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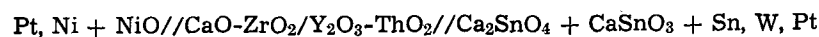
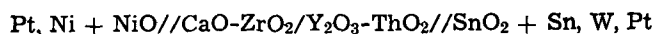
## Electrochemical Determination of the Stability of Mono- and Dicalcium Stannates

K. T. Jacob and J. C. Chan<sup>1</sup>

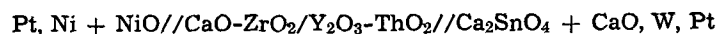
*Department of Metallurgy and Materials Science, University of Toronto, Ontario, Canada M5S 1A4*

### ABSTRACT

The thermodynamic properties of mono- and dicalcium stannates have been determined in the temperature range 973°-1423°K from the electromotive force measurements on solid oxide galvanic cells



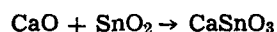
and



The Gibbs free energy changes accompanying the formation of the stannates from component oxides may be represented by the equations



$$\Delta G^\circ = -17,040 + 0.85T (\pm 300) \text{ cal}$$



$$\Delta G^\circ = -17,390 + 2.0T (\pm 300) \text{ cal}$$

The partial pressures of the tin bearing oxide species resulting from the decomposition of the stannates have been calculated as a function of the oxygen partial pressure by combining the results of this study with published information on the partial pressures and composition of oxide species over stannic oxide.

Quantitative information on the stability of calcium stannates is of importance in the pyrometallurgy of tin and its alloys. Tin smelting slags frequently contain considerable amounts of calcium oxide. Recently Shelley and Shelley (1) have illustrated the importance of calcium oxide in increasing the solubility of stannic oxide in glassy matrix. The traditional use of stannic oxide as an opacifier in glass is related to its precipitation as  $\text{CaSnO}_3$ ,  $\text{CaSnTiO}_5$ , etc. Application of alkaline-earth stannates as dielectric materials (2) has raised considerable interest in the stability of these compounds under different environmental conditions. The tendency of these compounds to change composition at high temperatures and reducing conditions, due to the volatilization of  $\text{SnO}$  and its polymeric forms, can be quantitatively assessed from an accurate knowledge of the stabilities and published information (3) on the vapor composition and pressures over  $\text{Sn} + \text{SnO}_2$  mixtures.

The phase diagram (2,4) indicates the occurrence of two compounds in the  $\text{CaO-SnO}_2$  system; mono- and dicalcium stannates. The oxygen chemical potential

in equilibrium with tin and stannic oxide was measured by Belford and Alcock (5) using a galvanic cell incorporating a yttria-doped thoria electrolyte and  $\text{Ni} + \text{NiO}$  reference electrode, in the temperature range 773°-1023°K. In this study the Gibbs free energies of formation for calcium stannates were measured using a similar technique. Equilibration of tin with two adjoining phases of the  $\text{CaO-SnO}_2$  system fixes the oxygen potential, measurement of which permits the calculation of the partial and integral thermodynamic properties of the system.

### Experimental

*Materials.*—The stannic oxide was supplied by the British Drug House Limited and was 99.95% pure. Calcium oxide was prepared by calcination of calcium carbonate, 99.99% pure, supplied by the Electronic Space Products Incorporated. The stannates were prepared by mixing fine powders of the component oxides in the required stoichiometric ratio, compacting the mixture into pellets, and sintering at 1273°K in oxygen atmosphere for 8 hr in a closed platinum dish. X-ray diffraction analysis of the products confirmed the formation of the stannates.

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Key words: thermodynamics, solid electrolyte, galvanic cell, calcium stannates, vaporization.

Tin of 99.99+ purity was supplied by the Fisher Scientific Company. Calcia-stabilized zirconia tubes were supplied by the Zirconia Corporation of America. Thoria pellets stabilized by 15 mole per cent (m/o) yttria, were prepared from mixed nitrate solution by evaporation and subsequent decomposition. The resulting powder was pressed into pellets at a pressure of 30 tons/sq in.<sup>-1</sup>, and sintered under an atmosphere of 90% N<sub>2</sub> + 10% H<sub>2</sub> at 2073°K. The argon gas used as the atmosphere for the emf runs was 99.98% pure, and was dried by passing through magnesium perchlorate and deoxidized by passage through a column of titanium granules maintained at 1170°K.

**Apparatus.**—It has been observed in earlier studies (6,7) that at temperatures above 1273°K the calcia-stabilized zirconia electrolyte is corroded by pure stannic oxide in equilibrium with tin. Preliminary studies indicated that yttria-doped thoria electrolyte, used by Belford and Alcock (5) up to a temperature of 1023°K, is suitable in contact with pure stannic oxide till 1173°K and in contact with the stannates till 1423°K. At higher temperatures, discoloration of the electrolyte was noticed.

