$\rightarrow SnO^{2+}(solv) + 2H_3O^+(solv) + 2SO_4^{2-}(solv)$$
$$+ (x-1)H_2O(solv) \tag{1}$$

$$SnO^{2+}(solv) + 2H_3O^+(solv) \rightarrow Sn^{4+}(solv) + 3H_2O \tag{2}$$

$$Sn^{4+}(solv) + SO_4^{2-}(solv) \rightarrow SnSO_4^{2+}(solv) \tag{3}$$

$$SnSO_4^{2+}(solv) + SO_4^{2-}(solv) + 2H_2O(solv)$$
$$\rightarrow Sn(SO_4)_2 \cdot 2H_2O(s) \tag{4}$$

neglecting the concentration-dependent equilibria associated with H_2O in H_2SO_4.

Partially complexed (viz. solvated) species of $SnSO_4^{2+}$ and Sn^{4+} have been suggested to occur when stannic sulfates is dissolved in H_2SO_4.[27,28] However, the existence of $H_2Sn(SO_4)_3$ and $H_2Sn(SO_4)_3 \cdot H_2O$ claimed in several papers[19,21,28] could not be confirmed as solid products up to 95 wt% H_2SO_4 in this study.

Tin as reactant. The reaction between tin and sulfuric acid is slow and depends on the H_2SO_4 concentration, the reaction temperature, the tin form and the reaction atmosphere. Generally the reaction speed increases with

Table 1. Tin sulfates and oxide sulfate prepared (phase-pure) from various tin sources and different concentrations of conc. H_2SO_4, with or without passing $O_2(g)$ through the reaction mixture.

Reaction product	Phase no. in Table 2	Reactants: H_2SO_4 plus	Wt% H_2SO_4	$t/°C$
$SnSO_4$	I	g-Sn and $O_2(g)$	50–95	r.t.
$SnSO_4$	I	g-Sn	50–95	r.t.
$SnSO_4$	I	p-Sn and $O_2(g)$	50–95	r.t.
$SnSO_4$	I	p-Sn	50–95	r.t.
$SnSO_4$	I	p-Sn	50–70	95
$SnSO_4$	I	p-Sn and $O_2(g)$	50–55	95
$SnSO_4$	I	g-Sn	50–65	95
$Sn(SO_4)_2 \cdot 2H_2O(A)$	II	$SnO_2 \cdot xH_2O$	80	95
$Sn(SO_4)_2 \cdot 2H_2O(A)$	II	g-Sn and $O_2(g)$	70	95
$Sn(SO_4)_2 \cdot 2H_2O(A)$	II	g-Sn	75	95
$Sn(SO_4)_2 \cdot 2H_2O(B)$	III	$SnO_2 \cdot xH_2O$	85–95	95
$Sn(SO_4)_2 \cdot 2H_2O(B)$	III	g-Sn and $O_2(g)$	85	95
$Sn(SO_4)_2 \cdot 2H_2O(B)$	III	g-Sn	85	95
$Sn(SO_4)_2 \cdot 2H_2O(B)$	III	p-Sn and $O_2(g)$	85	95
$Sn(SO_4)_2 \cdot 2H_2O(B)$	III	g-Sn	85	95
$Sn(SO_4)_2 \cdot 4H_2O^a$	IV	g-Sn and $O_2(g)$	60	95
$Sn_6O(SO_4)_9$	V	g-Sn and $O_2(g)$	95	95
$Sn_6O(SO_4)_9$	V	g-Sn	95	95
$Sn_6O(SO_4)_9$	V	p-Sn and $O_2(g)$	95	95
$Sn_6O(SO_4)_9$	V	p-Sn	95	95
$Sn(SO_4)_2$	VI	g-Sn	95	230
$Sn(SO_4)_2$	VI	p-Sn	95	230

[a] This compound has been obtained only in one case by this procedure.

Table 2. Products (see Table 1 for the composition of phases I—VI) resulting from the reaction of $SnO_2 \cdot xH_2O$-am, p-Sn or g-Sn and 50–95 wt% H_2SO_4, with or without passing oxygen through the reaction mixture at temperatures between r.t. and 230 °C.

