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Thermodynamic stability of Sb_2O_4 by a solid oxide electrolyte e.m.f. method

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The standard Gibbs energy change for the reaction Sb_2O_3 (orthorhombic) + $\frac{1}{2}O_2(g) \rightleftharpoons Sb_2O_4$ (orthorhombic) was measured using the following galvanic cell: Pt, Sb_2O_3(ortho), Sb_2O_4 (ortho), platinum black |15 wt % Y_2O_3-stabilized $ZrO_2|O_2$(air, $P_{O_2} = 0.21$ atm), Pt over the range 585 to 828 K. Reproducible e.m.f. values were obtained only when the otherwise poorly electronic conducting oxide mixture was blended with platinum black. The standard Gibbs energy change for this reaction was found to be ($\Delta G^\circ_R \pm 0.81$) (kJ) = $-168.33 + 0.09019\,T$/K. This yielded the standard Gibbs energy of formation ΔG°_f of Sb_2O_4(ortho) to be as follows: [ΔG°_f(Sb_2O_4, ortho) ± 1.61] (kJ) = $-854.69 + 0.33614\,T$/K. A third-law treatment yielded a value of −880.55 (±1.21) kJ mol^{-1} for $\Delta H^\circ_{f,298}$ of Sb_2O_4(ortho).

1. Introduction

Antimony sesquioxide Sb_2O_3 in the orthorhombic (ortho) modification (known as valentinite) encapsulated in stainless steel is often used as a neutron start-up facility in contact with beryllium in fast breeder nuclear reactors [1, 2]. The utility of such a facility has been limited by a rather low [3] temperature of melting (929 K) of Sb_2O_3(ortho). Though Sb_2O_3 is less stable thermodynamically compared even to the oxide of nickel [2, 4, 5] which is a component of stainless steel, still Sb_2O_3 was compatible with stainless steel owing to its lower chemical reactivity in its solid state. However, in the molten state it could be reactive enough to lead to clad failure. As this poses a serious limitation on the temperature range of utility of Sb_2O_3–Be neutron start-up facility, use of Sb_2O_4 with a much higher melting point [3] (> 1400 K under 0.1 MPa) has been contemplated. Hence, the equilibrium oxygen pressure over the buffer mixture Sb_2O_3(ortho)/Sb_2O_4(ortho) has to be measured precisely in order to estimate the stability of the higher antimony oxide. There has been no reliable Gibbs energy data on Sb_2O_4 though its equilibrium oxygen pressure has been reported [3] to be 6.0 MPa at its melting temperature of 2093 K. In this investigation, the oxygen potential of Sb_2O_3(ortho)/Sb_2O_4(ortho) has been reported from e.m.f. results using 15 wt % yttria stabilized zirconia as electrolyte.

2. Experimental procedure

2.1. Materials

The Sb_2O_3(ortho) of purity better than 99.999% (Johnson and Mathey, UK) was oxidized by heating in air at 773 K for 100 h and the product was identified to be pure Sb_2O_4(ortho) by X-ray diffraction within the limits of its detection. The electrolyte was made of 15 wt % yttria stabilized zirconia (15 YSZ) one end closed tube with closed end flat (Corning, USA) having the dimensions of 9.7 mm i.d., 12.5 mm o.d. and 305 mm length. Thermocouple-grade platinum wire was used as electrical lead on both sides.

Two batches of pellets of equimolar mixtures of Sb_2O_3(ortho)/Sb_2O_4(ortho) were made with and without the addition of platinum black to study the effect of electron exchange reaction (between the two phases in the electrode) in establishing an open-cell equilibrium voltage. The batch of pellets with platinum black was prepared by intimately mixing the oxide with half their weight of platinum black. Both batches of pellets were compacted under pressure of 100 MPa into cylinders of dimension 12 mm diameter and 3 mm thickness.

2.2. Galvanic cell assembly

A two-compartment galvanic cell assembly described earlier [6, 7] was used in this investigation. A Pt–10% Rh/Pt thermocouple calibrated with the freezing points of tin, bismuth, zinc, antimony, silver and gold was used to measure the temperature. Purified argon [6, 7] was used as a cover gas and air/platinum was used as the reference electrode. The internal consistency was checked by varying the 1 : 1 ratio of Sb_2O_3(ortho)/Sb_2O_4(ortho) to the extent of 10% blended with platinum black.

