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Letter to the Editors

Determination of thermodynamic stability of $CrSbO_4$ using oxide solid electrolyte

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Abstract

An isothermal section of the phase diagram of the system Cr–Sb–O at 873 K was established by isothermal equilibration and X-ray diffraction analysis of quenched samples. Making use of the coexistence of the only ternary oxide $CrSbO_4$(s) identified in the system with Cr_2O_3(s) and Sb_2O_3(s,l), the galvanic cell

$$\mathrm{Pt}, \mathrm{Cr_2O_3(s)}, \mathrm{Sb_2O_3(s,l)}, \mathrm{CrSbO_4(s)}\ |15\ \mathrm{CSZ}|\ \mathrm{air}\ (P_{O_2} = 0.21\ \mathrm{atm}),\ \mathrm{Pt}$$

(where 15 CSZ stands for 15 wt% CaO stabilized ZrO_2 electrolyte tube) was designed to measure its Gibbs energy of formation. The emf of the cell was measured over the temperature range 770–982 K. The results could be summarized by the expressions:

$$E \pm 0.5\ (\mathrm{mV}) = 874.25 - 0.45952\ T\ (\mathrm{K}) \quad (770\text{–}920\ \mathrm{K}),$$

$$E \pm 0.2\ (\mathrm{mV}) = 1003.58 - 0.59859\ T\ (\mathrm{K}) \quad (931\text{–}982\ \mathrm{K}).$$

The break in the plot of emf as a function of temperature at 930 K yielded a value of 50 kJ mol^{-1} for the enthalpy of fusion of Sb_2O_3 in agreement with the literature. From the emf results the standard Gibbs energy of formation, ΔG_f^0 ($CrSbO_4$), was calculated to be

$$\Delta G_f^0\ (\mathrm{CrSbO_4}) \pm 4.1\ (\mathrm{kJ\ mol^{-1}}) = -1074.84 + 0.34002\ T\ (\mathrm{K}) \quad (770\text{–}920\ \mathrm{K})$$

and

$$\Delta G_f^0\ (\mathrm{CrSbO_4}) \pm 4.0\ (\mathrm{kJ\ mol^{-1}}) = -1088.32 + 0.35365\ T\ (\mathrm{K}) \quad (931\text{–}982\ \mathrm{K}).$$

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1. Introduction

The antimony sesquioxide, Sb_2O_3 (valentinite), encapsulated in AISI type 316 stainless steel (SS) is often used in the Auxiliary Neutron Source (ANS) of liquid metal cooled fast breeder reactors (LMFBRs). Though it is well known that Sb_2O_3 is not thermodynamically compatible with SS because of its much lower stability compared with the oxides of the metals present in SS, still its use in ANS was resorted to for kinetic reasons. However, the extensive attack of the cladding by the oxides of antimony was established earlier by out of pile compatibility studies carried out by Swaminathan et al. [1]. Further, antimony is also a fission product, albeit a minor one [2] it has a deleterious effect on the SS cladding [1]. Therefore, thermodynamic characterisation of all the phases present in M–Sb–O systems (where M = Fe, Ni and Cr) is of relevance to nuclear technology. As a part

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of the on going project on the characterisation of the ternary oxides in the M–Sb–O systems, investigation of the system Cr–Sb–O was conducted.

No reliable phase diagram information on the system Cr–Sb–O is available in the literature. The existence of a ternary oxide, $CrSbO_4$, binary oxides Sb_2O_3, Sb_2O_4 and Cr_2O_3 and intermetallics CrSb and $CrSb_2$ [3] at temperatures above 800 K have been reported. The ternary oxide $CrSbO_4$ is reported to have a tetragonal rutile-type structure with space group $P4_2|mnm$, $Z = 1$ [4]. Its thermal expansion was studied by Mohan Rao et al. [5] by employing powder X-ray diffraction (XRD) technique. Studies on the isothermal section of the ternary phase diagram were carried out in the initial part of this investigation. Based on the ternary phase relations, a solid state cell was designed to measure the standard Gibbs energy of formation of $CrSbO_4$.