Reactants and conditions	Wt% H_2SO_4									
	50	55	60	65	70	75	80	85	90	95
p-Sn; r.t.	I ——————————————————————————————————>									
p-Sn, $O_2(g)$; r.t.	I ——————————————————————————————————>									
g-Sn; r.t.	I ——————————————————————————————————>									
g-Sn, $O_2(g)$; r.t.	I ——————————————————————————————————>									
p-Sn; 95 °C	I ————————————————————> I/II —> I/III —> III —> III/V —> V (VI[a])									
p-Sn, $O_2(g)$; 95 °C	I ——> I/II ————————> I/III —> II/III ——————> III —> III/V —> V (VI[a])									
g-Sn; 95 °C	I ——————————————> I/II —> II ——————> III —> III/V —> V (VI[a])									
g-Sn, $O_2(g)$; 95 °C	I/L[b] ——> IV[c] —> I/II —> II ——> II/III ——————> III —> III/V —> V (VI[a])									
$SnO_2 \cdot xH_2O$; 95 °C	L[b] ——————————————————————> II[d] —> II ——> III ——————————> (VI[a])									

[a] Long-term heating at ca. 230 °C. [b] L denotes unidentified hydrolysis product(s). [c] This compound has been obtained only in one case. [d] Plus minor amounts of L.

increasing H_2SO_4 concentration and reaction temperature, decreasing particle size of the tin (p- vs. g-Sn) and is moreover enhanced when $O_2(g)$ is passed through the reaction mixture. Also the products depend on the factors mentioned above: At r.t., the role of the tin form, the H_2SO_4 concentration and O_2 in the atmosphere is rather insignificant, and the only reaction product is $SnSO_4$. However, when the temperature is increased to 95 °C and higher temperatures these factors become important (Tables 1 and 2) and different reaction products with Sn in oxidation states +2, +3.3 (average) and +4 are obtained depending on the synthesis conditions. Table 2 shows that the form of the tin has a particular effect on the product at concentrations between ca. 60 and ca. 80 wt% H_2SO_4.

The progressing reaction between Sn and conc. H_2SO_4 is evidenced by the dissolution of Sn in addition to the evolution of H_2 and the deposition of a white solid product. A minor amount of a yellow deposite on the wall and the neck of the reaction vessel above the solution was proved to be elementary sulfur by PXD and mass spectrometry. This sulfur originates from the reduction of H_2SO_4 by the atomic hydrogen which is formed initially when Sn is dissolved.

Characterization. Five different tin sulfates and one oxide sulfate can be obtained by the reaction between tin and conc. H_2SO_4 on appropriate variation of the synthesis conditions (Tables 1 and 2). The finding that two-phase mixtures are obtained at some intermediate concentrations is attributed to kinetical factors like concentration fluctuations in the reaction vessel, and to the fact that once a wrong, but nearly equilibrium situation has been established it requires redissolving to be rectified.

Two hitherto unreported compounds, $Sn(SO_4)_2 \cdot 4H_2O$ and $Sn_6O(SO_4)_9$, have been prepared and two different modifications (designated A and B) of $Sn(SO_4)_2 \cdot 2H_2O$ have been identified. A phase with the latter composition have been reported earlier (according to another method of preparatation),[19,29] but since only a few, somewhat approximate *d*-values were reported in Ref. 30 the identity has not been established.

Except for $SnSO_4$ whose structure[4,5] was known in advance, and $Sn_6O(SO_4)_9$ for which satisfactory indexing has not been obtained, the PXD patterns for the phase-pure synthesis products have been indexed by the TREOR program.[25] All reflections have been accounted for and good figures of merit have been obtained for the unit-cell data listed in Table 3. Together with the TG and DTA data presented below, the information in Table 3 serves as characterization documentation for the compounds obtained in this study.

$Sn_6O(SO_4)_9$ is the first example of a tin oxide sulfate which contains tin atoms in two oxidation states ($+2$ and $+4$; average $+3.3$). Tin in both oxidation states is reported for the structurally well characterized hydroxide sulfate $Sn_7(OH)_{12}(SO_4)_2$.[9]

Anhydrous $Sn(SO_4)_2$ has been mentioned in the literature,[13,17,18,31] but its preparation and characterization has remained unexplored. In addition to the route outlined in Table 1, $Sn(SO_4)_2$ can be prepared by dissolving any other of the five compounds in Tables 1 and 2 in 95 wt% H_2SO_4 and heating the reaction mixture until the volume of the solution is reduced appropriately by heating at 230–300 °C. The subsequently deposited product is then anhydrous $Sn(SO_4)_2$.

