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X-ray Diffraction and Mössbauer Analyses of SnO Disproportionation Products

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Abstract

The disproportionation of SnO in the temperature range 200–750 °C for varying lengths of time from 0.5 to 100 h was investigated. The reaction starts at about 250 °C producing metallic tin and an intermediate oxide whose formula has been confirmed as Sn_3O_4. In the temperature range 250–425 °C the disproportionation proudcts are metallic tin and the intermediate oxide. In the temperature range between 425 °C and 550 °C, Sn_3O_4 slowly decomposes to Sn and SnO_2, after the complete disappearance of SnO. Over 550 °C the disproportionation products are the thermodynamically stable phases Sn and SnO_2.

Introduction

Tin monoxide heated in vacuum undergoes a disproportionation reaction, whose products are metallic tin and SnO_2 and/or, depending on the temperature, an intermediate oxide (**IO**) containing Sn(II) and Sn(IV).

It has been established that the thermodynamically-stable phases of the Sn–O system in the range 300–1000 °C are SnO–gas, Sn–liq and SnO_2–sol [1]. Therefore, the **IO**, whose controversal existence [2, 3] has been finally evidenced by X-ray diffraction [4, 5], is a metastable phase. The composition and the mechanism of formation of this phase have been debated for a long time. The formulae Sn_2O_3 [6], Sn_3O_4 [7] and Sn_5O_6 [8] correspond respectively to the disproportionation reactions

$$3SnO \longrightarrow Sn_2O_3 + Sn \qquad (1)$$

$$4SnO \longrightarrow Sn_3O_4 + Sn \qquad (2)$$

$$6SnO \longrightarrow Sn_5O_6 + Sn, \qquad (3)$$

and have therefore been proposed for the **IO**.

On the basis of thermo-e.m.f., Mössbauer spectroscopy and X-ray diffraction measurements, it has been found [9] that the method of SnO preparation markedly influences its initial content of Sn(IV) (up to 30% SnO_2) and the behaviour of the disproportionation reaction. The **IO** has been observed in the disproportionation of SnO samples with initial SnO_2 content less than 1%. Samples with more than 1% SnO_2 disproportionate on dissolving increasing quantities of Sn(IV) in the SnO lattice. The problem of the **IO** composition is not dicussed in ref. [9]. Reaction (2) has been considered the more realistic one on the basis of analytical determinations of metallic tin in the disproportionation products [10, 11], whereas from Mössbauer measurements and from the determination of the Sn(II):O ratio by means of analytical methods, reaction (1) has been suggested [5, 12]. Very recently reaction (2) has been re-proposed in a Mössbauer study by measuring the percent atom distribution of tin among the different oxidation states in the disproportionation products obtained after heating for 100 h at 450 °C [13].

The aim of the present work is to investigate the behaviour of the disproportionation as a function of temperature and time and to confirm the correctness of formula (2) for the **IO**. For this purpose a discussion of X-ray and Mössbauer measurements on the disproportionation products is presented.

Experimental

Tin monoxide, obtained from $SnCl_2$ and NH_4OH as described in [14], was heated in glass or quartz-evacuated bulbs (oxygen partial pressure ≃1–2 mPa), at temperatures and times given in Table I.

The phases occurring in the disproportionation products were firstly identified by X-ray diffraction analysis (radiation Cu-Kα; $\lambda = 0.15418$ nm) and then Mössbauer spectra were taken at room temperature on a constant acceleration spectrometer using a

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source of ^{119}Sn in $CaSnO_3$ with 15 mCi nominal activity. A standard minimization routine allowed the spectral profiles to be fitted with a number of lorentzian lines. The quantitative evaluation of the disproportionation products was done in the thin-absorber approximation, by utilizing the values 0.11 and 0.47, respectively, as room temperature recoil-free factor ratios f(0):f(IV) and f(II):f(IV) (where, 0, II and IV are the oxidation states of tin). These values were calculated on the basis of Mössbauer measurements on equimolecular mechanical mixtures (Sn + SnO_2) and (SnO + SnO_2).

