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# Determination of standard Gibbs energies of formation of ternary oxides in the system Co-Sb-O by solid electrolyte emf method

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An isothermal section of the phase diagram of the system Co-Sb-O at 873 K was established by isothermal equilibration and XRD analyses of quenched samples. The following galvanic cells were designed to measure the Gibbs energies of formation of the three ternary oxides namely $CoSb_2O_4$, $Co_7Sb_2O_{12}$ and $CoSb_2O_6$ present in the system.

| | | | |
|---|---|---|---|
| Chromel, Mo, Sb, CoO, $CoSb_2O_4$ | 15 CSZ | NiO, Ni, Mo, Chromel | I |
| Pt, CoO, $Co_7Sb_2O_{12}$, $CoSb_2O_4$ | 15 CSZ | air ($P_{o_2} = 0.21$ atm), Pt | II |
| Pt, $Co_7Sb_2O_{12}$, $CoSb_2O_6$, $CoSb_2O_4$ | 15 CSZ | air ($P_{o_2} = 0.21$ atm), Pt | III |

where 15 CSZ stands for $ZrO_2$ stabilized by 15 mol % CaO. The reversible emfs obtained could be represented by the following expressions.

$$E_{\mathrm{I}} \pm 0.5\,(\mathrm{mV}) = 120.7 - 0.04924\,T(\mathrm{K}) \quad (795\text{–}954\ \mathrm{K})$$

$$E_{\mathrm{II}} \pm 0.5\,(\mathrm{mV}) = 1106.3 - 0.3992\,T(\mathrm{K}) \quad (790\text{–}1040\ \mathrm{K})$$

$$E_{\mathrm{III}} \pm 0.4\,(\mathrm{mV}) = 967.9 - 0.4395\,T(\mathrm{K}) \quad (855\text{–}1035\ \mathrm{K})$$

The standard Gibbs energies of formation of $CoSb_2O_4$, $Co_7Sb_2O_{12}$ and $CoSb_2O_6$ were computed from the emf expressions:

$$\Delta G_f^\circ\,(CoSb_2O_4) \pm 4.3\,(\mathrm{kJ\ mol^{-1}}) = -1006.3 + 0.3549\,T(\mathrm{K})$$

$$\Delta G_f^\circ\,(Co_7Sb_2O_{12}) \pm 10.5\,(\mathrm{kJ\ mol^{-1}}) = -2834.5 + 0.9190\,T(\mathrm{K})$$

$$\Delta G_f^\circ\,(CoSb_2O_6) \pm 4.5\,(\mathrm{kJ\ mol^{-1}}) = -1379.9 + 0.5115\,T(\mathrm{K})$$

The reasonability of the above data were assessed by computing the entropy change for the solid-solid reactions leading to the formation of ternary oxides from the respective pairs of constituent binary oxides. 

## 1. Introduction

The thermodynamic stabilities of inter-oxide compounds in the systems M-Sb-O (where M = Fe, Cr or Ni) are of relevance in evaluating the Fission Product-Clad Chemical Interaction (FPCCI) in Fast Breeder Reactors (FBRs) since antimony is one of the deleterious fission products though minor in yield [1]. In addition, $Sb_2O_3$ (in the valentinite form) encapsulated in stainless steel was found to pose compatibility problem when used in the neutron source which is an in-core component in some FBRs [2]. Hence, a systematic investigation of the stabilities of ternary oxides in the systems Cr-Sb-O and Ni-Sb-O were carried out by Swaminathan and Sreedharan by employing the familiar solid oxide electrolyte emf technique [3, 4]. Though cobalt is neither a constituent of the structural alloy of FBRs nor a fission product still the stabilities of inter-oxide compounds in the system Co-Sb-O would be of considerable interest in understanding the systematic trend if any among the isomorphous analogs of triad elements Fe, Co and Ni. To facilitate an investigation of the stabilities of ternary compounds $CoSb_2O_4$, $Co_7Sb_2O_{12}$ and $CoSb_2O_6$ present in the system Co-Sb-O, no reliable phase diagram has so far been reported in the literature. However, three intermetallic phases CoSb, $CoSb_2$ and $CoSb_3$ and four binary oxides CoO, $Co_3O_4$, $Sb_2O_3$ and $Sb_2O_4$ are known to be stable in the temperature range of 800–1100 K [5]. On the basis of these information a systematic study of the phase diagram of the system Co-Sb-O as well as the thermodynamic stabilities of the ternary oxides in this system were undertaken.

The present study may also be of relevance to materials science and technology owing to the use of $CoSb_2O_6$ as an oxidation catalyst [6], metal oxide resistor material [7] as well as in ion exchange [8]. Besides $CoSb_2O_6$, $Co_7Sb_2O_{12}$ finds application in ZnO varistors [9]. Incidentally, $CoSb_2O_6$ crystallizes in a trirutile type structure with space group $P4_2/mnm$ [10] while $Co_7Sb_2O_{12}$ exists as a spinel (space group Fd 3m) [11] and $CoSb_2O_4$ exhibits $Pb_3O_4$ structure which is isomorphous with $NiSb_2O_4$ with space group $P4_2/mbc$ [12].

