

# A Thermodynamic Study of Tin Oxides by Coulometric Titration

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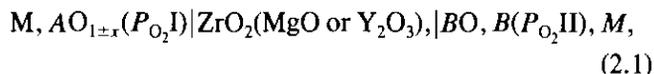
The nonstoichiometries of tin oxides have been studied by coulometric titration, using solid state electrolytes (YSZ) between 694 K and 990 K. The nonstoichiometry ( $X$ ) and the oxygen partial pressure ( $P_{O_2}$ ) vary as  $x \propto P_{O_2}^{-1/6}$  near 900 K. A phase  $Sn_3O_4$  between the Sn and  $SnO_2$  in the range of 969–732 K. The Gibbs free energy change of formation of  $Sn_3O_4$  is given by  $\Delta G_{Sn_3O_4}^\circ = -1,163,960 + 417.36 T$  (J/mol). © 1994 Academic Press, Inc.

## 1. INTRODUCTION

Over the past 30 years, tin oxide materials have been continually used in many fields (1–10) and studied theoretically (11–13). In addition to the two common stoichiometric compounds,  $SnO_2$  and  $SnO$ , there are other stoichiometric and nonstoichiometric compounds in the system Sn–O (14–21). The Gibbs free energy change of the formation of  $SnO_2$  and  $SnO$  as stoichiometric compounds has been reported in the literature (22–26), but that of nonstoichiometric tin oxides ( $SnO_{2-x}$ ) has not been reported to date. The aim of this paper is to study the oxygen defect concentration ( $x$ ) in  $SnO_{2-x}$  and the Gibbs free energy change of the formation of nonstoichiometric phases.

## 2. EXPERIMENTAL PROCEDURE

Coulometric titration has been used to study the nonstoichiometries of  $Ag_2S$  (27, 28), nickel oxides (29), and some nonstoichiometric oxides in the system  $V_2O_5$ – $V_2O_4$  (30, 31), because its accuracy is greater than that of a thermobalance. The electric cell used in the coulometric titration procedure is



where  $M$  is the electrode material,  $AO$  and  $BO$  are appropriate oxides, and  $(P_{O_2}I)$  and  $(P_{O_2}II)$ , are the equilibrium oxygen fugacity of the nonstoichiometric oxide and the oxygen fugacity of the reference electrode, respectively.

The electromotive force  $E$  of the cell may be expressed as

$$E = (RT/4F) \ln(P_{O_2}II/P_{O_2}I), \quad (2.2)$$

where  $R$  is the gas constant,  $T$  is the temperature in K, and  $F$  is Faraday's constant.

From the value of current ( $I_i$ ), titration time ( $t_i$ ), and specimen weight ( $W_{SnO_2}$ ), the value of the nonstoichiometry in  $SnO_{2-x}$  ( $X$ ) may be expressed as

$$X = X_{(ref)} + \frac{2G_{SnO_2}}{W_{SnO_2}} \cdot \sum [I_i t_i / 4F - \Delta N_{O_2}(\text{space})], \quad (2.3)$$

where  $X_{(ref)}$  is the nonstoichiometry in the starting  $SnO_{2-x}$  sample,  $G_{SnO_2}$  is the gram molecular weight of  $SnO_2$ , and  $\Delta N_{O_2}(\text{space})$  is the change in the amount of oxygen gas in the titration room.

In general, the initial  $X_{(ref)}$  and the  $\Delta N_{O_2}(\text{space})$  can be regarded as zero, because the oxygen defect in the sample  $SnO_2$  vanishes and the oxygen fugacity in the titration room is very low.

The Gibbs free energy change of  $SnO_{2-x}$  can be calculated by the formula

$$\Delta G = -4EF = -RT \ln(P_{O_2}II/P_{O_2}I), \quad (2.4)$$

since  $P_{O_2}II$  is given.

The raw materials tested by us in coulometric titration are listed in Table 2.1 and the coulometric titration cells are illustrated in Fig. 2.1.