Results

Table I reports the results of X-ray diffraction analysis for the various thermal treatments. We can deduce that: i) the disproportionation starts at a temperature between 250 °C and 275 °C (SnO remains unchanged after 100 h at 250 °C and is slightly disproportionated after 100 h at 275 °C); ii) the monoxide vanishes completely by heating for at least 1 h at 400 °C; iii) the disproportionation at temperatures higher than 400 °C (when the starting SnO is completely transformed) produces SnO_2, besides metallic tin and **IO**; iv) prolonged heating at 525 °C or heating for a short time at higher temperatures does not give rise to the **IO**, metallic tin and SnO_2 being the only products of disproportionation in these conditions.

The Mössbauer measurements, carried out on most of the samples of Table I, substantially confirm the X-ray diffraction results and allow a quantitative evaluation of the occurring phases through the calculation of the relative areas of the spectral components. In Table II the mean values of the hyperfine parameters of the identified spectral

TABLE I. X-ray Diffraction Analysis of SnO Disproportionation Products.

Thermal treatment time (h)/ temperature (°C)	SnO	Sn	IO	SnO_2
100/200	a			
100/250	a			
100/275	a	b	b	
100/300	b	b	a	
1/350	a	b	b	
3/350	a	a	a	
10/350		a	a	
100/350		a	a	
0.5/400	b	a	a	
1/400		a	a	
10/400		a	a	
0.5/450		a	a	b
1/450		a	a	b
3/450		a	a	b
10/450		a	a	b
30/450		a	a	b
100/450[c]		a	a	b
1/500		a	a	b
18/500		a	a	a
1/525		a	a	b
100/525		a		a
100/550		a		a
100/575		a		a
24/600		a		a
1/630		a		a
30/700[c]		a		a
1/750		a		a
64/750		a		a

[a]Appreciable amount or unique component. [b]Low amount or traces. [c]Data of ref. [13].

TABLE II. Mean Hyperfine Parameters (mm/s) of Spectral Components Corresponding to the Various Oxidation States of Tin: Isomer Shift (*IS*) Referred to SnO_2, Quadrupole Splitting (*QS*) and FWHM (*W*).

	IS[a]	*QS*[b]	*W*[c]
Sn(O)	2.56		0.92
Sn(II) in SnO	2.63	1.36	0.86
Sn(II) in IO	2.56	2.00	0.90
Sn(IV) in IO	0.07	0.52	0.92
Sn(IV) in SnO_2	0.00	0.44	0.82

[a]±0.02 mm/s. [b]±0.04 mm/s. [c]±0.04 mm/s.

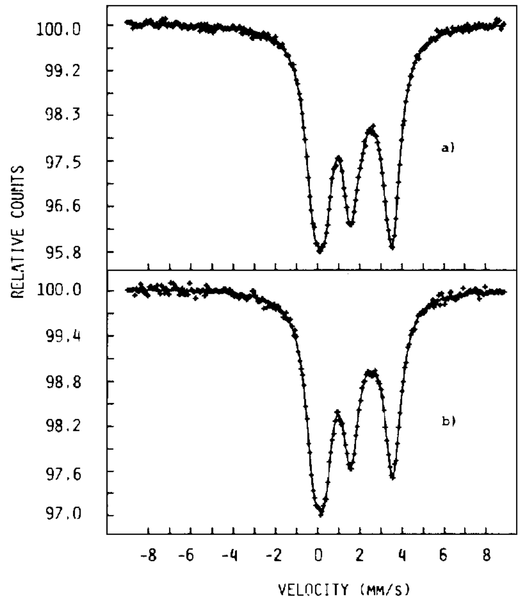

Fig. 1. Room temperature Mössbauer spectra of samples heated 0.5 h at (a) 400 °C and (b) 450 °C.