2. Experimental

2.1. Materials

Cr (Aldrich, USA), Sb, Sb_2O_3 and Cr_2O_3 (Johnson Matthey, UK) of purity better than 99.99% were used as the starting materials. Sb_2O_4 was prepared by oxidation of Sb_2O_3 in air at 823 K. $CrSbO_4$ was prepared from an equimolar mixture of Cr_2O_3 and Sb_2O_4 which was compacted into cylindrical pellets of 10 mm diameter and 5 mm thickness in a hydraulic press at a pressure of 100 MPa. These pellets were heated in air in two steps of 873 and 1173 K, for a total period of 72 h. This process was repeated at least twice to complete the reaction. Formation of the inter-oxide compound was verified by XRD within 5 mass% limit of detection of a second phase. A 15 wt% calcia-stabilized zirconia tube (Yamori, Japan) with one flat closed end having the dimensions 12.5 mm OD, 9.5 mm ID and 305 mm length and density better than 98% of theoretical value was used as solid electrolyte in a two compartment cell assembly. Its helium leak rate was tested by a quadrupole mass spectrometer based leak detector and was found to be within specified limits.

2.2. Procedure

2.2.1. Phase equilibrium studies

Mixtures of various phases as given in Table 1 were made by grinding the component phases in an agate mortar. The resulting powders were compacted into pellets as described earlier. Those mixtures which require vacuum heat treatment were encapsulated in evacuated silica ampoules after outgassing up to 473 K prior to vacuum sealing. Powder mixtures stable in air were heat treated in the ambient atmosphere. All the heat treatments were carried out at an isothermal temperature of 873 K for a total period of 600 h with at least one intermediate grinding and recompaction followed by air quenching. The phase identification in the equilibrated samples was accomplished using XRD.

2.2.2. Emf studies

The two compartment cell assembly for the emf measurements used in the study was described earlier [6–9]. The absence of asymmetric potential was ensured by nearly null emf (±0.5 mV) obtained over the range 700–1200 K when the cell was heated in the isothermal zone of the furnace with both sides air ($P_{O_2} = 0.21$ atm)/Pt as electrodes. The emf of the cell

$$\text{Pt, air } (P_{O_2} = 0.21 \text{ atm})\ |15\ \text{CSZ}|\ O_2\ (1\ \text{atm}),\ \text{Pt}$$

was also tested in the same temperature range and was found to deviate by less than 1 mV from the theoretical value. Helium gas of spectroscopy purity, dried by passing through columns of silica gel and outgassed molecular sieve (Linde 4A) was used as inert gas cover

Table 1
Phase equilibrium studies on the Cr–Sb–O system at 873 K

S. No.	Before equilibration		Condition of equilibration	After equilibration phases found
	Phases	Cr:Sb:O		
1	Cr_2O_3, Sb_2O_4	2:1:5	Air	Cr_2O_3, $CrSbO_4$
2	Cr_2O_3, Sb_2O_4	2:4:11	Air	$CrSbO_4$, Sb_2O_4
3	Cr_2O_3, Sb_2O_4	2:2:7	Air	$CrSbO_4$
4	Cr_2O_3, Sb_2O_4	2:6:15	Vacuum[a]	$CrSbO_4$, Sb_2O_3, Sb_2O_4
5	Cr_2O_3, Sb_2O_3	1:1:3	Vacuum[a]	Cr_2O_3, Sb_2O_3
6	Cr_2O_3, Sb_2O_4	2:2:7	Vacuum[a]	$CrSbO_4$, Cr_2O_3, Sb_2O_3
7	Cr, Sb_2O_3	1:2:3	Vacuum[a]	Cr_2O_3, Sb_2O_3, Sb
8	Cr, Sb_2O_3	2:2:3	Vacuum[a]	Cr_2O_3, Sb
9	Cr, Sb, Cr_2O_3	1:1:1	Vacuum[a]	Cr_2O_3, Sb, $CrSb_2$
10	Cr, Sb, Cr_2O_3	4:3:3	Vacuum[a]	Cr_2O_3, CrSb, $CrSb_2$
11	Cr, Sb, Cr_2O_3	4:1:3	Vacuum[a]	Cr_2O_3, Cr, CrSb

[a] Static vacuum in sealed silica ampoules.

for the test electrode. The temperature of the galvanic cell was measured by a type S thermocouple (calibrated against the freezing point standard of high purity metals such as Sn, Zn, Sb and Ag). The hot junction of the thermocouple was located near the inner closed end of the solid electrolyte tube. The test electrode pellets were made from an equal weight ratio mixture of $CrSbO_4$ with two binary oxides which were found to coexist with it, namely Cr_2O_3 and Sb_2O_3. The emf of the galvanic cell of the following configuration were measured over the range 770–982 K

$$\text{Pt, } Cr_2O_3(s),\ Sb_2O_3(\text{s or l}),\ CrSbO_4(s)\ |15\ \text{CSZ}|\ \text{air } (P_{O_2} = 0.21\ \text{atm}),\ \text{Pt.} \qquad \text{(I)}$$

The reproducibility of the emf values was tested by thermal cycling and micropolarisation. The equilibrium at the measuring electrode was tested by a 10% variation in the relative ratios of coexisting phases in separate experiments designated as B and C.

