# Measurements of Standard Molar Gibbs Energies of Formation of $Sb_2O_3$, $ZnSb_2O_4$ and $MgSb_2O_4$ by EMF Method with Zirconia Solid Electrolyte*

By Iwao Katayama**, Shoji Sugimura** and Zensaku Kozuka**

Emf measurements of the following galvanic cells were carried out to determine the standard molar Gibbs energies of formation of $Sb_2O_3$, $ZnSb_2O_4$ and $MgSb_2O_4$:

$(-)$  Pt, Re|Sb, $Sb_2O_3$|$ZrO_2 + Y_2O_3$|air, Pt  $(+)$,

$(-)$  Pt, Re|Sb, ZnO, $ZnSb_2O_4$|$ZrO_2 + Y_2O_3$|air, Pt  $(+)$  and

$(-)$  Pt, Re|Sb, MgO, $MgSb_2O_4$|$ZrO_2 + Y_2O_3$|air, Pt  $(+)$.

The results were represented as follows:

1. $\Delta G^0/kJ \pm 0.47 = -686.2 + 0.2422\, T/K$  $(T/K < 904)$,
   $\Delta G^0/kJ \pm 0.70 = -643.1 + 0.1951\, T/K$  $(904 < T/K < 929)$  and
   $\Delta G^0/kJ \pm 0.53 = -687.8 + 0.2433\, T/K$  $(929 < T/K)$
   for  $2Sb(s, l) + 3/2 O_2(g) = Sb_2O_3(s, l)$.

2. $\Delta G^0/kJ \pm 0.70 = -170.4 + 0.2574\, T/K$  $(T/K < 904)$
   for  $2Sb(s) + 3/2 O_2(g) + ZnO(s) = ZnSb_2O_4(s)$.
   $\Delta G^0/kJ \pm 0.35 = -739.5 + 0.2869\, T/K$  $(T/K > 904)$
   for  $2Sb(l) + 3/2 O_2(g) + ZnO(s) = ZnSb_2O_4(s)$.
   $\Delta G^0/kJ \pm 1.2 = 27.0 - 0.0153\, T/K$  $(T/K < 904)$,
   $\Delta G^0/kJ \pm 1.1 = 96.4 - 0.0918\, T/K$  $(904 < T/K < 929)$  and
   $\Delta G^0/kJ \pm 0.9 = 51.8 - 0.0435\, T/K$  $(929 < T/K)$,
   for  $Sb_2O_3(s, l) + ZnO(s) = ZnSb_2O_4(s)$.

3. $\Delta G^0/kJ \pm 0.53 = -745.6 + 0.2720\, T/K$  $(945 < T/K < 1117)$
   for  $2Sb(l) + 3/2 O_2(g) + MgO(s) = MgSb_2O_4(s)$.
   $\Delta G^0/kJ + 1.1 = -58.0 + 0.0287\, T/K$  $(945 < T/K < 1117)$
   for  $Sb_2O_3(l) + MgO(s) = MgSb_2O_4(s)$.

## I.  Introduction

Thermodynamic properties of oxides are very important from both the academic and industrial viewpoints, and established values are required. In the course of our program of mea-surements of the standard molar Gibbs energy of formation of oxides and double oxides, a devised measuring method was applied to the oxides, whose thermodynamic values had not been established.

In the present work, the standard molar Gibbs energies of formation of $Sb_2O_3$ was re-examined, and those of $ZnSb_2O_4$ and $MgSb_2O_4$ were obtained by emf measurements of gal-vanic cells with stabilized zirconia electrolyte.