TABLE III. Tin Concentration (at. pct.) in the Occurring Phases as Computed from Mössbauer Spectra.

Thermal treatment time (h)/ temp. (°C)	Sn(II) in SnO	Sn(0)	Sn(II) in IO	Sn(IV) in IO	Sn(IV) in SnO_2	Sn(II)/Sn(IV) in IO
0.5/400	27	15	40	18		2.2
0.5/450		17	61	22		2.8
1/350	92	3	(see text)	5		
1/400		17	59	24		2.5
1/450		18	60	22		2.7
1/630		50			50	
100/250	95	3	(see text)	2		
100/275	63	10	17	10		1.7
100/300	12	18	46	24		1.9
100/350		17	58	25		2.3
100/450[a]		26	50	23	1	2.2
100/525		45			55	

[a] Data of ref. [13].

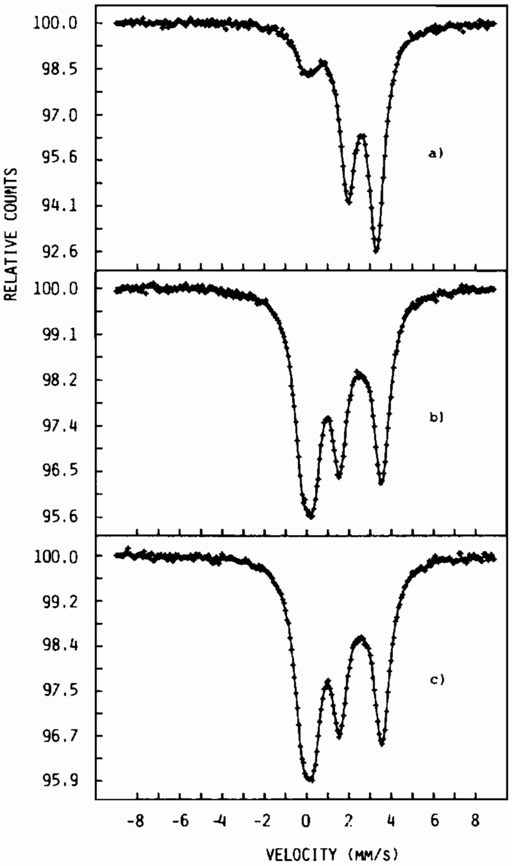

Fig. 2. Room temperature Mössbauer spectra of samples heated 1 h at (a) 350 °C. (b) 400 °C and (c) 450 °C.

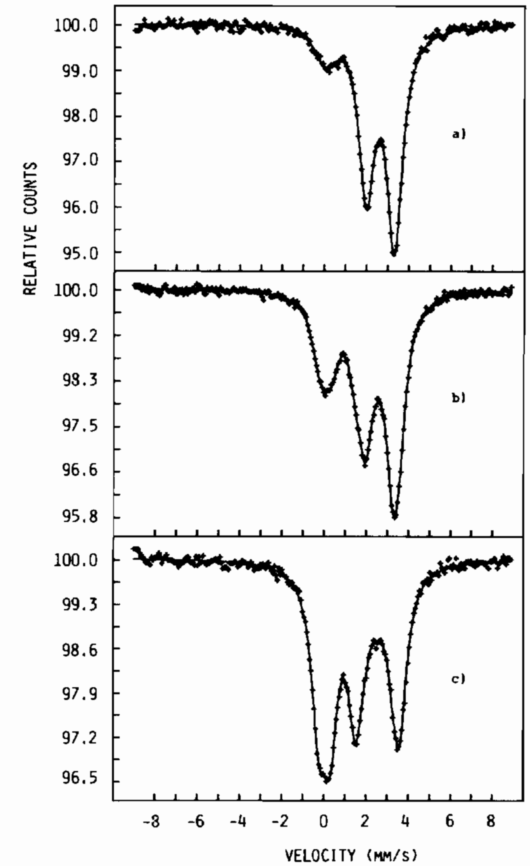

Fig. 3. Room temperature Mössbauer spectra of samples heated 100 h at (a) 250 °C, (b) 275 °C and (c) 300 °C.

components are given, corresponding to the different oxidation states of tin. Figs. 1–5 show the more significant spectra. For these, Table III gives the atomic concentrations of tin in the recognized phases as obtained by combining the computed subspectral areas with the recoil-free fraction ratios mentioned in the Experimental Section.