## 2. Experimental

### 2.1. Materials

Co (Robert Johnson), $Co_3O_4$ (Aldrich), Sb and $Sb_2O_3$ (Johnson Matthey) of purity better than 99.99% were used as starting materials. $Sb_2O_4$ was prepared by oxidation of $Sb_2O_3$ in air at 823 K with intermittent grinding of the product to ensure completion of oxidation. CoO was prepared by heating $Co_3O_4$ at 1273 K under a dynamic vacuum of 1 mPa. $CoSb_2O_6$ was synthesised by compacting an equimolar mixture of CoO and $Sb_2O_4$ 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 ambient air at 873 K and 1173 K for a total period of 96 h. This process was repeated at least twice to complete the reaction. Formation of ternary oxide was verified by powder X-ray Diffraction (XRD) technique within a 5 mass % limit of its detection of impurity phases. A 6 : 1 mixture of CoO and $CoSb_2O_6$ was likewise compacted after thorough mixing for the preparation of $Co_7Sb_2O_{12}$. The pellets were encapsulated in evacuated silica ampoules after outgassing at 473 K and was subsequently heat treated at 873 K for a prolonged period of 600 h. A similar heat treatment was given to pellets made from 1 : 1 mixture of CoO and $Sb_2O_3$ for the synthesis of $CoSb_2O_4$. A 15 mol % (15 CSZ) calcia-stabilised zirconia tube (Yamari, Japan) with one end closed and closed end flat of dimensions 12.5 mm OD, 9.5 mm ID and 305 mm long with density better than 98% of the theoretical value, was used as the solid electrolyte in two compartment cell assembly for the galvanic cell configurations employing air/Pt as reference electrode. The same material in the form of cylindrical discs of diameter 12.5 mm and 1.5 mm thickness (Yamari, Japan) was used as the solid electrolyte in the other cell with solid electrodes arranged in a stacked pellet configuration.

### 2.2. Procedure

#### 2.2.1. Phase equilibrium studies

Mixtures of various phases as given in Table I were made by grinding the component phases in an agate mortar. The resulting mixtures were compacted into pellets as described earlier. Those mixtures which require vacuum heat treatment were encapsulated in silica ampoules. The ampoules were outgassed at temperatures up to 473 K prior to sealing under vacuum. 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 was accomplished using XRD.

#### 2.2.2. Emf studies

The following galvanic cells,

| | | | |
|---|---|---|---|
| Chromel, Mo, Sb, CoO, $CoSb_2O_4$ | 15 CSZ | NiO, Ni, Mo, Chromel | I |
| Pt, CoO, $Co_7Sb_2O_{12}$, $CoSb_2O_4$ | 15 CSZ | air ($P_{o_2} = 0.21$ atm), Pt | II |
| Pt, $Co_7Sb_2O_{12}$, $CoSb_2O_6$, $CoSb_2O_4$ | 15 CSZ | air ($P_{o_2} = 0.21$ atm), Pt | III |

were studied over the temperature ranges 795–954 K, 790–1040 K and 855–1035 K respectively.

An open cell stacked pellet assembly described elsewhere [13] was used for measurements on cell I. In order to prevent the attack of electrical lead wires and contact foils by antimony, a molybdenum foil of 12 mm

TABLE I Results of phase equilibrium studies of the Co-Sb-O system at 873 K

| S. no. | Before equilibration: Phases | Before equilibration: Co : Sb : O | Condition of equilibration | After equilibration phases found |
|---|---|---|---|---|
| 1. | $Co_3O_4$, $Sb_2O_4$ | 3 : 3 : 10 | air | $Co_3O_4$, $CoSb_2O_6$ |
| 2. | $Co_3O_4$, $Sb_2O_4$ | 3 : 8 : 20 | air | $CoSb_2O_6$, $Sb_2O_4$ |
| 3. | $Co_3O_4$, $Sb_2O_4$ | 3 : 6 : 10 | air | $CoSb_2O_6$ |
| 4. | $Co_3O_4$, $Sb_2O_4$ | 6 : 3 : 14 | vacuum* | $Co_3O_4$, $CoSb_2O_6$, $Co_7Sb_2O_{12}$ |
| 5. | CoO, $Sb_2O_4$ | 9 : 4 : 17 | vacuum* | CoO, $Co_7Sb_2O_{12}$, $CoSb_2O_4$ |
| 6. | $Co_3O_4$, $Sb_2O_4$, $Sb_2O_3$ | 9 : 6 : 22 | vacuum* | $CoSb_2O_4$, $CoSb_2O_6$, $Co_7Sb_2O_{12}$ |
| 7. | CoO, $Sb_2O_3$ | 2 : 2 : 5 | vacuum* | CoO, $CoSb_2O_4$ |
| 8. | CoO, $Sb_2O_3$ | 1 : 4 : 7 | vacuum* | $CoSb_2O_4$, $Sb_2O_3$ |
| 9. | CoO, $Sb_2O_3$ | 1 : 2 : 4 | vacuum* | $CoSb_2O_4$ |
| 10. | $Co_3O_4$, $Sb_2O_4$ | 3 : 10 : 24 | vacuum* | $CoSb_2O_6$, $Sb_2O_3$ |
| 11. | CoO, $Sb_2O_3$, Sb | 1 : 3 : 4 | vacuum* | $CoSb_2O_4$, Sb |
| 12. | CoO, $Sb_2O_3$ | 3 : 2 : 6 | vacuum* | CoO, Sb |
| 13. | CoO, Co, Sb | 2 : 4 : 1 | vacuum* | CoO, $CoSb_3$, Sb |
| 14. | CoO, Co, Sb | 3 : 5 : 1 | vacuum* | CoO, $CoSb_2$, $CoSb_3$ |
| 15. | CoO, Co, Sb | 3 : 3 : 1 | vacuum* | CoO, CoSb, $CoSb_2$ |
| 16. | CoO, Co, Sb | 3 : 1 : 1 | vacuum* | CoO, CoSb, Co |