For the standard molar Gibbs energy of for-mation of $Sb_2O_3$ some investigators[1]-[8] have

measured by the emf method. At higher temperatures the values have tended to agree well except one[5], but at lower temperatures some difference can be found. For the standard molar Gibbs energies of formation of $ZnSb_2O_4$ and $MgSb_2O_4$ no values have been reported hitherto.
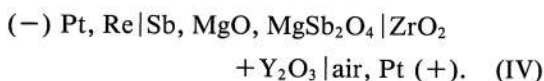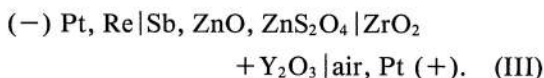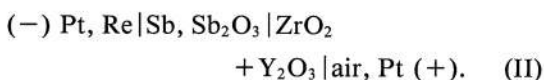
## II.  Experimental

Principle: A solid oxide electrochemical cell I is constructed on the assumption that the transference number of oxygen ion in a solid electrolyte is very nearly equal to unity.

$$(-) \, P_{O_2}(\text{I}) \,|\, ZrO_2 + Y_2O_3 \,|\, P_{O_2}(\text{II}) \, (+), \quad \text{(I)}$$
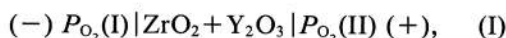
where $P_{O_2}$ is oxygen pressure. Based on the emf of cell I, oxygen pressure of the electrode is obtained according to eq. (1) with known oxygen pressure of the reference electrode:

$$E = (RT/4F) \ln \left[ (P_{O_2}(\text{II})/P^0)/(P_{O_2}(\text{I})/P^0) \right],$$
$$\text{(1)}$$

where $E$ is the emf of cell I, $R$ the gas constant (8.3144 J/mol K), $T$ the thermodynamic temperature (K), $F$ the Faraday constant (96485 C/mol) and $P^0$ a standard pressure (101.325 kPa). In this study the air, Pt electrode was used as a reference and emfs of the following cells were measured:

$$(-) \, Pt, \, Re \,|\, Sb, \, Sb_2O_3 \,|\, ZrO_2$$
$$+ Y_2O_3 \,|\, \text{air, Pt } (+). \quad \text{(II)}$$

$$(-) \, Pt, \, Re \,|\, Sb, \, ZnO, \, ZnS_2O_4 \,|\, ZrO_2$$
$$+ Y_2O_3 \,|\, \text{air, Pt } (+). \quad \text{(III)}$$

$$(-) \, Pt, \, Re \,|\, Sb, \, MgO, \, MgSb_2O_4 \,|\, ZrO_2$$
$$+ Y_2O_3 \,|\, \text{air, Pt } (+). \quad \text{(IV)}$$

The relation between the emf of cell (II) and the standard molar Gibbs energy of formation represented by the reaction (a) can be obtained from the eqs. (2) and (3) on the assumption of unit activities for metal(Sb) and the corresponding sesquioxide ($Sb_2O_3$).

$$2Sb(s, l) + 3/2 O_2(g) = Sb_2O_3(s, l). \quad \text{(a)}$$
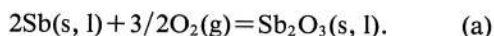
$$E_{\text{II}} = (RT/4F) \ln \left[ (P_{O_2}(\text{in air})/P^0) \right.$$
$$\left. / (P_{O_2}(Sb, Sb_2O_3)/P^0) \right]. \quad \text{(2)}$$

$$\Delta G^0 = -RT \ln \left[ a_{Sb_2O_3} \right.$$
$$\left. / (a_{Sb}^2 (P_{O_2}(Sb, Sb_2O_3)/P^0)^{3/2}) \right]. \quad \text{(3)}$$