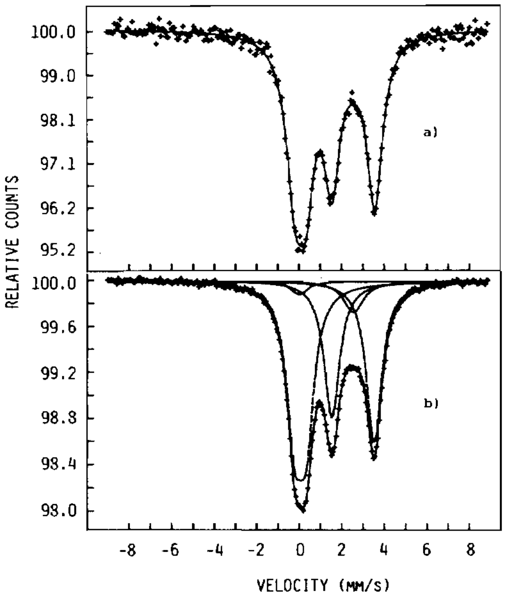

Fig. 4. Room temperature Mössbauer spectra of samples heated 100 h at (a) 350 °C and (b) 1 h at 450 °C.

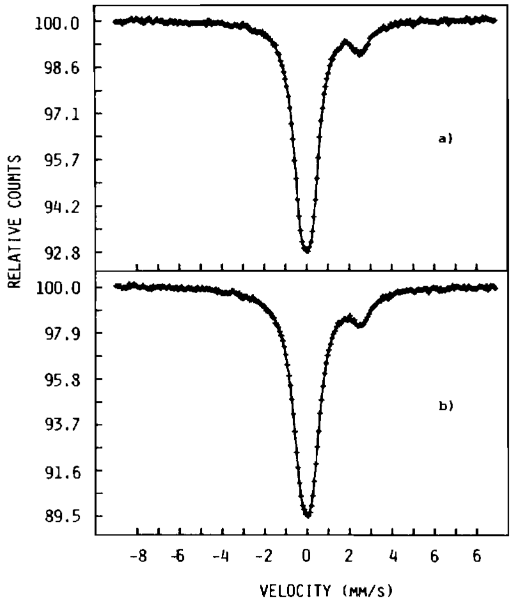

Fig. 5. Room temperature Mössbauer spectra of samples heated 100 h at (a) 525 °C and (b) 1 h at 630 °C.

Discussion

In order to choose the correct disproportionation reaction and then the correct formula for the **IO**, two difficult analytical methods may be followed: a) the dosage of metallic tin in the disproportionation products [10] and b) the indirect dosage of the Sn:O ratio in **IO** [5]. As mentioned in the Introduction, method a) leads to reaction (2), according also to other results [7].

Mössbauer spectroscopy confirms the above analytical results, as already noticed in [13], with the advantage of overcoming the difficult quantitative separation of the disproportionation products. Data in Table III indeed demonstrate that the ratio Sn(II):Sn(IV) in **IO** is closer to the value pertaining to Sn_3O_4 (Sn(II):Sn(IV) = 2) than to that pertaining to Sn_2O_3 (Sn(II):Sn(IV) = 1). The result is reasonably good if we consider that the spectral components are poorly resolved (see Figs. 1–5 and particularly 4b) and that even small variations of temperature (room) may influence the recoil-free factor ratios, as reported in temperature-dependent measurements of β-tin SnO_2 and SnO f factors [15–17]. Due to the low consistency of f factor absolute values reported in the literature, we have utilized the relative values determined as given in the Experimental, in order to obtain the phase-concentration evaluations in our samples.