3. Results and discussion

The following two series of galvanic cells were studied:

$$\text{Pt, } Sb_2O_3\text{(ortho), } Sb_2O_4\text{(ortho)} \; |15\,\text{YSZ}|O_2(\text{air, } P_{O_2} = 0.21\,\text{atm}),\ \text{Pt} \qquad \text{I}$$

$$\text{Pt, } Sb_2O_3\text{(ortho), } Sb_2O_4\text{(ortho), Pt black} \; |15\,\text{YSZ}|O_2(\text{air, } P_{O_2} = 0.21\,\text{atm}),\ \text{Pt} \qquad \text{II}$$

Cell I did not give rise to any reproducible value in the temperature range of 700 to 929 K. Beyond this temperature, the melting of Sb_2O_3 resulted in the attack of

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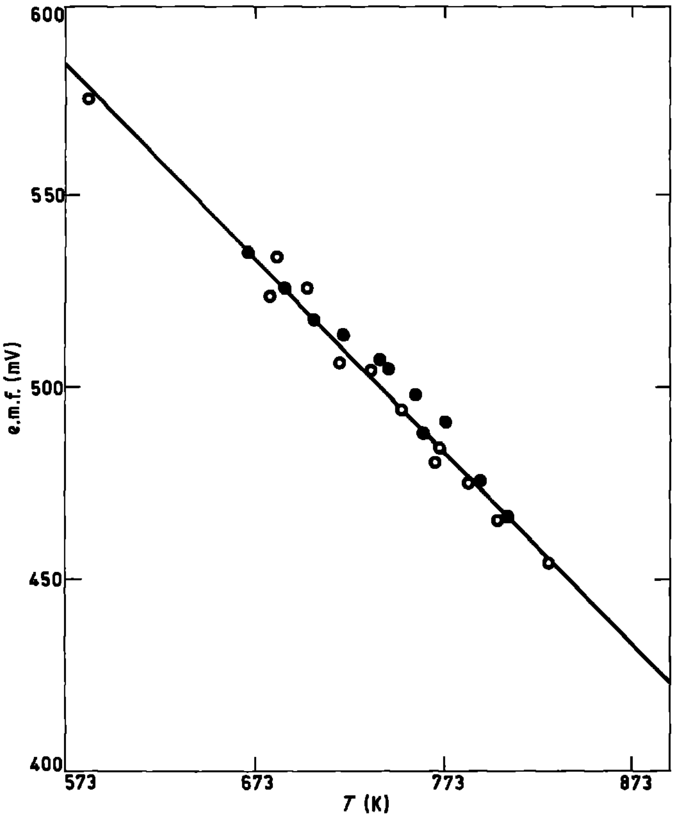

Figure 1 The e.m.f. of the cell Pt, Sb_2O_3(ortho), Sb_2O_4(ortho), Pt black | 15 YSZ | O_2(air, P_{O_2} = 0.21 atm), Pt. (●) and (○) are different runs.

the platinum lead wires. The failure of cell I to give rise to a reproducible voltage was likely to be due to the lack of the electron exchange reaction between the two oxides. The white colour of the two oxides itself is indicative of their poor electronic conduction. Good electronic conductivity is usually a characteristic of good and reversible electrodes according to Heyne [8]. To prove this conjecture, cell II was studied in which the two oxides were blended with platinum black to facilitate electron exchange reaction in the electrodes. The e.m.f. results on cell II shown in Fig. 1 proved that the addition of platinum black had helped in recording reproducible e.m.f. readings in thermal cycling as well as in two series of experimental runs with varying ratio of $Sb_2O_3|Sb_2O_4$. These results can be filled into the following least-square expression over the range 585 to 828 K:

$$(E \pm 4.2)\ (\text{mV}) = 872.32 - 0.50108\,T/K \quad (1)$$

For the reaction,

$$Sb_2O_3(\text{ortho}) + \tfrac{1}{2}O_2(g) \rightleftharpoons Sb_2O_4(\text{ortho}) \quad (2)$$

the standard Gibbs energy change $\Delta G^\circ_{(2)}$ can be calculated to be as follows after correcting for the standard state of oxygen in the air reference electrode in cell II:

$$(\Delta G^\circ_{(2)} \pm 0.81)\ (\text{kJ}) = -168.33 + 0.09019\,T/\text{K} \quad (3)$$

$$(585 \text{ to } 828\,\text{K})$$

This expression would lead to the following equation for the equilibrium oxygen partial pressure for the mixture of Sb_2O_4 and Sb_2O_3:

$$(\log P_{O_2} \pm 0.12) = 9.42 - 17585/T \quad (4)$$

At 1273 K, the dissociation of Sb_2O_4 will not yield more than 40 volume p.p.m. of oxygen and when encapsulated in stainless steel this may not give rise to a serious compatibility problem, so that it can be used

TABLE I Computation of free energy functions for the formation of Sb_2O_3(ortho) and Sb_2O_4(ortho)