*static vacuum in sealed silica ampoules.

diameter and 0.1 mm thickness was employed as spacer between the identical chromel leads and the electrode pellets. For the galvanic cells II and III, a two compartment cell assembly with 15 CSZ tube separating the two electrode compartments was employed, the details of which are described elsewhere [14–17]. Helium gas of spectroscopic purity, dried by passage through columns of silica gel and outgassed molecular sieve (Linde 4A), was used as the common inert gas in cell I and for protecting the test electrode in cells II and III. The cells were located in the isothermal zone of a bifilar wound furnace with an earthed shield to ground the induced electrical noise. The absence of spurious contribution to cell emf was confirmed by nearly null emf values ($\pm 0.5$ mV) obtained with a symmetrical cell employing identical Ni/NiO pellet electrodes in cell I together with Mo spacers and chromel lead wires in the temperature range 700–1200 K. Similar null emf (within $\pm 1$ mV) was obtained over the same temperature range with a symmetric cell in the two compartment configuration when both platinum electrodes were exposed to ambient air. The temperature measurements were made by a type S thermocouple duly calibrated at the freezing points of Sn, Zn, Sb and Ag. The performance of cell I was checked using $Ni + NiO$ and $Cu + Cu_2O$ as electrodes. The emf was close to derived values computed from the standard Gibbs energies of formation of NiO and $Cu_2O$ assessed by Kellog [18]. In the case of two compartment cell assembly, the emf of the cell, Pt, air ($P_{O_2} = 0.21$ atm) $\|$ $O_2$ (1 atm), Pt was also tested over the above temperature range and was found to deviate by less than 1 mV from the derived value calculated using the Nernst equation.

The test electrode for cell I was made from a mixture of $CoO|CoSb_2O_4|Sb$ in the weight ratio 2 : 2 : 1 and the reference electrode, Ni|NiO was taken in the weight ratio 5 : 1. These mixtures were separately ground and compacted into discs of 10 mm diameter and 1–2 mm thickness as mentioned above. For cell II, a mixture of $CoO|Co_7Sb_2O_{12}|CoSb_2O_4$ and for cell III $Co_7Sb_2O_{12}|CoSb_2O_6|CoSb_2O_4$ in an equal weight ratio were ground and similarly compacted. These electrode compositions were nominal. A 10% variation in the weight ratio of all the three test electrodes was made in order to ascertain the existence of composition independent emf values. This procedure ensured that these three phases were truly in equilibrium with each other. The emfs obtained with different ratios of phases at the electrode are identified by separate designations such as A, B & C in Tables II–IV. Titanium sponge pieces in suitable location away from the cell leads were used as '*in situ*' oxygen getters in both the cell configurations. The reproducibility of the emf values were tested by thermal cycling and micropolarisation.

TABLE II Emf of cell I

| S. no. | $T$(K) | $E$(mV) |
|---|---|---|
| Cell A | | |
| 1 | 879.5 | 76.9 |
| 2 | 868.5 | 77.5 |
| 3 | 889.5 | 76.0 |
| 4 | 901.0 | 75.9 |
| 5 | 815.0 | 80.4 |
| 6 | 837.0 | 80.2 |
| 7 | 858.0 | 78.8 |
| 8 | 880.0 | 77.2 |
| 9 | 901.0 | 75.7 |
| 10 | 828.0 | 80.3 |
| 11 | 848.0 | 78.7 |
| 12 | 869.0 | 77.4 |
| 13 | 892.0 | 76.8 |
| 14 | 912.0 | 76.5 |
| 15 | 923.0 | 75.9 |
| 16 | 933.0 | 75.3 |
| Cell B | | |
| 17 | 816.0 | 80.1 |
| 18 | 846.0 | 79.4 |
| 19 | 879.5 | 77.7 |
| 20 | 912.5 | 76.4 |
| 21 | 932.0 | 75.7 |
| 22 | 954.0 | 74.6 |
| Cell C | | |
| 23 | 866.0 | 77.7 |
| 24 | 877.0 | 77.5 |
| 25 | 856.5 | 78.5 |
| 26 | 835.5 | 79.9 |
| 27 | 856.5 | 79.1 |
| 28 | 878.0 | 77.9 |
| 29 | 866.5 | 78.1 |
| 30 | 845.0 | 79.5 |
| 31 | 824.0 | 80.4 |
| 32 | 835.5 | 80.0 |
| 33 | 857.0 | 78.4 |
| 34 | 878.5 | 77.5 |
| 35 | 898.5 | 75.6 |
| 36 | 889.5 | 76.2 |
| 37 | 846.0 | 78.8 |
| 38 | 856.5 | 78.5 |
| 39 | 869.0 | 77.8 |
| 40 | 878.5 | 77.1 |
| 41 | 890.0 | 76.4 |
| 42 | 900.5 | 75.9 |
| Cell D | | |
| 43 | 795.0 | 81.8 |
| 44 | 815.0 | 81.2 |
| 45 | 836.0 | 79.7 |
| 46 | 858.0 | 79.2 |
| 47 | 879.5 | 77.4 |
| 48 | 901.0 | 76.1 |
| 49 | 825.5 | 80.0 |
| 50 | 847.5 | 78.5 |
| 51 | 868.0 | 77.2 |
| 52 | 888.5 | 76.1 |
| 53 | 909.5 | 75.6 |
| 54 | 930.0 | 75.1 |