A schematic diagram of the apparatus is shown in Fig. 1. The Ni + NiO reference electrode was placed inside a closed end, flat bottomed, lime-zirconia tube, with a platinum wire spring loaded against the reference electrode. The platinum lead is enclosed in an alumina sheath, through which prepurified argon gas is passed at a rate of 100 ml/min<sup>-1</sup>. The lime-zirconia tube is placed inside an alumina tube, one end of which is attached to a yttria-doped thoria pellet by means of alumina cement and glass seals. The outer end of the lime-zirconia tube and the surfaces of the yttria-thoria pellets were polished with diamond paste to facilitate good contacts when pressed together. The entire assembly was mounted inside a reaction tube in a vertical molybdenum wound resistance furnace in such a way that the assembly could be moved up and down through a sliding rubber seal.

Pellets of Sn + SnO<sub>2</sub> were made by compacting a mixture of their powders in the molar ratio 1:2. The pellet was placed inside an alumina crucible which was supported on an alumina tube. The pellet was pressed down against the bottom of the alumina crucible with a spring loaded ring sleeve of alumina. When the Sn + SnO<sub>2</sub> pellets of 1:2 mixture were heated under inert gas, fine droplets of molten tin were found to be held against the yttria-thoria pellet by surface tension. They do not settle to the bottom of the alumina crucible unless the ratio of tin in the pellets is increased.

Electrical contact between the Sn + SnO<sub>2</sub> pellet and the platinum wire passing over the outside of the alumina tube, e, was affected by lowering the overhanging electrolyte-tube onto the pellet. Attack of the platinum contact by the molten tin was observed, but was minimized by recessing the platinum lead in a small groove cut into the yttria-thoria pellet and then adding a 1 cm long tungsten wire extension to the platinum-lead to make contact with the Sn + SnO<sub>2</sub> pellet. Times varying from 30 min to 3 hr were found necessary to attain equilibrium emf's. The emf's were measured with "Solartron" digital voltmeter, which has an input impedance of 10<sup>12</sup> ohms. The design of the emf cell permitted the electrolyte material to be detached from the Sn + SnO<sub>2</sub> pellet during heating and cooling periods. Pellets containing tin and a mixture of stannates were prepared in a manner similar to the Sn + SnO<sub>2</sub> pellets; the respective stannates being mixed in 1:1 molar ratio. Reversible emf's of the following cells were measured as a function of temperature

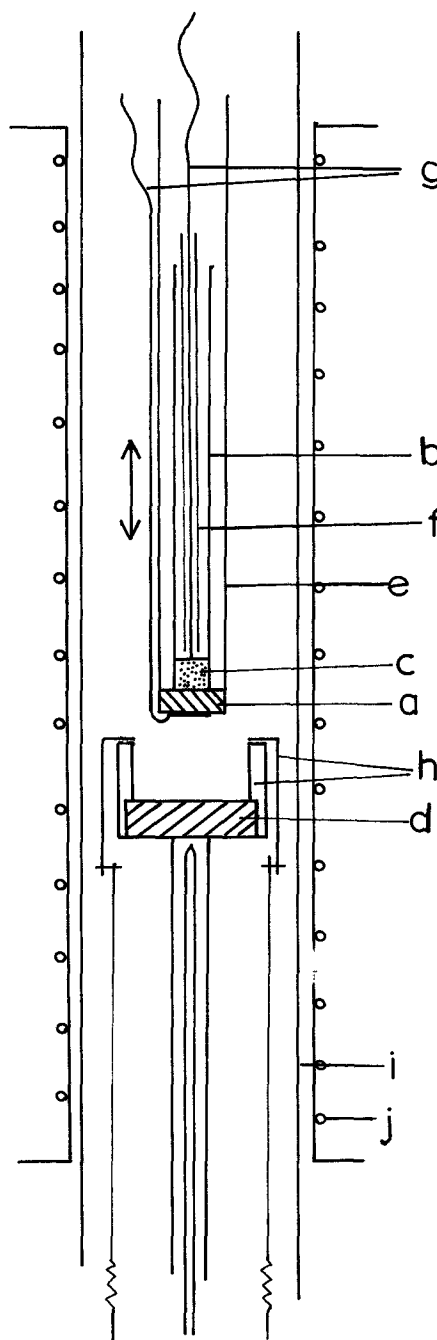
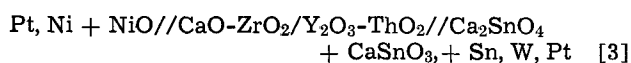
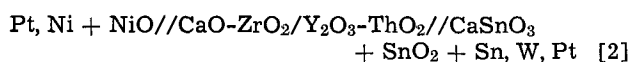
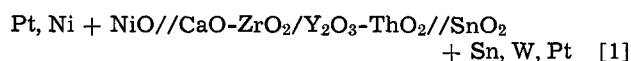
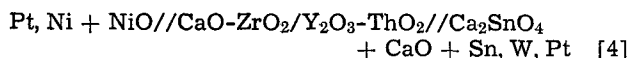