Substance	Value of ϕ(J K^{-1} mol^{-1})				Remarks
	600 K	700 K	800 K	900 K	
Sb_2O_3(ortho)	−152.555	−162.024	−171.453	−180.694	Using S°_{298} Sb_2O_3(c), C°_p(Sb_2O_3, ortho)*, ΔH°_f (cubic to ortho) from Barin and Knacke [9]
O_2(g)	−210.989	−213.588	−216.110	−218.315	Computed from Barin and Knacke [9]
Sb(s)	−50.593	−52.805	−54.976	−57.075	Computed from Barin and Knacke [9]
Sb_2O_4(ortho)	−150.579	−161.122	−171.572	−181.771	Computed from Samsonov [11]

*Parametric equation for C°_p is identical for ortho and cubic forms of Sb_2O_3 [9].

TABLE II Change in free energy function for the reactions involving Sb_2O_3 and Sb_2O_4

Reaction No.	$\Delta\phi$ (J K^{-1} mol^{-1}) = $A + BT$
(1) $Sb_2O_3(\text{ortho}) + \frac{1}{2}O_2(g) \rightleftharpoons Sb_2O_4(\text{ortho})$	106.243 + 0.00207 T
(2) $2Sb(s) + 2O_2(g) \rightleftharpoons Sb_2O_4(\text{ortho})$	379.808 + 0.01179 T

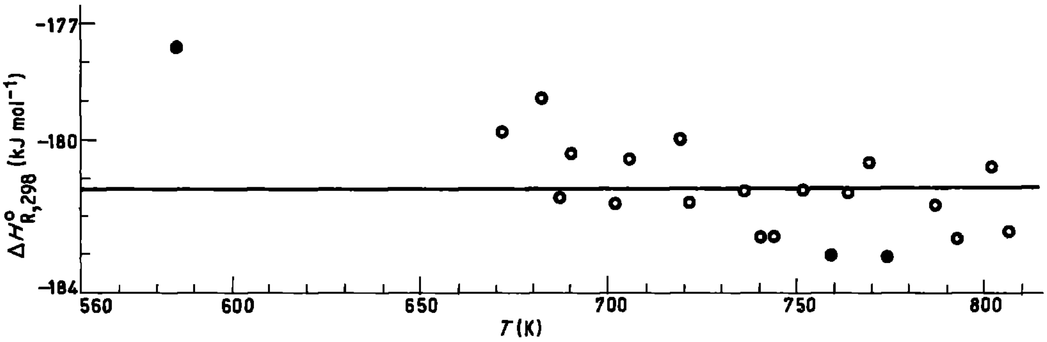

Figure 2 Third-law plot for the standard enthalpy change at 298.15 K for the formation of Sb_2O_4(ortho) from Sb_2O_3(ortho).

as a substitute for the stainless-steel encapsulated Sb_2O_3 in neutron start-up facility for fast breeder reactors provided that it meets with other requirements. Since the thermodynamic data on the high temperature phase transformation of Sb_2O_4 are not known, these values should not strictly be extrapolated beyond 1000 K. However, even on such an extrapolation to 2093 K, a value of 1.02 for log P_{O_2} of Sb_2O_3/Sb_2O_4 could be calculated which is of the same order of the value of 1.77 reported in the literature which value was again an extrapolated estimate [3].

The stable form of Sb_2O_3 is the cubic (c) form from room temperature up to 846 K beyond which it is reported to transform into the orthorhombic (valentinite) modification having a melting point 929 K [9]. However, the orthorhombic form once formed does not readily transform into cubic form [10] over the entire range of temperature. In addition, it is in the valentinite form that Sb_2O_3 has been used in the neutron start-up facility. Hence in the present work, the attempt was made to measure the oxygen potential as described above in the Sb_2O_3(ortho)/Sb_2O_4(ortho) mixture rather than in the mixture of the equilibrium phases Sb_2O_3(c)/Sb_2O_4(ortho) even in the temperature range of 585 to 828 K which is below the cubic-to-ortho transition temperature. The equilibrium being of metastable nature in this measurement, it becomes necessary to confirm the absence of temperature dependent errors in the e.m.f. results by a third-law treatment.