## 3. Results and discussion

### 3.1. Phase equilibrium studies

The results of phase equilibrium studies are summarised in Table I. The column one of this table lists the compounds/elements taken, together with the composition expressed in atom ratios. Phase analyses after the heat treatment in either air or vacuum are also given in Table I. The average composition of the samples are shown by filled circles in Fig. 1. By combining information on the average composition with the phase analyses of equilibrated samples tie-lines were constructed. The equilibrium diagram thus established shows three 3-phase regions which are useful to the present study.

These three phase fields, namely $CoO/CoSb_2O_4/Sb$, $CoO/C0_7Sb_2O_{12}/CoSb_2O_4$ and $Co_7Sb_2O_{12}/CoSb_2O_6/CoSb_2O_4$ establish an unique oxygen potential at constant temperature. The oxygen potential can be measured by solid state cells based on stabilized-zirconia

TABLE III Emf of cell II

| S. no. | $T$(K) | $E$(mV) |
|---|---|---|
| Cell A | | |
| 1 | 807.0 | 784.0 |
| 2 | 823.5 | 777.6 |
| 3 | 790.0 | 791.0 |
| 4 | 823.0 | 778.4 |
| 5 | 840.0 | 770.0 |
| 6 | 857.0 | 764.0 |
| 7 | 873.5 | 757.8 |
| 8 | 873.0 | 758.1 |
| 9 | 888.0 | 751.8 |
| 10 | 904.0 | 744.8 |
| 11 | 921.0 | 739.0 |
| 12 | 913.0 | 741.4 |
| 13 | 929.0 | 736.0 |
| 14 | 936.5 | 733.1 |
| 15 | 944.0 | 730.0 |
| 16 | 952.0 | 727.0 |
| 17 | 960.0 | 723.3 |
| 18 | 967.5 | 719.7 |
| 19 | 976.5 | 716.0 |
| 20 | 983.5 | 713.1 |
| 21 | 991.5 | 710.1 |
| 22 | 1010.0 | 703.1 |
| 23 | 1016.0 | 700.2 |
| 24 | 1024.0 | 697.1 |
| 25 | 1031.0 | 694.8 |
| 26 | 921.0 | 738.0 |
| 27 | 880.0 | 754.1 |
| 28 | 928.0 | 735.5 |
| 29 | 975.5 | 716.5 |
| 30 | 1024.0 | 697.3 |
| Cell B | | |
| 31 | 896.0 | 748.9 |
| 32 | 911.0 | 742.6 |
| 33 | 928.0 | 736.0 |
| 34 | 943.0 | 730.0 |
| 35 | 958.5 | 724.2 |
| 36 | 975.5 | 717.0 |
| 37 | 990.0 | 711.4 |
| 38 | 981.5 | 715.0 |
| 39 | 965.5 | 721.6 |
| 40 | 951.0 | 726.8 |
| 41 | 936.0 | 732.2 |
| 42 | 919.0 | 739.0 |
| 43 | 903.0 | 746.3 |
| 44 | 887.5 | 752.5 |
| 45 | 872.0 | 758.0 |
| 46 | 919.0 | 739.0 |
| 47 | 847.5 | 767.8 |
| 48 | 896.5 | 748.9 |
| 49 | 943.5 | 729.6 |
| 50 | 990.0 | 711.3 |
| 51 | 1039.5 | 691.4 |