Fig. 1. Schematic diagram of the electrochemical cell assembly; (a) Y<sub>2</sub>O<sub>3</sub>-ThO<sub>2</sub> pellet, (b) CaO-ZrO<sub>2</sub> tube, (c) Ni + NiO reference electrode, (d) Sn + SnO<sub>2</sub> electrode, (e) alumina tube, (f) alumina sheath (argon inlet), (g) platinum leads, (h) alumina crucibles and rings for spring loading the Sn + SnO<sub>2</sub> electrode against the alumina container, (i) alumina reaction tube, (j) molybdenum resistance furnace.



and



The reversibility of the cells was checked by passing a small current ( $\approx 50 \mu\text{A}$ ) through the cell for 2-5 min in either direction, and it was found that the emf

returned to its initial value in a few minutes, after which it remained constant for up to 8 hr. Emf's were also found to be independent of the flow rate of inert gas through the cell.

### Results and Discussion

The emf's were reproducible within  $\pm 2$  mV on repeated temperature cycling. The emf's of cells [3] and [4] were found to be a linear function of temperature, as shown in Fig. 2, in the temperature range 975°-1423°K. At lower temperatures higher emf's were observed which tend to increase with time, suggesting that equilibrium may not have been attained. The emf's of cells [1] and [2] varied linearly with temperature in the range 875°-1175°K, above which the emf's were found to decrease with time. Reproducible emf's could not be obtained once the cells were heated above 1175°K. Examination of the cell components indicated that SnO vapor penetrated the  $Y_2O_3$ - $ThO_2$  pellets and the supporting alumina tube above 1175°K.

The emf of cell [2] was on the average 2.5 mV above the emf of cell [1]. If the solid solubility of calcium oxide in stannic oxide is negligible, the emf's of cells [1] and [2] should be identical. While the slightly higher emf obtained with cell [2] indicates some solid solubility, it is not possible to calculate the solubility limit accurately from the present results because of a scatter of  $\pm 2$  mV in the measured emf. The variation of the emf's of cells [1], [3], and [4] with temperature may be represented by the equations

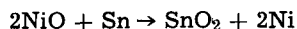
$$E_1 = 300.5 - 0.1088T (\pm 2) \text{ mV}$$

$$E_3 = 492.7 - 0.143T (\pm 2) \text{ mV}$$

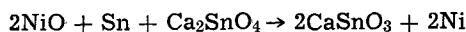
$$E_4 = 485.2 - 0.1032T (\pm 2) \text{ mV}$$

The emf of cell [1] obtained in this study is almost identical to that reported by Belford and Alcock (5). Recent work by Carbo-Nover and Richardson (7) have confirmed that both solid and liquid SnO are

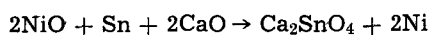
unstable below 1373°K and decompose to a mixture of Sn and  $SnO_2$ . Above 1373°K, liquid SnO is the stable phase in equilibrium with tin. Information on electrolytic conduction domains for both calcia-zirconia and yttria-thoria has been reviewed by Patterson (8). An analysis of the emf of bioelectrolyte cells has been proposed by Shores and Rapp (9), which indicates that at the oxygen potentials prevailing at the electrodes employed in this study, significant electronic contributions to the total conductivity of the electrolyte would be absent. Therefore, the standard free energy changes accompanying the following cell reactions can be calculated from the measured emf



$$\Delta G^\circ = -27,720 + 10.04T (\pm 200) \text{ cal}$$



$$\Delta G^\circ = -45,455 + 13.19T (\pm 200) \text{ cal}$$

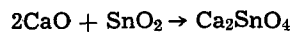


$$\Delta G^\circ = -44,765 + 10.89T (\pm 200) \text{ cal}$$

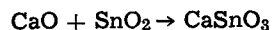
Using a value of

$$\Delta G^\circ = -55,965 + 20.29T \text{ cal}$$

for the standard free energy of formation of NiO (10), the free energy of formation of calcium stannates from the component oxides can be obtained from the above equations