The spectrum of SnO (not reported) is a strongly asymmetric doublet. We have found that this asymmetry decreases when the oxide is dispersed and ground in alumina powder, as otherwise reported on a SnO/MgO powder mixture [19]. This characteristic is attributed to the texture present in the SnO crystal powder and not to the Goldanskii–Karyagin effect, according also to refs. [17–20]. The doublet associated to the Sn(II) in the **IO** is also rather asymmetric (Fig. 4b). This suggests that a crystallographic relationship of reciprocal orientation exists in the phase transformation SnO → Sn_3O_4.

As previously observed [12, 13], the quadrupole splitting of the Sn(II) subspectrum in the **IO** is greater than that of SnO (see Table II), being an indication of a different coordination for tin–oxy-

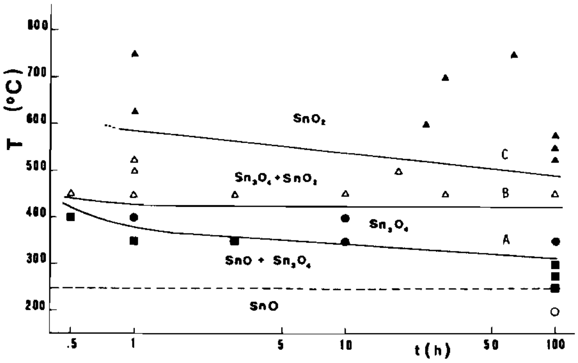

Fig. 6. Temperature transformation–time diagram of SnO obtained by combining X-ray and Mössbauer results. Tin oxides in the disproportionation product are: ○ SnO; ■ SnO + Sn_3O_4; ● Sn_3O_4; △ Sn_3O_4 + SnO_2; ▲ SnO_2 (see text).