TABLE IV Emf of cell III

| S. no. | $T$(K) | $E$(mV) |
|---|---|---|
| Cell A | | |
| 1 | 904.0 | 570.8 |
| 2 | 920.0 | 563.6 |
| 3 | 935.0 | 557.3 |
| 4 | 951.0 | 550.5 |
| 5 | 966.0 | 543.2 |
| 6 | 951.0 | 549.5 |
| 7 | 920.0 | 563.2 |
| 8 | 905.0 | 570.5 |
| 9 | 967.0 | 542.3 |
| 10 | 983.0 | 536.3 |
| 11 | 904.5 | 570.5 |
| 12 | 921.5 | 562.8 |
| 13 | 937.5 | 556.0 |
| 14 | 953.0 | 548.6 |
| Cell B | | |
| 15 | 938.0 | 555.7 |
| 16 | 953.0 | 548.9 |
| 17 | 970.0 | 542.4 |
| 18 | 985.0 | 534.7 |
| 19 | 1001.5 | 528.1 |
| 20 | 970.0 | 541.5 |
| 21 | 929.0 | 559.6 |
| 22 | 944.0 | 553.1 |
| 23 | 960.0 | 545.6 |
| 24 | 976.5 | 538.9 |
| 25 | 991.5 | 532.1 |
| 26 | 1005.0 | 526.2 |
| 27 | 1020.0 | 519.4 |
| 28 | 1035.0 | 512.9 |
| Cell C | | |
| 29 | 855.0 | 591.5 |
| 30 | 871.0 | 584.9 |
| 31 | 887.5 | 577.0 |
| 32 | 888.5 | 576.9 |
| 33 | 904.0 | 571.5 |
| 34 | 919.5 | 564.7 |
| 35 | 936.0 | 557.5 |
| 36 | 896.5 | 574.5 |
| 37 | 913.0 | 567.6 |
| 38 | 929.0 | 559.2 |
| 39 | 863.5 | 587.9 |
| 40 | 888.0 | 577.1 |
| 41 | 920.0 | 564.3 |
| 42 | 952.0 | 549.1 |
| 43 | 983.5 | 535.4 |
| 44 | 1010.5 | 523.3 |

as the electrolyte. Incidentally the intermetallics CoSb and $CoSb_2$ are reported to exhibit compositional range of 48–51% and 64–67% of Sb respectively [5]. These intermetallics were found to coexist with CoO. In the absence of quantitative estimates of oxygen solubility limits in these intermetallics, these phases are represented only as points in the Co-Sb axis and tie-lines joining CoO are therefore shown as simple lines instead of as areas.

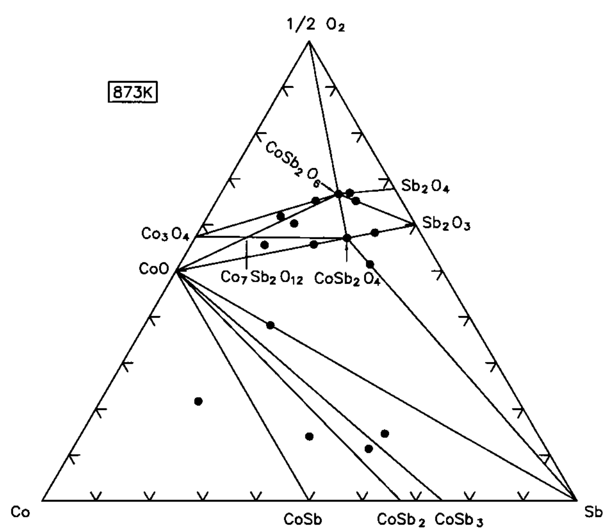


*Figure 1* Isothermal section of the phase diagram for the system Co-Sb-O at 873 K.

## 3.2. Emf measurements

The emf results on cells I, II and III are listed in Tables II–IV and are plotted in Figs. 2–4 respectively

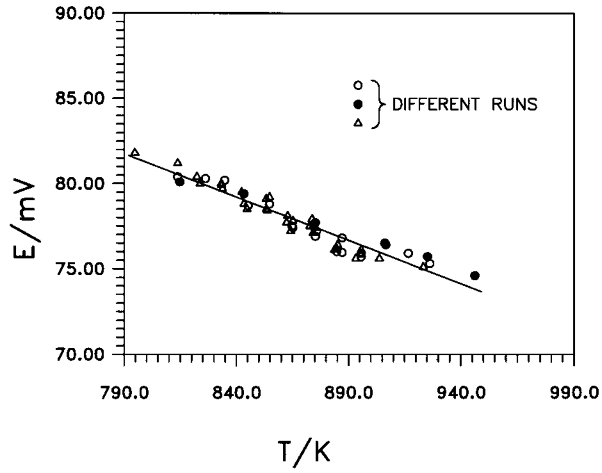


*Figure 2* Variation of the reversible emf of cell I with temperature.

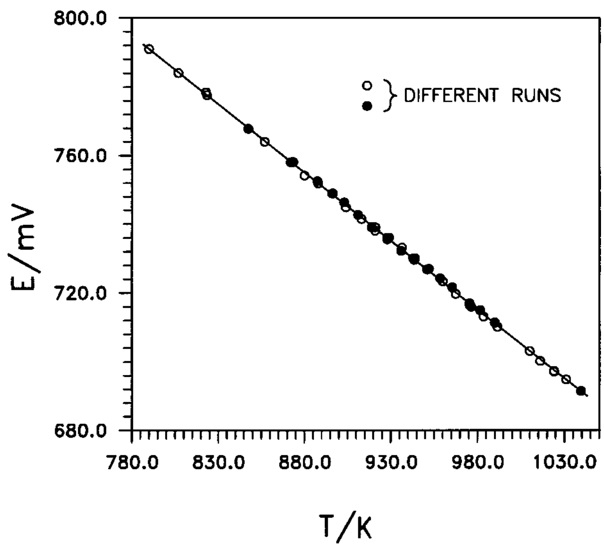


*Figure 3* Temperature dependence of the reversible emf of cell II.