The standard molar Gibbs energy of formation of $ZnSb_2O_4$ (or $MgSb_2O_4$) from $Sb_2O_3$ and $ZnO$ (or $MgO$) are derived from the emfs of cell (V) using eq. (4):

$$(-) \, Pt, \, Re \,|\, Sb, \, MO, \, MSb_2O_4 \,|\, ZrO_2$$
$$+ Y_2O_3 \,|\, Sb, \, Sb_2O_3 \,|\, Re, \, Pt \, (+) \quad \text{(V)}$$
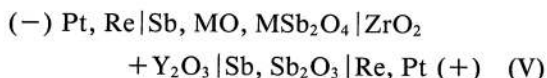
and

$$\Delta G^0 = -6 E_V F, \quad \text{(4)}$$

where $M = Zn$ or $Mg$. In this study cells (II), (III) and (IV) were used instead of cell (V), so we obtain $\Delta G^0_{MSb_2O_4}$ from eq. (5):

$$\Delta G^0_{MSb_2O_4} = -6(E_{\text{III}} - E_{\text{II}})F \quad \text{or}$$
$$-6(E_{\text{IV}} - E_{\text{II}})F. \quad \text{(5)}$$

Materials:Sb metal (99.999 mass% purity) was powdered in an agate mortar and mixed with $Sb_2O_3$ powder (99.999% purity) in a weight ratio (5:1) for an Sb, $Sb_2O_3$ electrode. $ZnSb_2O_4$(or $MgSb_2O_4$) was synthesized by heating a pressed pellet of equimolar mixture of $Sb_2O_3$ and $ZnO$ (or $MgO$) powder (99.0+% purity) at 973 K for 86.4 ks in a zirconia crucible placed in a silica tube filled with purified argon gas. Formation of the ternary compounds was confirmed by X-ray diffraction analysis. A three-phase electrode (Sb, MO, $MSb_2O_4$) was prepared by mixing the components in a molar ratio (6:1:1) and heating in a zirconia crucible placed in a sealed evacuated silica capsule at 900 K for 86.4 ks. Closed-end tubes of $0.92 ZrO_2 + 0.08 Y_2O_3$ electrolyte (8 mm in o.d.; 5 mm in i.d.; 300 mm long) were supplied by Nippon-Kagaku Togyo Co. Ltd. Apparatus and Procedure: Experimental details such as cell arrangement, furnace, temperature control and measurement and emf determination of cells have been outlined previously for the measurements of $\Delta G^0$ of $ZnO$ and $ZnGa_2O_4$[9]. A two- or three-phase electrode was put into the electrolyte tube. The space above the electrode in the tube was decreased by inserting a tight-fitting alumina tube in which a lead wire (Pt) was fixed with high-temperature zirconia-cement. At the start

of each experimental run the cell was evacuated and flushed with purified argon gas repeatedly, and heated in an argon gas atmosphere. Air was flushed at the flow rate of $5 \times 10^{-6}$ m$^3$s$^{-1}$ up to the Pt-painted bottom of the zirconia tube and the air/Pt electrode acted as a reference.

## III. Results and Discussion

### 1. Standard molar Gibbs energy of formation of Sb$_2$O$_3$

The experimental results from cell II are shown in Table 1. The data are listed in the order of measurements in each run. Sb, Sb$_2$O$_3$ electrode was not heat-treated before each experimental run, so it required a long time (28.8–36 ks) to obtain the first equilibrium emf at temperatures below the melting point of Sb. After that equilibrium emf was obtained in a shorter period of time (14.4–21.6 ks even at temperatures below the melting point of Sb) and stable emf held for a long time. As there exist melting points[10] of Sb(904 K) and Sb$_2$O$_3$(929 K) in this experimental temperature range, the emf-temperature plots for cell II are expected to consist of three linear segments. Jacob and Mathew[4] and Sugimoto et al.[6] observed them in the $E-T$ plots from the cell with Cu, Cu$_2$O or Pb, PbO reference electrode. Referring to their results, data in this study were analysed by the least squares

method in the three regions to give eqs. (6) to (8):

(i)    Below the melting point of Sb (904 K)

$$E/\text{mV} \pm 0.8 = 1184.9 - 0.4518\ T/\text{K}. \quad (6)$$

(ii)    Between the melting points of Sb and Sb$_2$O$_3$(929 K)

$$E/\text{mV} \pm 1.2 = 1110.6 - 0.3705\ T/\text{K}. \quad (7)$$

(iii)   Above the melting point of Sb$_2$O$_3$

$$E/\text{mV} \pm 0.9 = 1187.6 - 0.4538\ T/\text{K}. \quad (8)$$

Equations (6) to (8) were used to calculate the free energy-temperature expressions for the reaction (a) on the reasonable assumption that the oxygen solubility in Sb is very small[3][4].