For the third-law treatment, the free energy function, ϕ, for the Sb_2O_3(ortho) is needed. This was constructed using the C_p°, S_{298}° and $\Delta H^\circ_{\mathrm{trans},846\,\mathrm{K}}$ data listed in Barin and Knache [9] by appropriate integration. Similar free energy functions were also derived for Sb_2O_4(ortho) and O_2(g) using the literature [11, 9]; data interpolated from these expressions are listed in Table I. Also given in Table II is the expression for the change in ϕ corresponding to reaction (2). The standard enthalpy change for reaction (2) at 298 K, $\Delta H^\circ_{(2),298}$ is computed as follows:

$$\Delta H^\circ_{(2),298} = \Delta G^\circ_{(2),T} - T\Delta\phi \qquad (5)$$

The $\Delta H^\circ_{(2),298}$ so calculated for every measured value of e.m.f. of cell II is plotted against temperature of measurement in Fig. 2. This third-law plot shows the absence of any systematic trend in the derived values of $\Delta H^\circ_{(2),298}$. A value of -181.34 (± 0.98) kJ mol^{-1} could be calculated as a mean value.

Azad and co-workers [2] had determined the ΔG_f° (Sb_2O_3, ortho) to be as follows over the range 662 to 890 K using the same experimental set-up:

$$[\Delta G_f^\circ\ (Sb_2O_3,\ \mathrm{ortho}) \pm 0.80]\ (\mathrm{kJ\,mol^{-1}})$$
$$= -686.36 + 0.24594\,T/\mathrm{K} \qquad (6)$$

Equations 3 and 6 were combined to yield the following expression for ΔG_f° (Sb_2O_4, ortho):

$$[\Delta G_f^\circ\ (Sb_2O_4,\ \mathrm{ortho}) \pm 1.61]\ (\mathrm{kJ\,mol^{-1}})$$
$$= -854.69 \pm 0.33614\,T/\mathrm{K} \qquad (7)$$

To evaluate $\Delta H^\circ_{f,298}$ (Sb_2O_4, ortho) a third-law treatment identical to that adopted for $\Delta H^\circ_{(2),298}$ was used. For this purpose, the ΔG_f° (Sb_2O_3, ortho) computed

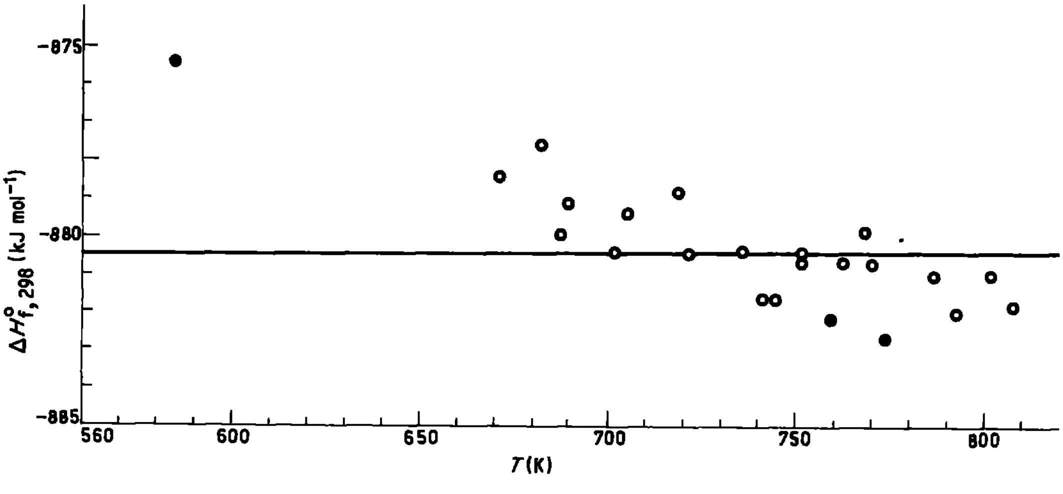

Figure 3 Third-law plot for the standard enthalpy of formation at 298.15 K of Sb_2O_4(ortho).

from Equation 6 at each temperature of this measurement was added to the directly measured value of $\Delta G^{o}_{(2),T}$ and was substituted in an expression similar to Equation 5 corresponding to the reaction

$$2Sb(s) + 2O_2(g) \rightleftharpoons Sb_2O_4(\text{ortho}) \qquad (8)$$

The expressions of $\Delta\phi_{(8)}$ used in this exercise are also listed in Table II. The third-law plot for $\Delta H^{o}_{f,298}$ (Sb_2O_4, ortho) in Fig. 3 yielded a mean value of -880.55 (± 1.21) kJ mol^{-1}.

4. Conclusion

It is difficult to apply solid electrolyte e.m.f. technique for the oxygen potential measurement to the electrodes made of only those oxides which are poor electronic conductors. In this work, intimate blending with platinum black was demonstrated to facilitate realization of equilibrium between the phases Sb_2O_3(ortho) and Sb_2O_4(ortho). By this method, it was possible to generate thermodynamic data for Sb_2O_4(ortho) which is likely to be a better substitute for the low-melting Sb_2O_3 in Sb_2O_3–stainless steel–beryllium facility for use as neutron start-up assembly.

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