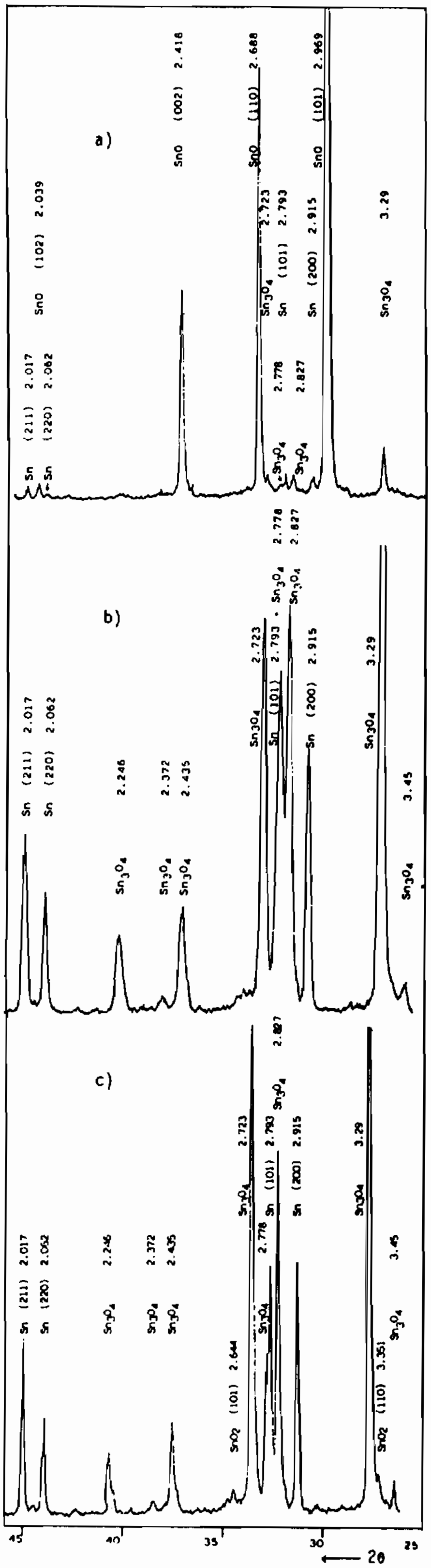

Fig. 7. X-ray diffraction patterns ($25 < 2\theta < 45$) of samples heated 1 h at (a) 350 °C, (b) 400 °C and (c) 450 °C.

gen. The square-based pyramid, where Sn(II) occupies the centre and oxygen atoms are at the base vertex (configuration of n.n. of tin in the SnO structure), has consequently a lower crystallographic symmetry than in SnO [5]. On the other hand, the parameters of Sn(IV) in **IO** are very similar to those of SnO_2, so that the n.n. distribution of Sn(IV) is practically the same in SnO_2 and in **IO**.

The composition of the disproportionation products as a function of temperature and length of treatment is given in Fig. 6, which combines the X-ray diffraction and Mössbauer spectroscopy results. The dotted line represents the temperature of the disproportionation onset (assumed time-independent). Curve A represents the time necessary, for a given temperature, to have complete disproportionation (disappearance of SnO), the final product being only the **IO**. The border line conditions to have SnO_2 in the final product or, in other words, the onset of **IO** decomposition, are given by curve B. Finally, curve C defines the treatment parameters over which the only oxide produced is SnO_2.

The temperature at which the reaction starts may be established at about 275 °C, according to X-ray results, although the Mössbauer spectrum of the 100 h/250 °C sample suggests a slightly lower value, displaying the presence of little amount of Sn(IV) in **IO** (Fig. 3a). In this case the higher sensitivity of the Mössbauer technique derives from the relatively higher value of the Sn(IV) recoil-free factor.

The usefulness of combining information derived from X-ray diffraction and Mössbauer spectroscopy arises also from data obtained on samples heated for

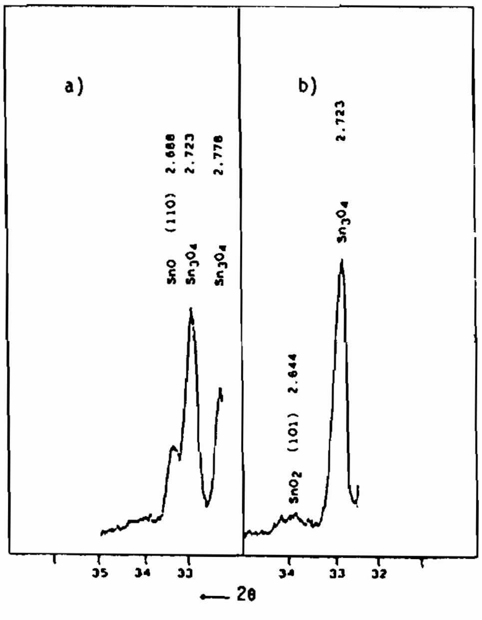

Fig. 8. Detail of X-ray diffraction patterns of samples heated 0.5 h at (a) 400 °C and (b) 450 °C.