A coulometric titration tube, with a certain mass of sample  $SnO_2$ , was heated in an electric resistance furnace. The accuracy of temperature control was  $\pm 0.5^\circ K$ . After heating to  $1123^\circ K$  the variation of electromotive force of cell was monitored for 16 hr. If the oxygen partial pressure fluctuated greatly the titration tube was assumed to be damaged and was replaced. The titration temperature was above  $973^\circ K$  and the dc voltage remained below 2.5 V. Under these conditions the transference number of the oxygen ion is close to unity. The titration time was more than 180 sec. After titration the change of electromotive force (EMF) was measured at the given temperature. The system was equilibrated for 4–6 hr, after the rate of change

TABLE 2.1.  
The Materials Used for Coulometric Titration

Item	Purity (%)	Content of impurity	Maker
Sn	>99.99	Sb < 0.001, Ce < 0.0002, Bi < 0.001	Shenyang
SnO	>99.8	Pb < 0.001, SnCl < 0.005, SnO < 0.001	Shanghai
SnO	>99.99	PbO < 0.0005, SbO < 0.001, Cl < 0.0005	Shanghai
CeO	>99.99	BaO < 0.001, Nd < 0.001, La < 0.001	JingShou

of EMF was less than  $\pm 1$  mV/hr. The final titration product was then quenched and examined by X-ray diffraction. It should be pointed that in these experiments no Sn-Pt alloys were found. That indicates the low rate of reaction between Sn and Pt.

### 3. RESULTS AND DISCUSSION

#### 3.1. Coulometric Titration of $\text{SnO}_{2-x}$

The equilibrium oxygen partial pressure over  $\text{SnO}_{2-x}$  shown in Fig. 3.1 as a function of  $X$  at 694, 720, 746, 783, 885, and 990 K. The plateau in the  $\ln P_{\text{O}_2}$  vs  $X$  relation in Fig. 3.1 corresponds to the  $\text{SnO}_{2-x} + \text{Sn}$  two-phase region and the maximum oxygen deficiency increased with increasing temperature. For example, the value of  $X$  is 0.034 at 990 K and decreases to 0.02 at 694 K. This means that the defect structure in  $\text{SnO}_{2-x}$  changes with temperature.

In general, the oxygen vacancy concentration  $X$  is related to the oxygen partial pressure  $P_{\text{O}_2}$  via the proportionality

$$X \propto P_{\text{O}_2}^{-1/n} \quad (3.1)$$

The relations between  $\ln X$  and  $\ln P_{\text{O}_2}$  in  $\text{SnO}_{2-x}$  at 990,

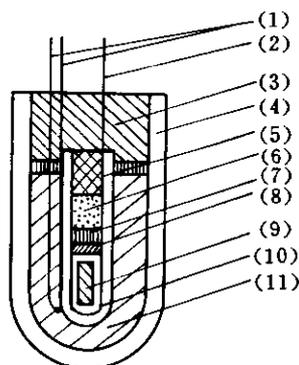


FIG. 2.1. The structure of the coulometric titration tube with NiO + Ni reference electrode: (1, 2) Pt-Rh wire and Pt wire; (3, 5) boron oxide; (4)  $\text{Al}_2\text{O}_3$  tube; (6)  $\text{B}_2\text{O}_3 + \text{Al}_2\text{O}_3$  cement; (7)  $\text{Al}_2\text{O}_3$  cement; (8) Alumina plate; (9) Sample with Pt; (10) YSZ tube; (11) Ni + NiO.

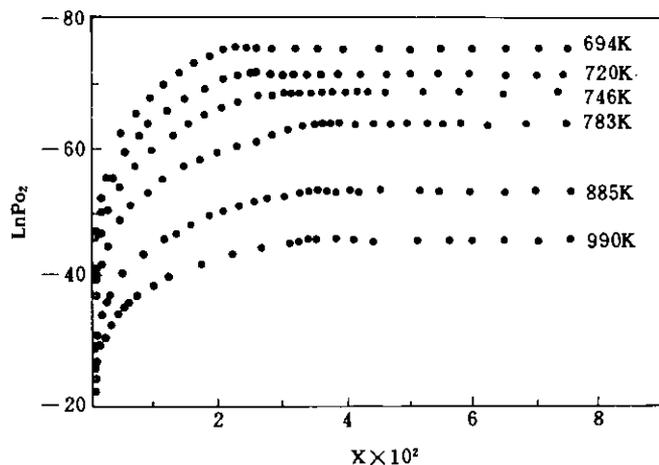


FIG. 3.1. Variation of  $\ln P_{\text{O}_2}$  with value  $X$  in  $\text{SnO}_{2-x}$ .

885, 783, 746, and 720 K are shown in Fig. 3.2. the straight lines have slopes ranging from  $-1/5.7$  to  $-1/8.3$  in the region  $X < 0.022$ .

#### 3.2. The Standard Gibbs Free Energy Change of Formation of $\text{SnO}_2$

The plateau in  $P_{\text{O}_2}$  for  $x > 0.03$  in Fig. 3.1 indicates the coexistence of two phases.