$$\Delta G^\circ = -17,040 + 0.85T (\pm 300) \text{ cal}$$



$$\Delta G^\circ = -17,390 + 2.0T (\pm 300) \text{ cal}$$

Figure 3 shows the integral free energy and enthalpy of mixing in the CaO-SnO<sub>2</sub> system. The uncertainty limits on second law enthalpies are also indicated on the diagram. Within experimental error limits the integral heat of formation of dicalcium stannate is a linear additive function of the heats of formation of monocalcium stannate and pure calcium oxide. A slightly higher entropy of formation appears to be responsible for the high temperature stability of the dicalcium stannate with respect to monocalcium stannate and calcium oxide.

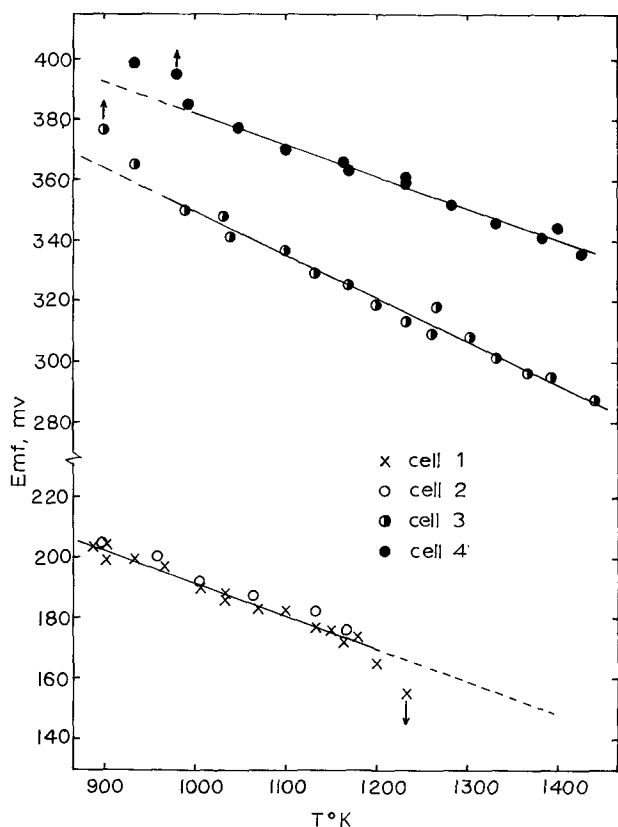


Fig. 2. The temperature dependence of the emf's of cells [1], [2], [3], and [4].

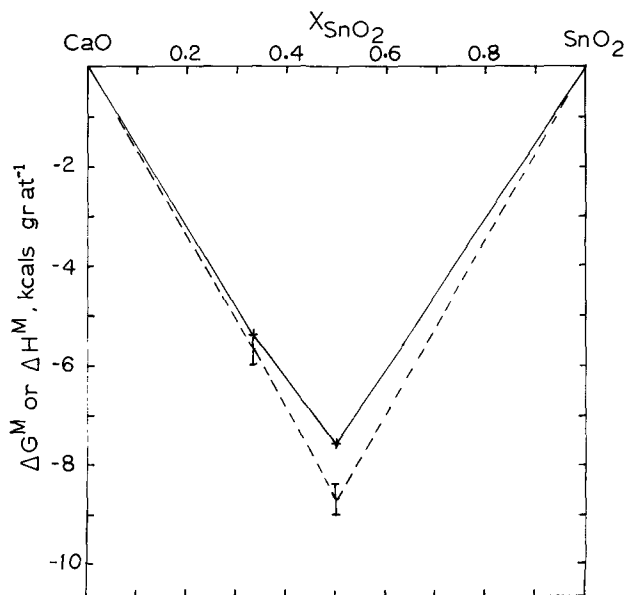


Fig. 3. The integral free energy and enthalpy of mixing in the CaO + SnO<sub>2</sub> system; —  $\Delta G^M$ , 1000°K; - - -  $\Delta H^M$ .