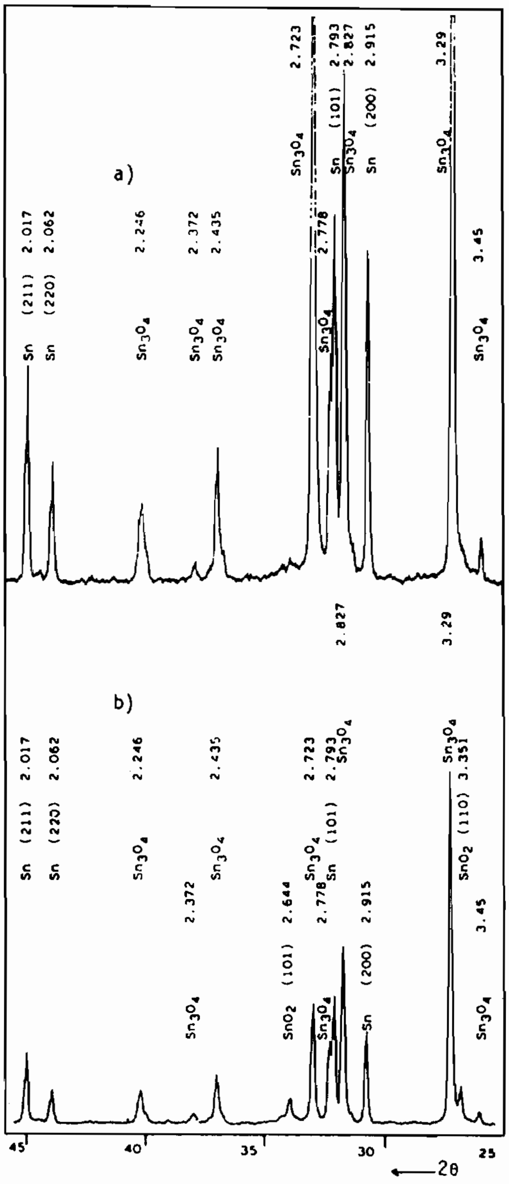

Fig. 9. X-ray diffraction patterns ($25 < 2\theta < 45$) of samples heated 100 h at (a) 350 ℃ and (b) 450 ℃.

1 h at 350 ℃, 400 ℃ and 450 ℃ (Figs. 2 and 7). The presence of **IO** is clearly evidenced by the diffraction pattern of Fig. 7a, whereas the Mössbauer spectrum of Fig. 2a gives only the Sn(IV) component of **IO**, the Sn(II) one being too weak to be resolved (Table III).

Up to 425 ℃ the only disproportionation product is the **IO**. We observe that at 450 ℃ formation of the **IO** proceeds very fast (SnO is completely transformed after 0.5 h at 450 ℃, as evidenced by the diffraction profiles of Fig. 8 and by the Mössbauer spectra of Fig. 1 and data of Table III). SnO_2 instead increases very slowly, its concentration being not greater than 1% even after 100 h heating, according to Figs. 4b and 9b. Very probably, at temperatures over about 425 ℃ the **IO** begins to decompose slowly in Sn and SnO_2 according to the scheme

$$Sn_3O_4 \longrightarrow Sn + 2SnO_2 \qquad (4)$$

and, in addition, the SnO_2 occurrence in the disproportionation products follows the complete disappearance of SnO in the zone (Sn_3O_4 + SnO_2) of Fig. 6.

At about 550 ℃ and over the disproportionation runs according to the scheme

$$2SnO \longrightarrow Sn + SnO_2 \qquad (5)$$

the SnO_2 being the only oxide recognizable in the final product, even by heating for only 1 h (see Figs. 7c and 9b). In this case the more valuable information derives from the X-ray diffraction data, it being very difficult to resolve the weak Mössbauer component of Sn(IV) in SnO_2 from the Sn(IV) in **IO** (Fig. 4b).

During disproportionation, whatever the scheme followed, there are no more than three condensed phases presented simultaneously.

Conclusions

Tin monoxide begins to disproportionate at about 275 ℃. In the temperature range 275–425 ℃ the disproportionation products are metallic tin and the intermediate oxide Sn_3O_4. In the temperature range 425–550 ℃, after the complete transformation of SnO, the intermediate oxide decomposes slowly in Sn and SnO_2, according to reaction (4). At about 550 ℃ and over, the disproportionation proceeds rapidly according to reaction (5) to form the thermodynamically-stable condensed phases Sn and SnO_2.

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