X-ray diffraction was measured on the final product of titration at 885 K. These patterns demonstrate the coexistence of two phases ( $\text{Sn} + \text{SnO}_2$ ), as is also confirmed by the phase diagram of the Sn-SnO<sub>2</sub> system (19) (Fig. 3.3). This shows that a two-phase mixture ( $\text{Sn} + \text{SnO}_2$ ) is present above 450°C (723° K).

The temperature depends of the equilibrium oxygen partial pressure  $P_{\text{O}_2}$  over the mixture of Sn + SnO<sub>2</sub> is

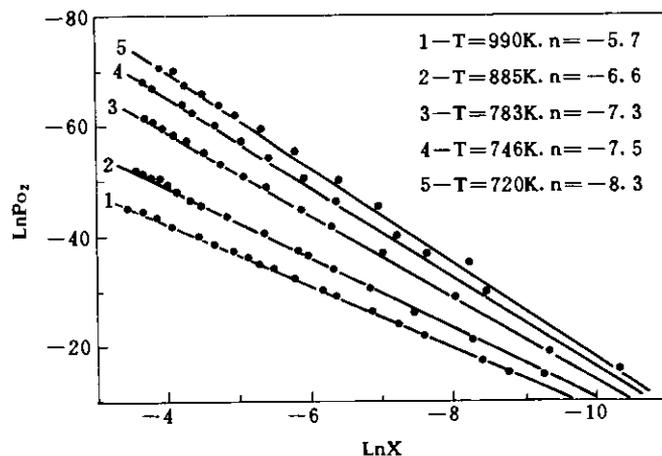
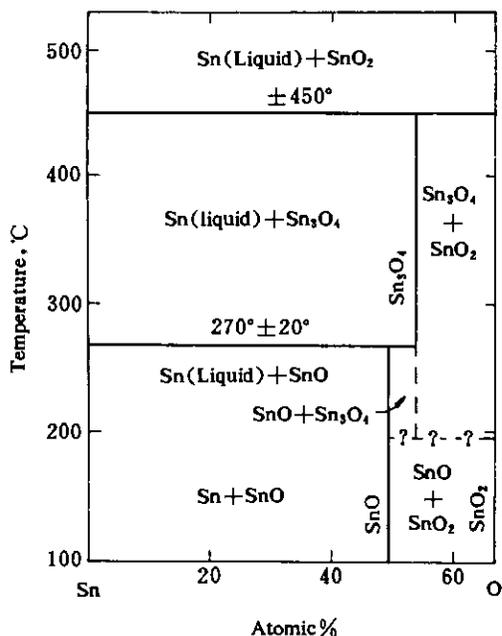


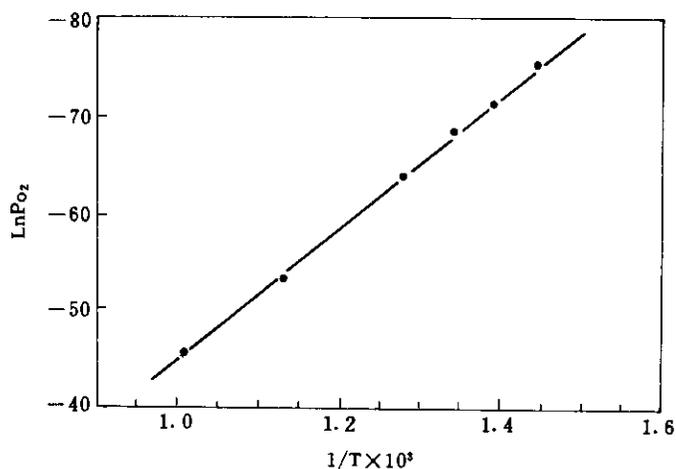
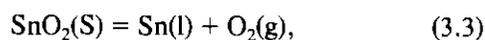
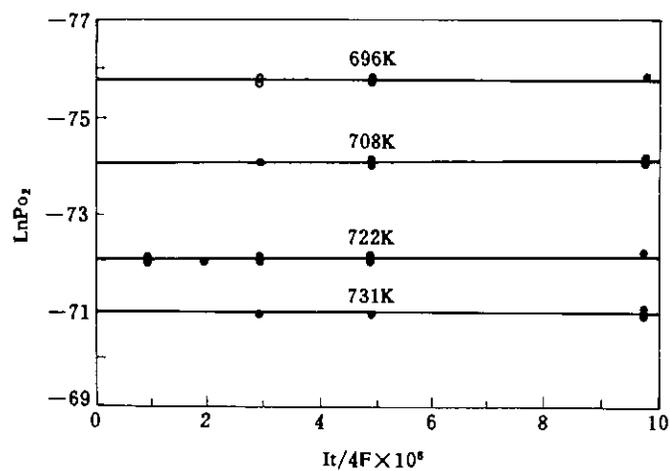
FIG. 3.2. Relation between  $\ln X$  and  $\ln P_{\text{O}_2}$  in  $\text{SnO}_{2-x}$ .