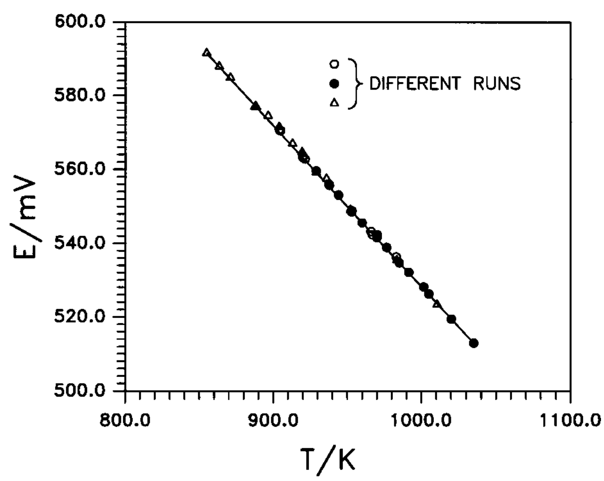


*Figure 4* Temperature dependence of the reversible emf of cell III.

as a function of temperature. The emf appears to vary linearly with temperature. The least-square regression analyses give the following expressions valid over the respective temperature ranges listed in parenthesis.

$$E_{\mathrm{I}} \pm 0.5\,(\mathrm{mV}) = 120.7 - 0.0492\,T(\mathrm{K}) \quad (795\text{–}954\ \mathrm{K}) \tag{1}$$

$$E_{\mathrm{II}} \pm 0.5\,(\mathrm{mV}) = 1106.3 - 0.3992\,T(\mathrm{K}) \quad (790\text{–}1040\,\mathrm{K}) \tag{2}$$

$$E_{\mathrm{III}} \pm 0.4\,(\mathrm{mV}) = 967.9 - 0.4395\,T(\mathrm{K}) \quad (855\text{–}1035\,\mathrm{K}) \tag{3}$$

The overall virtual reaction corresponding to 6F of electricity for the galvanic cell I is

$$\mathrm{CoO} + 3\mathrm{NiO} + 2\mathrm{Sb} \rightarrow \mathrm{CoSb_2O_4} + 3\mathrm{Ni} \tag{4}$$

The standard Gibbs energy change corresponding to reaction (4) is calculated from the emf using the Nernst equation, ($\Delta G^{\mathrm{o}}_{\mathrm{R}} = -6\mathrm{FE}$)

$$\Delta G^{\mathrm{o}}_{\mathrm{R(4)}} \pm 0.3\,(\mathrm{kJ\,mol^{-1}}) = -69.9 + 0.0285\,T(\mathrm{K}) \tag{5}$$

By combining Equation 5 with the literature data for $\Delta G^{\mathrm{o}}_{\mathrm{f}}$ of NiO and CoO [18,15], the standard Gibbs energy of formation, $\Delta G^{\mathrm{o}}_{\mathrm{f}}$ ($CoSb_2O_4$) could be calculated and is given below

$$\begin{aligned}\Delta G^{\mathrm{o}}_{\mathrm{f}}\,(\mathrm{CoSb_2O_4}) &\pm 4.3\,(\mathrm{kJ\,mol^{-1}})\\ &= -1006.3 + 0.3549\,T(\mathrm{K})\end{aligned} \tag{6}$$

The uncertainty limit in $\Delta G^{\mathrm{o}}_{\mathrm{f}}$ ($CoSb_2O_4$) is obtained by combining the uncertainty limit of ±3 kJ estimated for 3 moles of NiO from its $\Delta G^{\mathrm{o}}_{\mathrm{f}}$ (NiO) value assessed by Kellog [18] and uncertainty limit of ±1 kJ for CoO [19] with the uncertainty limit in Equation 5. The temperature dependent term in the above expression (6) which is related to the entropy of formation of the compound appears to be quite reasonable as it is comparable with twice the value of the relative partial molar entropy of oxygen.

The overall virtual reaction corresponding to 4F of electricity for the galvanic cell II is,

$$6\mathrm{CoO} + \mathrm{CoSb_2O_4} + \mathrm{O_2} \rightarrow \mathrm{Co_7Sb_2O_{12}} \tag{7}$$

The standard Gibbs energy change corresponding to reaction (7) was calculated from the emf expression (2) after correcting for standard state of oxygen in the reference air/Pt electrode of cell II using Nernst equation

$$\Delta G^{\mathrm{o}}_{\mathrm{R(7)}} \pm 0.2\,(\mathrm{kJ\,mol^{-1}}) = -427.0 + 0.1411\,T(\mathrm{K}) \tag{8}$$

By combining Equation 8 with the literature data on CoO [15] and $\Delta G^{\mathrm{o}}_{\mathrm{f}}$ ($CoSb_2O_4$) derived above, the $\Delta G^{\mathrm{o}}_{\mathrm{f}}$ ($Co_7Sb_2O_{12}$) could be calculated and is given below:

$$\begin{aligned}\Delta G^{\mathrm{o}}_{f}\,(\mathrm{Co_7Sb_2O_{12}}) &\pm 10.5\,(\mathrm{kJ\,mol^{-1}})\\ &= -2834.5 + 0.9190\,T(\mathrm{K})\end{aligned} \tag{9}$$

The uncertainty limit in $\Delta G^{\mathrm{o}}_{\mathrm{f}}$ ($Co_7Sb_2O_{12}$) is obtained by combining the uncertainty limit in Equations 6 and 8 with an uncertainty limit of 6 kJ estimated for 6 moles of CoO [19]. The temperature dependent term in the above expression (9) which is related to the entropy of formation of the compound appears to be quite reasonable as it compares well with six times the value of the relative partial molar entropy of oxygen.