3. Results and discussions

3.1. Phase equilibrium studies

The composition of phase mixtures initially taken and phase analyses of the same after equilibration at 873 K in the appropriate environment are listed in Table 1. The initial compositions of the mixtures are shown in Fig. 1 by filled circles. The analyses of equilibrated samples facilitated the determination of tie-lines which are also shown in Fig. 1. The absence of any other ternary compound in the temperature range of present study as well as the coexistence of $CrSbO_4$ with the sesquioxides of Cr and Sb facilitated the choice of coexisting phases used in making the test electrode of the galvanic cell.

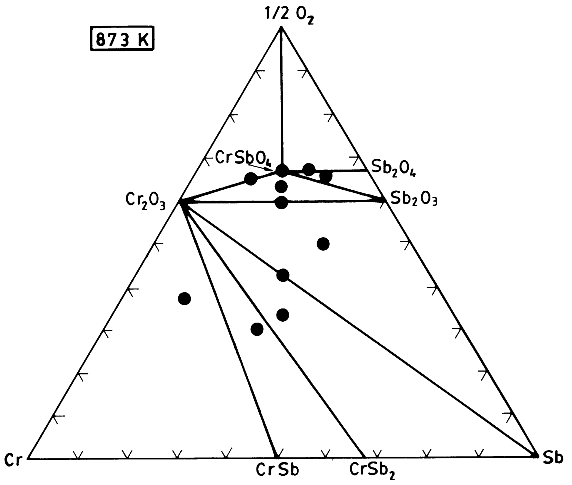

Fig. 1. Isothermal section of the phase diagram for the system Cr–Sb–O at 873 K.

3.2. Emf measurements

The results of the emf of cell (I) are listed in Tables 2 and 3 and are plotted in Fig. 2. Within experimental uncertainty the emf appears to vary linearly with temperature with a change of slope at 930 K. The least-square regression analyses give

$$E \pm 0.5\ (\text{mV}) = 874.25 - 0.45952\ T\ (\text{K}) \quad (770\text{–}920\ \text{K}), \qquad (1)$$

Table 2
Emf for the cell Pt, $Cr_2O_3(s)$, $Sb_2O_3(s)$, $CrSbO_4(s)$ | 15 CSZ | air ($P_{O_2} = 0.21$ atm), Pt

S. No.	T (K)	E (mV)	Run
1	799.5	506.9	A
2	819.7	497.7	A
3	836.1	490.1	A
4	854.2	482.3	A
5	872.1	473.7	A
6	887.6	466.9	A
7	903.0	459.1	A
8	916.1	453.4	A
9	820.0	498.1	B
10	836.8	490.2	B
11	854.2	481.9	B
12	870.7	474.6	B
13	887.5	466.5	B
14	769.7	520.1	B
15	785.1	513.8	B
16	800.2	507.0	B
17	819.7	497.1	B
18	837.8	488.6	B
19	854.6	481.1	B
20	871.1	473.5	B
21	887.2	466.3	B
22	902.4	459.4	B
23	920.1	451.3	B
24	786.0	513.1	C
25	802.7	505.5	C
26	821.2	497.1	C
27	836.6	490.0	C
28	854.1	481.8	C
29	870.1	474.6	C
30	778.6	516.9	C
31	794.4	509.2	C
32	810.3	501.1	C
33	829.2	492.5	C
34	846.1	485.2	C
35	863.2	477.3	C
36	879.2	469.8	C
37	895.0	463.4	C
38	909.8	456.3	C

Table 3
Emf result for the cell Pt, Cr_2O_3(s), Sb_2O_3(l), $CrSbO_4$(s) | 15 CSZ | air ($P_{O_2} = 0.21$ atm), Pt

S. No.	T (K)	E (mV)	Run
1	935.8	443.6	A
2	951.2	434.0	A
3	982.3	415.8	A
4	934.8	444.2	B
5	950.7	434.0	B
6	935.8	443.3	B
7	942.5	439.7	B
8	966.5	425.2	B
9	981.7	415.8	B
10	931.1	446.1	C
11	942.9	439.2	C
12	959.2	429.5	C
13	974.8	420.2	C
14	982.2	415.5	C

$$E \pm 0.2\ (\mathrm{mV}) = 1003.58 - 0.59859\ T\ (\mathrm{K}) \quad (931\text{–}982\ \mathrm{K}). \tag{2}$$