Chemical analysis. The composition of selected samples from different batches of the phase-pure (according to PXD) reaction products was verified by TG analysis

(*vide infra*). As a consistency test the composition of $Sn(SO_4)_2 \cdot 2H_2O$ was also verified by quantitative chemical analysis. A weighed amount (ca. 1.4 g) of the compound was added to 300 ml distilled H_2O in a beaker and stirred. A rapid hydrolysis to a colloid precipitate of $SnO_2 \cdot xH_2O$ was seen within the first half hour. The solution and precipitate was left for 2 d, subjected to frequent interruptions by stirring. The precipitate was then filtered off, washed several times with distilled H_2O, and the ashless filter paper with the precipitate was incinerated at 400 and 950 °C, and finally cooled to r.t. and weighed. This gave an observed Sn content of 34.47 wt% as compared with the calculated content of 34.27 wt% for $Sn(SO_4)_2 \cdot 2H_2O$. The sulfur was determined from the filterate as $BaSO_4$: obs. 17.89 wt%, calc. 18.44 wt%.

Oxidation state test. The oxidation state of Sn in selected samples of phase-pure reaction products was checked by the classical qualitative analysis test by $HgCl_2$ [reduction of $HgCl_2(aq)$ to $Hg_2Cl_2(s)$ and $Hg(1)$ on oxidation of $Sn^{2+}(aq)$ to $Sn^{4+}(aq)$]. Deoxygenated distilled H_2O was used for these tests which gave positive confirmation of Sn^{2+} only for $SnSO_4$ and $Sn_6O(SO_4)_9$.

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–1f and temperature regions and relative mass losses for the occurring decompostion reactions are summarized in Table 4. The agreement between observed and calculated ($\Delta m/m_0$) values is generally good, and the TG data accordingly serve to confirm the composition of the synthesized compounds.

The decomposition of $SnSO_4$ into SnO_2 and SO_2 (Fig. 1a) and of $Sn(SO_4)_2$ into SnO_2 and SO_3 (Fig. 1f) takes place in one step, whereas the TG curves for the other compounds show two or more features (Figs. 1b–1e; Table 4). The DTA curve of $SnSO_4$ (Fig. 1a) shows an additional exothermic peak at around 500 °C which according to Donaldson and coworkers[8,11] reflects the crystallization of SnO_2 after its initial formation in the amorphous state. Following Donaldson and coworkers $SnSO_4$ experiences an internal redox process owing to the fact that SnO_2 is more stable than SnO under the given conditions. The DTA curve for $Sn(SO_4)_2$

Table 3. Unit-cell data at r.t. for tin sulfates obtained by synthesis in conc. H_2SO_4 (see Tables 1 and 2).

Compound	Symmetry	*a*/pm	*b*/pm	*c*/pm	$\alpha/°$	$\beta/°$	$\gamma/°$	$V/10^6$ pm³	$M(20)^a$
$SnSO_4$	Orthorhombic	880.4(1)	532.9(1)	711.9(1)				334.02(4)	148.9
$Sn(SO_4)_2 \cdot 2H_2O(A)$	Triclinic	518.9(1)	554.2(1)	679.0(1)	76.90(1)	102.69(1)	79.23(1)	179.71(3)	134.9
$Sn(SO_4)_2 \cdot 2H_2O(B)$	Monoclinic	970.5(1)	565.2(1)	703.3(1)		106.86(1)		369.21(3)	144.5
$Sn(SO_4)_2 \cdot 4H_2O$	Monoclinic	873.6(2)	710.6(1)	871.0(1)		104.68(1)		523.0(2)	80.5
$Sn_6O(SO_4)_9$	Unsuccessful indexing								
$Sn(SO_4)_2^b$	Monoclinic	1164.2(1)	1066.5(1)	504.5(1)		113.70(1)		573.56(6)	192.3
$Sn(SO_4)_2^c$	Orthorhombic	768.3(2)	754.2(2)	515.0(1)				298.4(1)	120.2