Table I. Standard free energy change accompanying the volatilization of SnO<sub>2</sub> (3)

Reaction	$\Delta G^\circ$ , cal
$\text{SnO}_2(\text{s}) \rightarrow \text{SnO}(\text{g}) + \text{O}_2(\text{g})$	$138,420 - 60.947T$
$2\text{SnO}(\text{g}) \rightarrow \text{Sn}_2\text{O}_3(\text{g})$	$-64,570 + 30.76T$
$3\text{SnO}(\text{g}) \rightarrow \text{Sn}_3\text{O}_3(\text{g})$	$-131,740 + 67.84T$
$4\text{SnO}(\text{g}) \rightarrow \text{Sn}_4\text{O}_4(\text{g})$	$-200,220 + 102.68T$

The mass-spectrometric studies of Colin, Drowart, and Verhaegen (3) have shown that the vapor above stannic oxide consists of Sn, SnO, Sn<sub>2</sub>O<sub>2</sub>, Sn<sub>3</sub>O<sub>3</sub>, and Sn<sub>4</sub>O<sub>4</sub> species. On the basis of their mass-spectrometric measurements and earlier studies of the vapor pressures over Sn + SnO<sub>2</sub> mixtures, the standard free energy changes for the reactions involved in the vaporization of stannic oxide have been derived (3), and are summarized in Table I. Due to the change in the stoichiometry of the oxide during vaporization, the volatility of stannic oxide and the stannates would be dependent on the oxygen partial pressure as discussed by Kellogg (11). The partial pressures of the oxide species over mono- and dicalcium stannates can readily be calculated by combining the information in Table I with the results of the present study. Figure 4 shows the variation of the partial pressure of the various gaseous species over mono- and dicalcium stannates with the oxygen partial pressure at 1400°K. The pressures of SnO and its polymeric forms increase as the oxygen partial pressure decreases, until pure liquid tin is obtained as a separate phase by the reduction of the stannates. A further decrease in the oxygen partial pressure results in a decrease in the partial pressure of the oxide species. The main contribution to the total pressure arises from SnO species. The relative contribution of the polymeric species to the total pressure increases as the oxygen pressure is reduced, and attains a maximum value at the oxygen partial pressure corresponding to the reduction of the stannates to form liquid tin. The total

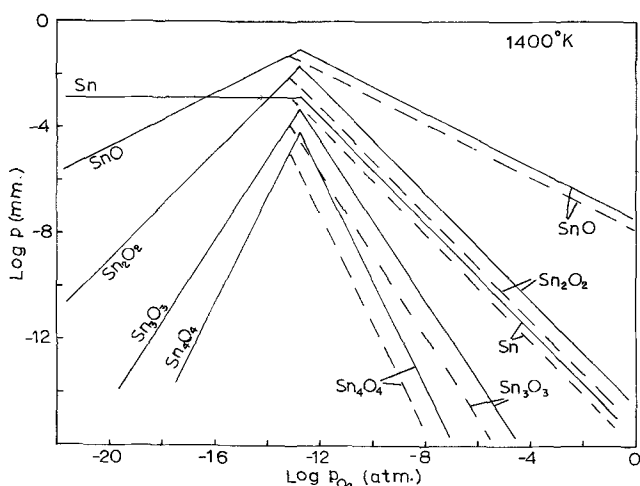


Fig. 4. The partial pressures of the tin bearing oxide species in equilibrium with the stannates at 1400°K as a function of the oxygen partial pressure; — monocalcium stannate, - - - dicalcium stannate.

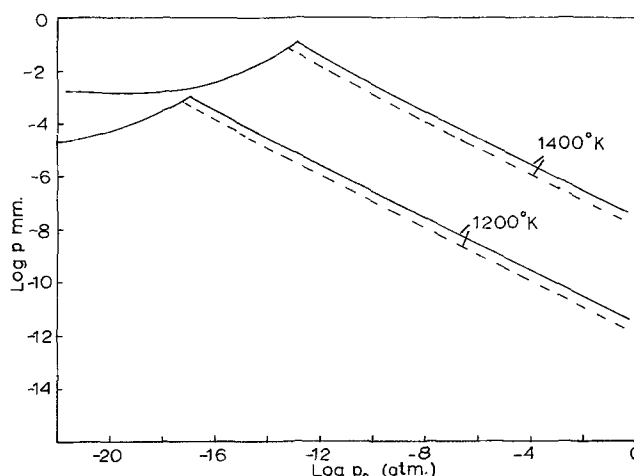


Fig. 5. The total vapor pressure over the stannates as a function of the oxygen partial pressure; — monocalcium stannate, - - - dicalcium stannate.

pressure, obtained as a summation of the individual partial pressures over mono- and dicalcium stannates, is shown in Fig. 5, as a function of the oxygen partial pressure. If the stannates are kept under an inert gas or in vacuum, the volatility would be restricted by the requirement that  $P_{\text{SnO}} = 2P_{\text{O}_2}$ . The values for the partial and total pressures of the tin bearing oxide species, shown in Fig. 4 and 5, enable the estimation of the composition changes upon prolonged use of the stannates at high temperatures.

#### Acknowledgment

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