After correcting for the standard state of oxygen in the reference air electrode, the standard Gibbs energy change, ΔG^0_R, for the virtual cell reaction

$$Cr_2O_3(s) + Sb_2O_3(s\ \text{or}\ l) + O_2(g) \rightarrow 2CrSbO_4(s) \tag{3}$$

could be calculated by using the Nernst equation, $\Delta G^0_R = -4FE$ (corresponding to four faraday of electricity). The expressions so calculated from Eqs. (1) and (2) are

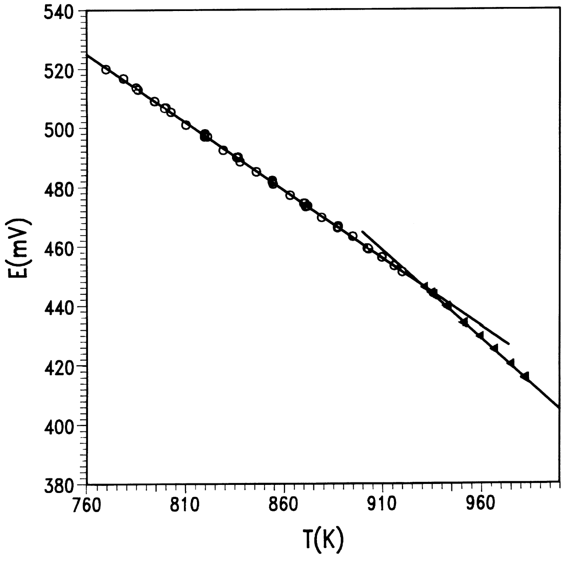

Fig. 2. Variation of the emf of the cell Pt, Cr_2O_3(s), Sb_2O_3 (s or l), $CrSbO_4$(s) | 15 CSZ | air ($P_{O_2} = 0.21$ atm), Pt with temperature.

$$\Delta G^0_R \pm 0.2\ (\mathrm{kJ\ mol^{-1}}) = -337.42 + 0.17735\ T\ (\mathrm{K}), \tag{4}$$

$$\Delta G^0_R \pm 0.08\ (\mathrm{kJ\ mol^{-1}}) = -387.33 + 0.23102\ T\ (\mathrm{K}), \tag{5}$$

valid over the ranges 770–920 and 931–982 K respectively. Since

$$\Delta G^0_R = 2\Delta G^0_f\,CrSbO_4 - \Delta G^0_f\,Cr_2O_3 - \Delta G^0_f\,Sb_2O_3 \tag{6}$$

the standard Gibbs energy of formation ΔG^0_f ($CrSbO_4$) from elements can be calculated by combining Eq. (4) or (5) with literature data on Cr_2O_3 [10] and Sb_2O_3 [11]:

$$\Delta G^0_f(CrSbO_4) \pm 4.1\ (\mathrm{kJ\ mol^{-1}}) = -1074.84 + 0.34002\ T\ (\mathrm{K}) \quad (770\text{–}920\ \mathrm{K}), \tag{7}$$

$$\Delta G^0_f(CrSbO_4) \pm 4.0\ (\mathrm{kJ\ mol^{-1}}) = -1088.32 + 0.35365\ T\ (\mathrm{K}) \quad (931\text{–}982\ \mathrm{K}). \tag{8}$$

The uncertainty limits in the values of ΔG^0_f ($CrSbO_4$) were assessed by combining the uncertainties in the ΔG^0_R (±0.2 or ±0.1 kJ) with those for Cr_2O_3 (±7 kJ mol^{-1}) and Sb_2O_3 (±0.8 or ±0.7 kJ mol^{-1}) obtained from literature [10,11]. Solving either pair of Eqs. (1) and (2) or (4) and (5) yielded a value of 930 K for the temperature of fusion of Sb_2O_3. Also, solving Eqs. (4) and (5) directly yielded a value of 50 kJ mol^{-1} for the apparent enthalpy of fusion of Sb_2O_3. These values are in reasonable agreement with 929 K and 54.8 kJ mol^{-1} respectively reported in the literature [12]. The agreement could be taken as absence of significant amount of terminal solubilities of coexisting phases in Sb_2O_3. However, this inference could not be taken as conclusive with reference to terminal solubilities owing to the rather limited temperature span of about 51 K above the melting point in the present measurement.