FIG. 3.3. Phase diagram of Sn-SnO<sub>2</sub> (19).

presented in Fig. 3.4. This is the line that can be represented by Eq. (3.2) using the least-squares method:

$$\ln P_{O_2} = 24.3 - 69,080/T. \quad (3.2)$$

Since the equilibrium oxygen partial pressure  $P_{O_2}$  corresponds to the reaction

FIG. 3.4. The relationship between  $\ln P_{O_2}$  and  $1/T \times 10^3$  for the SnO<sub>2</sub>(s) + Sn(l) system  $\ln P_{O_2} 1/T \times 10^3$ .FIG. 3.5. The relationship between  $\ln P_{O_2}$  and  $It/4F \times 10^6$  for the Sn<sub>3</sub>O<sub>4</sub>(s) + Sn(l) system.

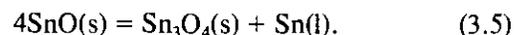
the standard Gibbs free energy change of formation of SnO<sub>2</sub> can be calculated as

$$\Delta G_{\text{SnO}_2}^{\circ} = -574330 + 202T \quad (\text{J/mol}). \quad (3.4)$$

These results agree with those already published (22, 24) within a few percent.

### 3.3. Coulometric Titration of Sn<sub>3</sub>O<sub>4</sub> + Sn System

The equilibrium oxygen partial pressure over the Sn + Sn<sub>3</sub>O<sub>4</sub> system between 696 and 731 K was measured by coulometric titration on a specimen which was the product of the disproportionation of SnO through the reaction

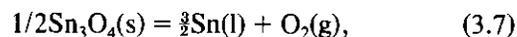


The presence of these products was confirmed by X-ray diffraction test and is in conformity with the phase diagram of Sn-SnO<sub>2</sub>.

$\ln P_{O_2}$  is independent of the amount of oxygen migration during the titration ( $It/4F$ ), as shown in Fig. 3.5, but  $\ln P_{O_2}$  does depend on the temperature, as shown in Fig. 3.6, which can be expressed by

$$\ln P_{O_2} = 25.1 - 70,000/T. \quad (3.6)$$

Since the equilibrium oxygen partial pressure  $P_{O_2}$  corresponds to the reaction



the standard Gibbs free energy change of formation of Sn<sub>3</sub>O<sub>4</sub> can be written as

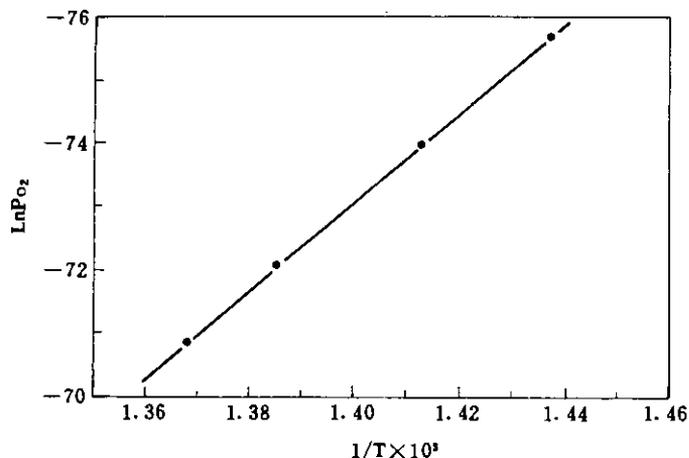


FIG. 3.6. The relationship between  $\ln P_{O_2}$  and  $1/T \times 10^3$  for the  $Sn_3O_4(s) + Sn(l)$  system.

$$\Delta G_{Sn_3O_4}^0 = -1,163,960 + 417.36 T \quad (\text{J/mol}). \quad (3.8)$$

Because information is not available on the standard Gibbs free energy change of formation of  $Sn_3O_4$ , the present results cannot be compared with other data.

#### 4. CONCLUSIONS

The maximum oxygen defect concentration in  $SnO_{2-x}$  is 0.034 at temperatures below 990 K and the oxygen deficiency ( $X$ ) increases with decreasing equilibrium oxygen partial pressure  $P_{O_2}$ .

In the temperature range 696–732 K, the standard Gibbs free energy change of formation of  $Sn_3O_4$  is given by the equation

$$\Delta G_{Sn_3O_4}^0 = -1,163,960 + 417.36 T \quad (\text{J/mol}).$$

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