*a*Figure of merit. *b*For unit-cell dimensions between 20 and 450 °C see Fig. 2. *c*Unit-cell dimensions between 500 and ca. 580 °C.
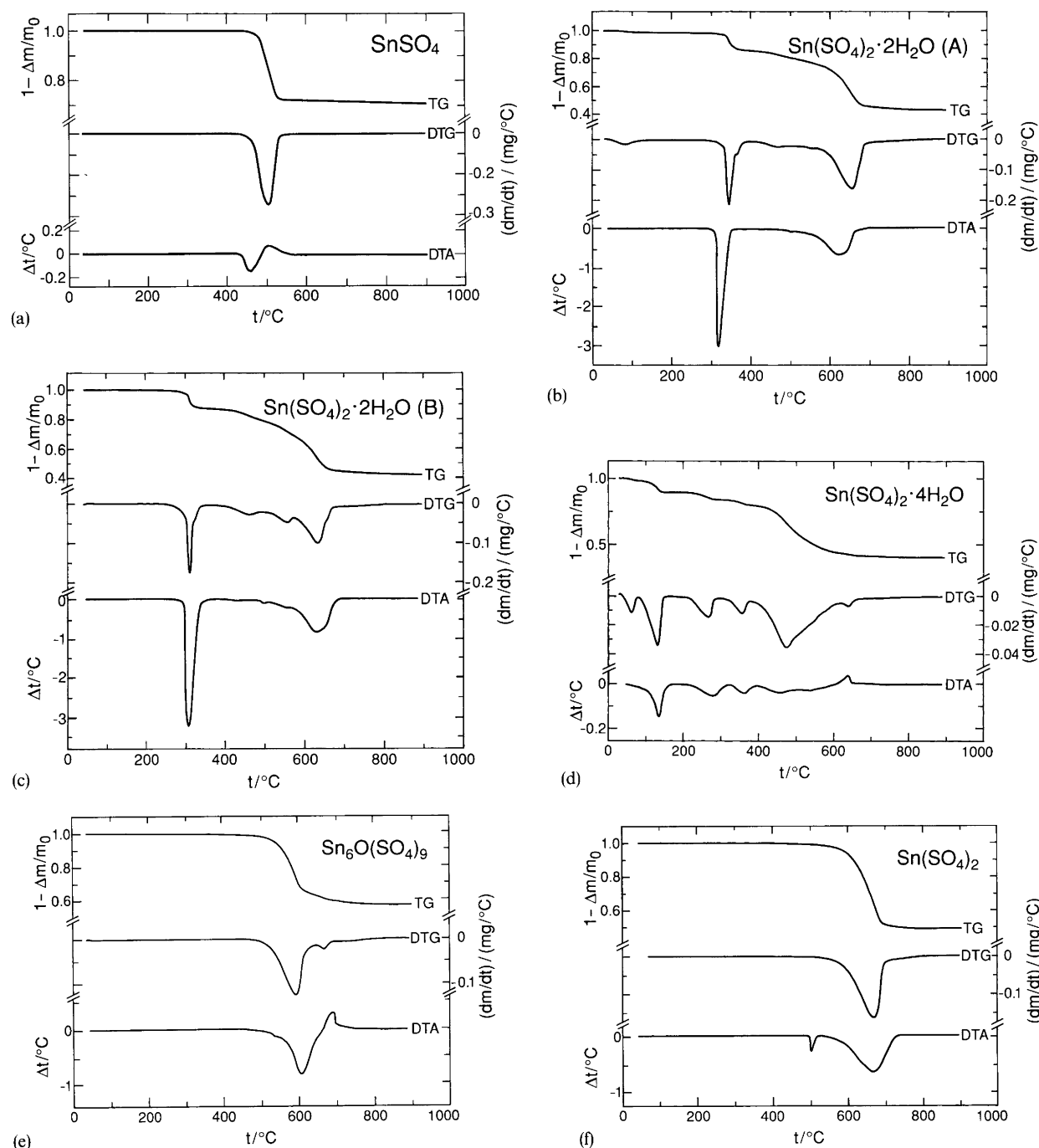
Fig. 1. TG, DTG and DTA data for (a) $SnSO_4$, (b) $Sn(SO_4)_2 \cdot 2H_2O(A)$, (c) $Sn(SO_4)_2 \cdot 2H_2O(B)$, (d) $Sn(SO_4)_2 \cdot 4H_2O$, (e) $Sn_6O(SO_4)_9$ and (f) $Sn(SO_4)_2$. The DTA scans are adjusted to a constant background signal.

(Fig. 1f) also shows an additional (in this case endo-thermic) peak at around 500 °C. However, this feature has its origin in a first-order phase transition in $Sn(SO_4)_2$ as manifested by high-temperature PXD. Using the indexing (*vide supra*) of the r.t. PXD films as the starting point, the temperature dependence of the unit-cell dimensions of the low-temperature modification of $Sn(SO_4)_2$ has been established (Fig. 2). The PXD pattern of the high-temerature modification (ca. 500–ca. 580 °C) has also been indexed with the unit-cell dimensions listed in

Table 3. There appears to be a certain relation between the metrics of the two cells, but this aspect will be returned to in a forthcoming paper.