A 'third law' analysis could not be carried out owing to the absence of reliable heat capacity measurements on $CrSbO_4$. Hence by 'second law' method a value of −1075 kJ mol^{-1} could be taken for the standard enthalpy of formation, ΔH^0_f ($CrSbO_4$), at 845 K which is the mean temperature of emf measurement as per Eq. (7) If Newman–Kopp's law could be assumed to be valid in the absence of experimental C^0_p data on $CrSbO_4$ then this value would amount to be the standard enthalpy of formation $\Delta H^0_{f,298}$ ($CrSbO_4$) at the standard temperature of 298 K. Taking into account the uncertainties in the $\Delta H^0_{f,298}$ for the formation of Cr_2O_3(s) and Sb_2O_3(s) the overall scatter in $\Delta H^0_{f,298}$ ($CrSbO_4$) was estimated to be ±15 kJ mol^{-1}.

In the absence of 'third law' analysis of the Gibbs energy data it becomes necessary to assess the reliability of slope of the emf measurements apart from the enthalpy and temperature of fusion of Sb_2O_3. An examination of the entropy term in Eq. (4) shows that the value of 177 J K^{-1} mol^{-1} for the relative partial molar entropy for one mole of O_2 should be considered as quite reasonable. This is in view of the fact that no significant deviation from stoichiometry was reported in the literature for the sesquioxides of Cr and Sb as well as for the ternary oxide and that the ΔG^0_R expression corresponding to the solidus range of Sb_2O_3 alone was considered in this context. A further evaluation of the reliability of the slope of the emf measurement was carried out by computing the Gibbs energy change $\Delta G_{f,ox}$ for the formation of $CrSbO_4$ from a solid–solid reaction between the two constituent oxides Cr_2O_3 and Sb_2O_5(s)

$$\Delta G_{f,ox}\,(CrSbO_4)\ (kJ\ mol^{-1}) = -14.28 - 0.02843\ T\ (K). \tag{9}$$

The value of 28 J K^{-1} mol^{-1} for $\Delta S^0_{f,ox}$ ($CrSbO_4$) could be considered as reasonably small as is to be expected of a solid–solid reaction. This upholds the reliability of the slope of the emf as a function of temperature in the present study.

For a comparison of the equilibrium oxygen pressures in the coexisting mixtures of significance in Cr–Sb–O system, plots of log P_{O_2} against reciprocal temperature are given in Fig. 3. This is consistent with coexistence of $CrSbO_4 + Cr_2O_3$ with Sb_2O_3, but not with Sb_2O_4. Nevertheless the line for equilibrium oxygen pressures for the three phase field $Cr_2O_3 +$ $CrSbO_4 + Sb_2O_3$ though lower is still close to that of Sb_2O_3/Sb_2O_4. It may be noted that the log P_{O_2} corresponding to Sb_2O_5/Sb_2O_4 is represented up to 798 K which is the temperature of dissociation of Sb_2O_5 [13] in pure O_2 at 1 atm. This is consistent with Fig. 1 valid at 873 K at which temperature Sb_2O_5 is not stable and hence not marked.

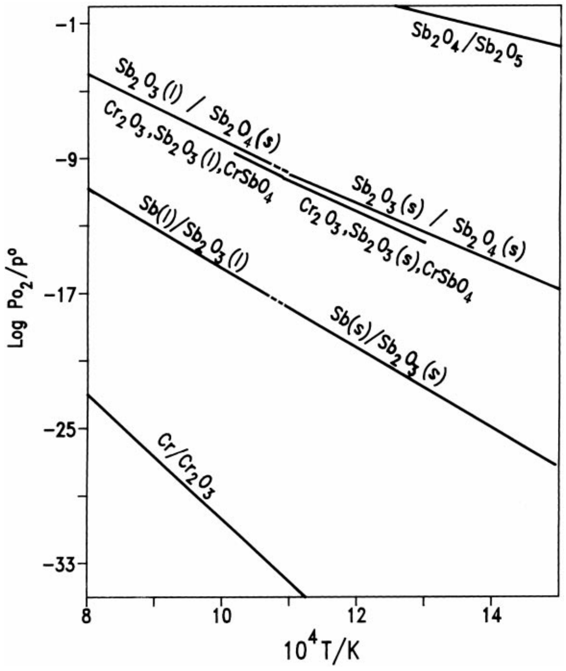

Fig. 3. Variation of the logarithm of oxygen partial pressure with reciprocal of absolute temperature for some condensed-phase mixtures in the system Cr–Sb–O.

4. Conclusion

An isothermal section of Cr–Sb–O system at 873 K was established from equilibration and phase identification study in quenched samples by XRD analysis. The standard Gibbs energy of formation of $CrSbO_4$, the only ternary oxide present in the system, was determined in the temperature range of 770–983 K using solid state electrochemical technique. The break in the emf–temperature plot showed good consistency with the data on the standard enthalpy of fusion of Sb_2O_3.

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