(i)    $\Delta G^0_{\text{Sb}_2\text{O}_3}/\text{kJ} \pm 0.47 = -686.2 + 0.2422\ T/\text{K}$
$$(T/\text{K} > 904). \quad (9)$$

(ii)    $\Delta G^0_{\text{Sb}_2\text{O}_3}/\text{kJ} \pm 0.70 = -643.1 + 0.1951\ T/\text{K}$
$$(904 < T/\text{K} < 929). \quad (10)$$

(iii)   $\Delta G^0_{\text{Sb}_2\text{O}_3}/\text{kJ} \pm 0.53 = -687.8 + 0.2433\ T/\text{K}$
$$(929 < T/\text{K}). \quad (11)$$

Figure 1 shows the standard molar Gibbs energy of formation of Sb$_2$O$_3$ by the emf method and compiled values in the literatures. At high temperatures, where both Sb and Sb$_2$O$_3$ are liquid, the values are in good agreement with one another except Hahn and Stevenson[5] and lie between the compiled values by Kubaschewski and Alcock[10] and Coughlin[11] or Wicks and Block[12]. The data

Table 1   Equilibrium emf $E$ and temperature $T$ for cell (II).

| Run 1 | $T/\text{K}$ | 883(i) | 824(i) | 848(i) | 951(iii) | 931(iii) | 911(ii) | 969(iii) |
|---|---|---|---|---|---|---|---|---|
| | $E/\text{mV}$ | 787.2 | 812.8 | 802.7 | 755.4 | 765.7 | 774.4 | 749.5 |
| Run 2 | $T/\text{K}$ | 860(i) | 886(i) | 785(i) | 915(ii) | 812(i) | 943(iii) | 923(ii) |
| | $E/\text{mV}$ | 795.4 | 783.6 | 830.5 | 771.9 | 818.3 | 760.0 | 768.5 |
| | 971(iii) | 953(iii) | 933(iii) | 900(i) | 922(ii) | 945(iii) | | |
| | 747.8 | 755.5 | 764.2 | 778.7 | 769.9 | 758.9 | | |
| Run 3 | $T/\text{K}$ | 879(i) | 906(ii) | 919(ii) | 836(i) | 982(iii) | 1004(iii) | |
| | $E/\text{mV}$ | 787.8 | 774.3 | 768.5 | 806.4 | 741.3 | 731.4 | |
| | 936(iii) | 1014(iii) | 991(iii) | 957(iii) | | | | |
| | 761.3 | 727.2 | 738.4 | 753.3 | | | | |
| Run 4 | $T/\text{K}$ | 805(i) | | | | | | |
| | $E/\text{mV}$ | 821.1 | | | | | | |