The TG and DTG characteristics for the forms A and B of $Sn(SO_4)_2 \cdot 2H_2O$ (Figs. 1b and 1c) are very similar apart from the fact that the dehydratization of form A as well as the terminal decomposition into SnO_2 take place at some 20 °C higher temperature than for form B. The thermal decomposition of $Sn(SO_4)_2 \cdot 4H_2O$ (Fig. 1d) takes place in four steps. First a conversion into

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Table 4. Summary of TG results for phase-pure reaction products.

Compound	Illustration no.	Decomposition reaction	Eqn.	$t_{start}/°C$	$t_{end}/°C$	$(\Delta m/m_0)$[a] obs.	$(\Delta m/m_0)$ calc.
$SnSO_4$	Fig. 1a	$SnSO_4(s) \rightarrow SnO_2(s) + SO_2(g)$	(5)	430	500	0.291	0.298
$Sn(SO_4)_2 \cdot 2H_2O(A)$	Fig. 1b	$Sn(SO_4)_2 \cdot 2H_2O(s) \rightarrow Sn(SO_4)_2(s) + 2H_2O(g)$	(6)	300	365	0.109	0.104
		$Sn(SO_4)_2(s) \rightarrow SnO_2(s) + 2SO_3(g)$	(7)	520	700	0.509	0.515
		$Sn(SO_4)_2 \cdot 2H_2O(s) \rightarrow SnO_2(s) + 2SO_3(g) + 2H_2O(g)$	(6+7)	300	700	0.561	0.565
$Sn(SO_4)_2 \cdot 2H_2O(B)$	Fig. 1c	$Sn(SO_4)_2 \cdot 2H_2O(s) \rightarrow Sn(SO_4)_2(s) + 2H_2O(g)$	(6)	300	350	0.109	0.104
		$Sn(SO_4)_2(s) \rightarrow SnO_2(s) + 2SO_3(g)$	(7)	500	700	0.508	0.515
		$Sn(SO_4)_2 \cdot 2H_2O(s) \rightarrow SnO_2(s) + 2SO_3(g) + 2H_2O(g)$	(6+7)	300	700	0.561	0.565
$Sn(SO_4)_2 \cdot 4H_2O$	Fig. 1d	$Sn(SO_4)_2 \cdot 4H_2O(s) \rightarrow Sn(SO_4)_2 \cdot 2H_2O(s) + 2H_2O(g)$	(8)	95	160	0.091	0.094
		$Sn(SO_4)_2 \cdot 2H_2O(s) \rightarrow Sn(SO_4)_2 \cdot H_2O(s) + H_2O(g)$	(9)	215	275	0.056	0.052
		$Sn(SO_4)_2 \cdot H_2O(s) \rightarrow Sn(SO_4)_2(s) + H_2O(g)$	(10)	320	400	0.054	0.055
		$Sn(SO_4)_2(s) \rightarrow SnO_2(s) + 2SO_3(g)$	(7)	420	700	0.500	0.515
		$Sn(SO_4)_2 \cdot 4H_2O(s) \rightarrow SnO_2(s) + 2SO_3(g) + 4H_2O(g)$	(8+9+10-7)	95	700	0.594	0.606
$Sn_6O(SO_4)_9$	Fig. 1e	$Sn_6O(SO_4)_9(s) \rightarrow Sn_6O_8(SO_4)_2(s) + 7SO_3(g)$	(11)	520	620	0.349	0.351
		$Sn_6O_8(SO_4)_2(s) \rightarrow 6SnO_2(s) + 2SO_2(g)$	(12)	650	750	0.122	0.124
		$Sn_6O(SO_4)_9(s) \rightarrow 6SnO_2(s) + 2SO_2(g) + 7SO_3(g)$	(11+12)	520	700	0.429	0.432
$Sn(SO_4)_2$	Fig. 1f	$Sn(SO_4)_2(s) \rightarrow SnO_2(s) + 2SO_3(g)$	(7)	580	730	0.515	0.515

[a]Note that m_0 refers to the mass at the start of the appropriate decomposition reaction.