The overall virtual reaction for the galvanic cell III corresponding to 4F of electricity could be given as

$$CoSb_2O_4 + O_2 \rightarrow CoSb_2O_6 \quad (10)$$

The third phase $Co_7Sb_2O_{12}$ being an inert component was included mainly to unequivocally fix the oxygen potential by phase rule consideration. The $\Delta G^o_R$ for the Equation 10 was calculated by combining expression (3) with Nernst equation after correcting for standard state of oxygen in the reference air/Pt electrode of cell III and is given by

$$\Delta G^o_{R(10)} \pm 0.2\,(\text{kJ mol}^{-1}) = -373.6 + 0.1566\,T(\text{K}) \quad (11)$$

By combining the Equations 6 and 11, an expression for $\Delta G^o_f$ $(CoSb_2O_6)$ was obtained and is given as

$$\Delta G^o_f\,(CoSb_2O_6) \pm 4.5\,(\text{kJ mol}^{-1}) = -1379.9 + 0.5115\,T(\text{K}) \quad (12)$$

The uncertainty limit in $\Delta G^o_f$ is obtained by combining those for Equations 6 and 11.

The expressions (6), (9) and (12) for the $\Delta G^o_f$ of the inter-oxide compounds included the uncertainties in the $\Delta G^o_f$ of the constituent binary oxides. However, the standard Gibbs energies of formation, $\Delta G^o_{f,ox}$ of the ternary oxides from the constituent binary oxides would be of greater relevance from the solid state chemistry point of view. The $\Delta G^o_{f,ox}$ $(CoSb_2O_4)$ corresponding to the reaction

$$CoO(s) + Sb_2O_3(s) \rightarrow CoSb_2O_4(s) \quad (13)$$

was calculated by combining $\Delta G^o_R$ for the cell I with $\Delta G^o_f$ of NiO [18] and $Sb_2O_3$ [20].

$$\Delta G^o_{f,ox}\,(CoSb_2O_4) = \Delta G^o_{R(4)} - \Delta G^o_f\,(Sb_2O_3, s) + 3\Delta G^o_f\,(NiO) \quad (14)$$

For computing $\Delta G^o_{f,ox}$ of $Co_7Sb_2O_{12}$ the reaction considered was

$$7CoO + Sb_2O_5 \rightarrow Co_7Sb_2O_{12} \quad (15)$$

The Gibbs energy change, $\Delta G^o_{f,ox}$ $(Co_7Sb_2O_{12})$ corresponding to the above reaction was computed from the following expressions by an appropriate combination of $\Delta G^o_{R(7)}$ with $\Delta G^o_f$ of necessary binary oxides.

$$\Delta G^o_{f,ox}\,(Co_7Sb_2O_{12}) = \Delta G^o_{R(7)} - \Delta G^o_f\,(Sb_2O_5) - \Delta G^o_f\,(CoO) + \Delta G^o_f\,(CoSb_2O_4) \quad (16)$$

Likewise, $\Delta G^o_{f,ox}$ $(CoSb_2O_6)$ was calculated from $\Delta G^o_{R(10)}$ by employing the expression

$$\Delta G^o_{f,ox}\,(CoSb_2O_6) = \Delta G^o_{R(10)} - \Delta G^o_f\,(CoO) - \Delta G^o_f\,(Sb_2O_5) + \Delta G^o_f\,(CoSb_2O_4) \quad (17)$$

for the following reaction

$$CoO + Sb_2O_5 \rightarrow CoSb_2O_6 \quad (18)$$

TABLE V $\Delta G^o_{f,ox}$ of inter-oxide compounds in the system Co-Sb-O

| Compound | $\Delta G^o_{f,ox}$ (kJ mol$^{-1}$) $= A + B\,T$(K) | Standard deviation kJ mol$^{-1}$ |
|---|---|---|
| $CoSb_2O_4$ | $-86.4 + 0.0385\,T$ | ±4.1 |
| $Co_7Sb_2O_{12}$ | $-205.5 - 0.0547\,T$ | ±5.8 |
| $CoSb_2O_6$ | $-152.1 - 0.0391\,T$ | ±5.8 |

For computing the numerical expressions for the above Equations one requires $\Delta G^o_f$ of $Sb_2O_5$ which is unstable in the temperature range of our consideration and is reported to dissociate into $Sb_2O_4$ and $O_2$ at 798 K in air. However, for the computation of $\Delta G^o_{f,ox}$ of inter-oxide compounds the following expression

$$\Delta G^o_f\,(Sb_2O_5) \pm 9.0\,(\text{kJ mol}^{-1}) = -994.2 + 0.4802\,T(\text{K}) \quad (19)$$

which is computed from the Gibbs energy data for $Sb_2O_5$ tabulated up to 798 K in the literature [21] is made use of. In making use of this expression its validity over a range extrapolated up to the temperature of the present measurement was assumed. These results are listed in Table V. The entropy change for the solid-solid reactions (13), (15) and (18) are not objectionably large as seen from the expressions listed in Table V and hence can be considered as reasonable.