(i):    below the melting point of Sb.
(ii):   between the melting points of Sb and Sb$_2$O$_3$.
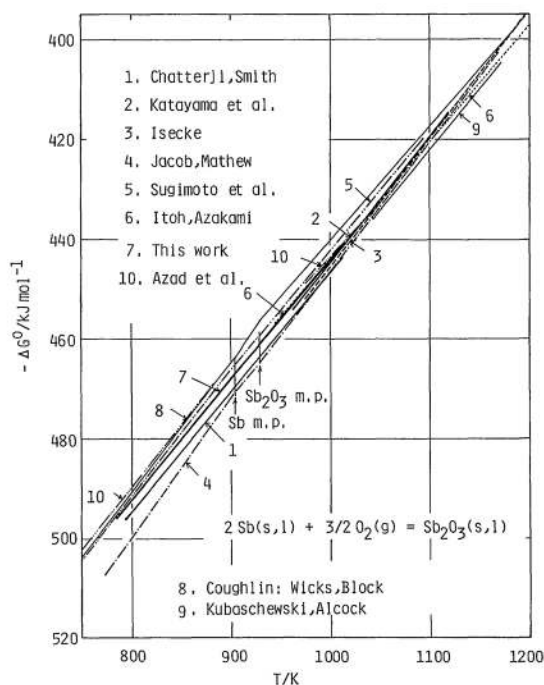(iii): above the melting point of Sb$_2$O$_3$.

Fig. 1  Standard molar Gibbs energy of formation of Sb$_2$O$_3$(s, l).

by Hahn and Stevenson differ too largely from those by other investigators, to be shown in Fig. 1 in their experimental temperature range (1073–1223 K). They found some difference in their own measurements with (1) Sb + Sb$_2$O$_3$ two phase mixtures and (2) Sb metal and oxide which was formed coulometrically. They used a long zirconia tube and CO/CO$_2$ or Ga, Ga$_2$O$_3$ reference electrode. The reasons of these discrepancies or the difference can not be explained. Judging from the fact that they ob-

tained too low values of emf, the effect of their cell structure or the property of the electrolyte seems to appear. The result obtained in this study is in excellent agreement with our previous values which was obtained from the cell with Fe, Fe$_x$O reference electrode, although the temperature dependence of emf is a little different. At low temperatures, where both Sb and Sb$_2$O$_3$ are solid, a little difference can be found. The reasons of the difference can not be explained from the kind of solid electrolyte, reference electrode, electrical contact materials for the electrodes and cell construction, because agreement in the values at higher temperatures is excellently good.

The melting points of Sb and Sb$_2$O$_3$ could not be determined in the present study from the emf-temperature relationship, because of the narrow temperature range between their melting points and of the small heat of fusion[10] of them.

## 2.  Standard Gibbs energy of formation of ZnSb$_2$O$_4$

Emf-values from cell III are shown in Table 2 in the order of the measurements. As the three-phase electrode was beforehand heat-treated, it required only a short period of time (about 10.8 ks) to obtain the first equilibrium emf. After that, emf was confirmed to be stable for 10.8–18 ks at the same temperature and then the cell temperature was changed to the next one. At each temperature emf value was confirmed to be stable for 7.2–43.2 ks after the equilibrium emf was obtained, so one run of the measurements lasted for (3–5)

Table 2  Equilibrium emf $E$ and temperature $T$ for cell (III).

| Run 1 | $T$/K | 886(s) | 932(l) | 913(l) | 931(l) | 954(l) | 933(l) | 899(s) |
|---|---|---|---|---|---|---|---|---|
|  | $E$/mV | 805.6 | 783.4 | 793.9 | 784.1 | 771.9 | 782.8 | 801.2 |
|  |  | 878(s) | 901(s) | 875(s) | 850(s) |  |  |  |
|  |  | 814.3 | 800.5 | 814.0 | 826.4 |  |  |  |
| Run 2 | $T$/K | 901(s) | 946(l) | 922(l) | 972(l) | 884(s) | 902(s) | 883(s) |
|  | $E$/mV | 801.0 | 777.5 | 790.2 | 762.7 | 810.0 | 800.8 | 810.8 |
|  |  | 856(s) | 909(l) | 933(l) | 875(s) | 970(l) | 876(s) |  |
|  |  | 821.6 | 796.4 | 784.2 | 812.6 | 764.4 | 812.3 |  |
| Run 3 | $T$/K | 876(s) | 892(s) | 899(s) | 940(l) | 870(s) | 919(l) | 947(l) |
|  | $E$/mV | 813.0 | 804.4 | 801.2 | 778.9 | 815.4 | 791.2 | 776.3 |
|  |  | 939(l) | 955(l) | 852(s) |  |  |  |  |
|  |  | 780.6 | 772.2 | 822.5 |  |  |  |  |