$Sn(SO_4)_2 \cdot 2H_2O$ at ca. 95 °C followed by the loss of one more H_2O at ca. 215 °C. The latter feature was not observed for the as-synthesized forms A and B of $Sn(SO_4)_2 \cdot 2H_2O$. $Sn(SO_4)_2 \cdot H_2O$ then decomposes into $Sn(SO_4)_2$ and finally into SnO_2. As seen from Fig. 1e and Table 4 the thermal decomposition of $Sn_6O(SO_4)_9$ takes place in two steps.
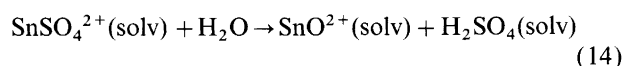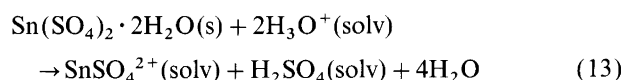
Hygroscopic behaviour. All the synthesized tin compounds, except $SnSO_4$, are hygroscopic. The following simple test is instructive: A small amount of a given (washed and dried; *vide supra*) compound is placed on a filter paper which in turn is placed on a Kleenex tissue. After exposure to moist air for about one week the Kleenex tissue was burned dark brown by evolved H_2SO_4, and PXD of the wet remains on the filter paper showed an amorphous substance, almost certainly $SnO_2 \cdot xH_2O$.

When say $Sn(SO_4)_2 \cdot 2H_2O$ (A or B) is subjected to a similar test of only one day duration the filter paper also contained a wet product. However, in this case the remains on the filterpaper proved to be a mixture of the amorphous substance and $Sn(SO_4)_2 \cdot 4H_2O$. The infer-

ence is accordingly that the tin(IV) sulfates hydrolysis by stepwise picking up H_2O from the air through the sequence of the increasing number of crystal waters.

Solubility in aqueous H_2SO_4 solutions. $Sn(SO_4)_2 \cdot 2H_2O$ (A or B) readily dissolves in ca. 10 wt% H_2SO_4. On increasing the concentration of the sulfuric acid the solubility of these compounds decreases gradually and they are in fact only very slightly soluble in 50 wt% H_2SO_4 at r.t. On heating to some 100 °C or higher temperatures the solubility in, say, 50 wt% H_2SO_4 has again become appreciable, and the resulting solution has a clear yellowish colour. Simlar results are obtained for the other compounds under investigation.

Our findings for $Sn(SO_4)_2 \cdot 2H_2O$ lead us (see also Refs. 1–3) to suggest the following reaction scheme for the dissolution process:

$$Sn(SO_4)_2 \cdot 2H_2O(s) + 2H_3O^+(solv)$$

$$\rightarrow SnSO_4^{2+}(solv) + H_2SO_4(solv) + 4H_2O \quad (13)$$

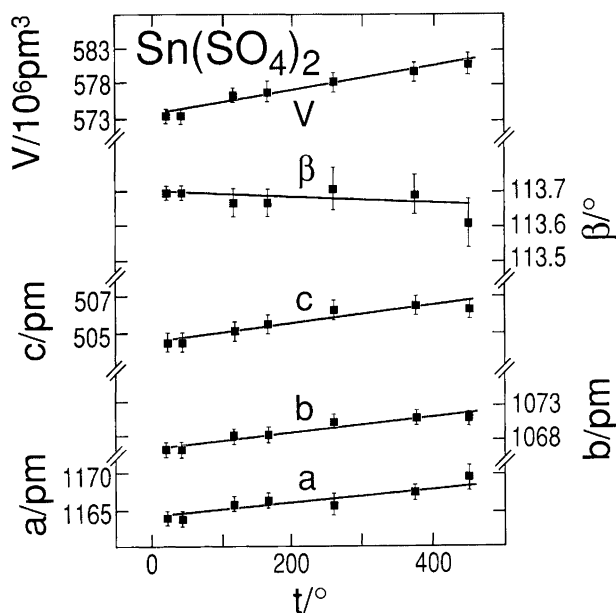$$SnSO_4^{2+}(solv) + H_2O \rightarrow SnO^{2+}(solv) + H_2SO_4(solv) \quad (14)$$

Fig. 2. Variation in unit-cell dimensions with temperature for the low-temperature modification of $Sn(SO_4)_2$. For the unit-cell dimensions of the high-temperature modification see Table 3. Thermal expansion coefficients for $Sn(SO_4)_2$ at 20–450 °C (in 10^{-6} K^{-1}): $\alpha_a = 8.4$, $\alpha_b = 10.7$, $\alpha_c = 10.2$, $\alpha_\beta \approx 0.00$, $\alpha_V = 29.0$.

where $SnO^{2+}(solv)$ probably is the abovementioned yellow species.

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