No reliable calorimetric data are available to facilitate calculation of the standard enthalpies of formation, $\Delta H^o_{f,298}$ for these ternary oxides. Hence, values of $-1006 \pm 15$, $-2835 \pm 20$ and $-1380 \pm 15$ kJ mol$^{-1}$ could be taken as reasonable estimates of standard enthalpies of formation, $\Delta H^o_{f,298}$ of the inter-oxide compounds $CoSb_2O_4$, $Co_7Sb_2O_{12}$ and $CoSb_2O_6$ respectively by second law.

The consistency of the Gibbs energy data on the inter-oxides determined from emf measurements with the phase diagram studies reported here was assessed as follows. For instance, in the region defined by the phases $CoSb_2O_6$, $Sb_2O_4$, $Sb_2O_3$ and $CoSb_2O_4$ at the four vertices of a quadrilateral in Fig. 1, two diagonal tie-lines are possible namely the one linking $CoSb_2O_6$ with $Sb_2O_3$ and $CoSb_2O_4$ with $Sb_2O_4$. By making use of the $\Delta G^o_f$ of the ternary phases from the expressions (6) and (12) and those for binary oxides from literature [20, 22], the $\Delta G^o_R$ for the balanced reaction

$$CoSb_2O_4 + 2Sb_2O_4 \rightarrow CoSb_2O_6 + 2Sb_2O_3 \quad (20)$$

was computed and at 873 K it was found to yield a value of −57.7 kJ. This upholds the fact that the pair of phases on the right hand side would form the tie-line. This inference is consistent with the experimental phase equilibrium studies (as shown in Fig. 1). A similar check was conducted for the region defined by the phases $Co_7Sb_2O_{12}$, $CoSb_2O_6$, $Sb_2O_3$ and $CoSb_2O_4$ in Fig. 1, by making use of the balanced reaction

$$Co_7Sb_2O_{12} + 6Sb_2O_3 \rightarrow CoSb_2O_6 + 6CoSb_2O_4 \quad (21)$$

This yielded a value of −250 kJ at 873 K for the Equation 21, confirming the tie-line between $CoSb_2O_6$

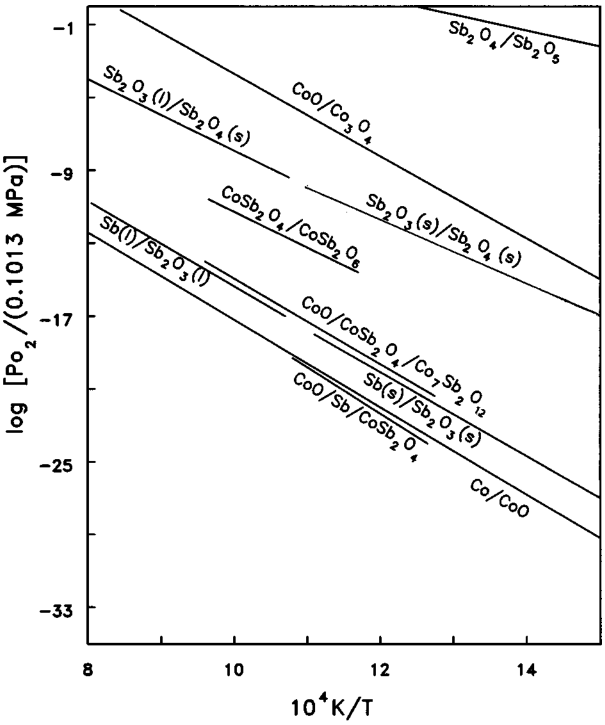


*Figure 5* Variation of the logarithm of oxygen partial pressure with reciprocal of absolute temperature for condensed phase mixtures in the system Co-Sb-O.

and $CoSb_2O_4$ in agreement with experimental phase analysis.

After establishing the reliability of Gibbs energy data it would be worthwhile to compare the relative stabilities of the different oxygen buffer mixtures of phases with a log $P_{o_2}$ - reciprocal absolute temperature diagram as shown in Fig. 5. This diagram shows not only the buffer mixtures employed in the emf studies on the three cells I, II and III but also the plots corresponding to the constituent binary oxides. There is no intersection of lines, signalling that the phase equilibria are invariant with temperature within the temperature range of measurements.

## 4. Conclusion

An isothermal section of the phase diagram for the system Co-Sb-O at 873 K was established in the study reported here. The standard Gibbs energies of formation of the three inter-oxide compounds are also reported here for the first time. The data were essentially derived from oxygen potential measurements from solid oxide electrolyte galvanic cells I, II and III whose equilibrium oxygen pressures could be represented by the following expressions.

$$\log\left[P_{o_2}/(0.1013\,\mathrm{MPa})\right]_{\mathrm{I}} = 9.90 - 26908/T(\mathrm{K}) \quad (22)$$

$$\log\left[P_{o_2}/(0.1013\,\mathrm{MPa})\right]_{\mathrm{II}} = 7.37 - 22301/T(\mathrm{K}) \quad (23)$$

$$\log[P_{o_2}/(0.1013\,\mathrm{MPa})]_{\mathrm{III}} = 8.18 - 19511/T(\mathrm{K}) \quad (24)$$


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