$\times$ 86.4 ks. The emf-temperature relationships are given by eqs. (12) and (13).

$$E/\text{mV} \pm 1.2 = 1231.6 - 0.4782\ T/\text{K}$$
$$(T/\text{K} < 904). \quad (12)$$

$$E/\text{mV} \pm 0.6 = 1277.1 - 0.5290\ T/\text{K}$$
$$(T/\text{K} > 904). \quad (13)$$

From eqs. (12), (13) and (1) we obtain eqs. (14) and (15).

$$\Delta G^0/\text{kJ} \pm 0.70 = -170.4 + 0.2574\ T/\text{K} \quad (14)$$

for

$$2\text{Sb(s)} + 3/2\text{O}_2(\text{g}) + \text{ZnO(s)} = \text{ZnSb}_2\text{O}_4(\text{s}) \quad (\text{b})$$

and

$$\Delta G^0/\text{kJ} \pm 0.35 = -739.5 + 0.2869\ T/\text{K} \quad (15)$$

for

$$2\text{Sb(1)} + 3/2\text{O}_2(\text{g}) + \text{ZnO(s)} = \text{ZnSb}_2\text{O}_4(\text{s}). \quad (\text{c})$$

Combining eqs. (12), (13), (6), (7), (8) and (5), we obtain eqs. (16) to (18)

$$\Delta G^0/\text{kJ} \pm 1.2 = 27.0 - 0.0153\ T/\text{K}$$
$$(T/\text{K} < 904), \quad (16)$$

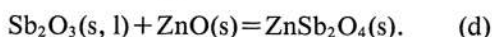$$\Delta G^0/\text{kJ} \pm 1.1 = 96.4 - 0.0918\ T/\text{K}$$
$$(904 < T/\text{K} < 929) \quad (17)$$

and

$$\Delta G^0/\text{kJ} \pm 0.9 = 51.8 - 0.0435\ T/\text{K}$$
$$(929 < T/\text{K}). \quad (18)$$

For the reaction (d)

$$\text{Sb}_2\text{O}_3(\text{s, l}) + \text{ZnO(s)} = \text{ZnSb}_2\text{O}_4(\text{s}). \quad (\text{d})$$

It seems that there have hitherto been no data to be compared with.

### 3. Standard Gibbs energy of formation of MgSb$_2$O$_4$

Emf values of cell (IV) are shown in Table 3, and the emf-temperature relationship is represented by eq. (19).

$$E/\text{mV} \pm 0.9 = 1287.7 - 0.5033\ T/\text{K}$$
$$(945 < T/\text{K} < 1117). \quad (19)$$

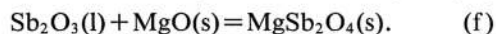From eqs. (19) and (1), eq. (20) is obtained for the reaction (e).

$$\Delta G^0/\text{kJ} \pm 0.53 = -745.6 + 0.2720\ T/\text{K}. \quad (20)$$

$$2\text{Sb(1)} + 3/2\text{O}_2(\text{g}) + \text{MgO(s)} = \text{MgSb}_2\text{O}_4(\text{s}). \quad (\text{e})$$

From eqs. (20) and (11), eq. (21) is obtained for the reaction (f).

$$\Delta G^0/\text{kJ} + 1.1 = -58.0 + 0.0287\ T/\text{K}$$
$$(945 < T/\text{K} < 1117). \quad (21)$$

$$\text{Sb}_2\text{O}_3(\text{l}) + \text{MgO(s)} = \text{MgSb}_2\text{O}_4(\text{s}). \quad (\text{f})$$

For this double oxide with Pb$_3$O$_4$ structure there are no data in the literature.

### IV. Conclusion

Emf measurements of the galvanic cells with solid electrolyte (ZrO$_2$ + Y$_2$O$_3$) were carried out to determine the standard molar Gibbs energies of formation of Sb$_2$O$_3$, ZnSb$_2$O$_4$ and MgSb$_2$O$_4$ using the air, Pt electrode as a reference. The results were represented as follows:

1.  $\Delta G^0/\text{kJ} \pm 0.47 = -686.2 + 0.2422\ T/\text{K}$
$$(T/\text{K} < 904),$$
$$\Delta G^0/\text{kJ} \pm 0.70 = -643.1 + 0.1951\ T/\text{K}$$
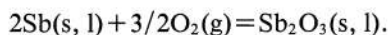$$(904 < T/\text{K} < 929)$$

and

Table 3  Equilibrium emf $E$ and temperature $T$ for cell (IV).

| Run 1 | $T/\text{K}$ | 1020 | 1064 | 953 | 1006 | 1117 | 1061 | 1110 | 1059 | 1069 |
|---|---|---|---|---|---|---|---|---|---|---|
| | $E/\text{mV}$ | 776.5 | 752.1 | 808.2 | 780.6 | 725.6 | 752.8 | 728.9 | 753.7 | 750.6 |
| Run 2 | $T/\text{K}$ | 945 | 989 | 1077 | 1028 | 990 | 1104 | | | |
| | $E/\text{mV}$ | 811.0 | 790.0 | 746.1 | 771.1 | 788.9 | 731.5 | | | |
| Run 3 | $T/\text{K}$ | 1102 | 1061 | 1105 | 1098 | 1105 | | | | |
| | $E/\text{mV}$ | 733.0 | 754.8 | 731.2 | 734.8 | 730.9 | | | | |

$$\Delta G^0/kJ \pm 0.53 = -687.8 + 0.2433\ T/K$$
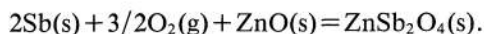
$$(929 < T/K)$$

for

$$2Sb(s,\ l) + 3/2O_2(g) = Sb_2O_3(s,\ l).$$

2.  $$\Delta G^0/kJ \pm 0.70 = -170.4 + 0.2574\ T/K$$

$$(T/K < 904)$$

for

$$2Sb(s) + 3/2O_2(g) + ZnO(s) = ZnSb_2O_4(s).$$
$$\Delta G^0/kJ \pm 0.35 = -739.5 + 0.2869\ T/K$$

$$(T/K > 904)$$

for

$$2Sb(l) + 3/2O_2(g) + ZnO(s) = ZnSb_2O_4(s).$$
$$\Delta G^0/kJ \pm 1.2 = 27.0 - 0.0153\ T/K$$

$$(T/K < 904),$$

$$\Delta G^0/kJ \pm 1.1 = 96.4 - 0.0918\ T/K$$

$$(904 < T/K < 929)$$

and

$$\Delta G^0/kJ \pm 0.9 = 51.8 - 0.0435\ T/K$$

$$(929 < T/K)$$

for

$$Sb_2O_3(s,\ l) + ZnO(s) = ZnSb_2O_4(s).$$

3.  $$\Delta G^0/kJ \pm 0.53 = -745.6 + 0.2720\ T/K$$

$$(945 < T/K < 1117)$$

for

$$2Sb(l) + 3/2O_2(g) + MgO(s) = MgSb_2O_4(s).$$
$$\Delta G^0/kJ + 1.1 = -58.0 + 0.0287\ T/K$$

$$(945 < T/K < 1117)$$

for

$$Sb_2O_3(l) + MgO(s) = MgSb_2O_4(s).$$
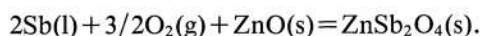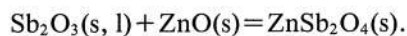
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