The Gibbs Free Energy of Formation of Y_2O_3 in the Temperature Region 1000—1150 K

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The Gibbs free energy of formation of Y_2O_3 ($\Delta G^\circ_{Y_2O_3}$) has been measured in the temperature region 1000—1150 K, and compared with literature values.^{1,2} The experiments give values for $\Delta G^\circ_{Y_2O_3}$ below the values given in the literature.^{1,2}

Compilations of the Gibbs free energy of formation of Y_2O_3 ^{1,2} are based on fairly old measurements. In connection with investigations on the electrolytic deposition of yttrium from fused fluorides containing Y_2O_3 , the Gibbs free energy of formation of Y_2O_3 has been measured in the temperature region 1000—1150 K by means of a formation cell of the type:

where X is a C/CO₂ ($p = 1$ atm), or Pt/O₂ ($p = 1$ atm) electrode.

EXPERIMENTAL

LiF and YF₃ (99.9 %) were used in molar ratio 3:1. The melting point of this mixture is 740 °C.³ 5 weight % Y_2O_3 (99.9 %) was added to the mixture to ensure complete saturation with respect to Y_2O_3 . The solubility of Y_2O_3 in the melt is approximately 2.5 weight % at 840 °C.⁴ The experiments were performed in a 5 cm internal diameter graphite cell. The cell is shown in Fig. 1. The cell was placed in a vertical Kanthal-wound furnace inside an inert atmosphere chamber, described elsewhere.⁵

LiF and YF₃ were weighed out in stoichiometric proportions, and 5 weight % Y_2O_3 was added. The salts were mixed and dried *in situ* at 300 °C and under dynamic vacuum of 0.02 Torr for at least 12 h. The mixture was then melted under He atmosphere.

The temperature in the melt was controlled with an on/off temperature controller and a chromel-alumel thermocouple. Temperature measurements were done with another chromel-alumel thermocouple contained inside a closed end molybdenum tube immersed in the melt, and a potentiometer.

The thermoelectrical electromotive force (TEMF) for the couples Y/C and Y/Pt was determined previously to the chain measurements as a function of temperature. These quantities represent a correction on the measured electromotive force (EMF).

The EMF's were recorded on a strip-chart recorder with input impedance 4 Mohm.

The potentials were stable at gas velocities above ~ 20 cm³/min. No time-dependence of the potentials was found.

The C/CO₂ electrode

This electrode has been used by several workers,⁶⁻¹⁰ in the cryolite system. The cell set-up in this investigation was:

with the cell reaction

The EMF of this cell is given by:

$$E_T = E^\circ_T + (RT/6F) \ln [(P_{CO_2})^{3/2}/a_{Y_2O_3}] \quad (2)$$

With $p_{CO_2} = 1$ atm and a saturated solution with respect to Y_2O_3 ($a_{Y_2O_3} = 1$), eqn. (2) gives $E_T = E^\circ_T$, and the Gibbs free energy change for reaction (1), ΔG°_T , is:

$$\Delta G^\circ_T = -6FE^\circ_T \quad (3)$$

Fig. 1. Cell used for the EMF measurements.

Fig. 2. EMF as function of T with the C/CO_2 ($p = 1$ atm) electrode.

With knowledge of standard Gibbs free energy of formation of CO_2 and ΔG°_T from eqn. (3), the standard Gibbs free energy of formation of Y_2O_3 ($\Delta G^\circ_{Y_2O_3}$) can be calculated:

$$\Delta G^\circ_{Y_2O_3} = 3/2 \Delta G^\circ_{CO_2} - \Delta G^\circ_T \quad (4)$$

The results from the experiments are given in Fig. 2, as measured EMF (E_T , V, corrected for TEMF) vs. thermodynamic temperature, T . The results are fitted to a straight line by means of a least-squares computer program:

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Fig. 3. EMF as function of T with the Pt/O_2 ($p = 1$ atm) electrode.

$$E_T = 2.3229 - 4.3890 \times 10^{-4} \times T \quad (5)$$

The estimated error in the EMF is ± 5 mV.

The Pt/O_2 ($p = 1$ atm) electrode

The cell set-up was:

with the cell reaction:

A saturated solution with respect to Y_2O_3 (i.e. $a_{Y_2O_3} = 1$) and an O_2 -pressure of 1 atm, give $E_T = E^\circ_T$, and the standard Gibbs free energy of formation of Y_2O_3 can be calculated directly from the measured EMF:

Table 1. Gibbs free energy of formation of Y_2O_3 , ΔG°_f .

Reference electrode (X)	Temp. K	Measured ΔG°_f , kJ	Lit. value ΔG°_f , kJ
$p = 1$ atm			
Pt/ O_2	1000	-1707.5	-1594.9(1)
C/ CO_2	1000	-1685.3	-1636.7(2)
Pt/ O_2	1050	-1692.4	-1584.4(1)
C/ CO_2	1050	-1672.7	-1623.7(2)
Pt/ O_2	1100	-1677.3	-1569.8(1)
C/ CO_2	1100	-1660.6	-1611.2(2)
Pt/ O_2	1150	-1661.8	-1551.0(1)
C/ CO_2	1150	-1648.0	-1598.2(2)

$$\Delta G^\circ_{Y_2O_3} = -6FE^\circ_T \quad (7)$$

The results from these experiments, presented as a plot of EMF *vs.* *T*, are given in Fig. 3. The results are fitted to a straight line by means of a least-squares computer program. The equation for the EMF (E_T, V) – *T* dependence is:

$$E_T = 3.4725 - 5.2450 \times 10^{-4} \times T \quad (8)$$

The estimated error in determining the EMF is ± 5 mV.

From the measured EMF (eqns. (5) and (8)), the free energy of formation of Y_2O_3 was calculated and compared with literature values. The results of this are given in Table 1. The literature values, marked (1) are taken from Wicks and Block's compilation of selected thermodynamic properties,¹ the values marked (2) are calculated by us from data found in Kubaschewski, Evans and Alcock's book on Metallurgical Thermochemistry.²

CONCLUSION

Table 1 shows that both reference electrodes gave Gibbs free energy of formation values for Y_2O_3 below the values found in the literature. The result indicates that the accepted value¹ for the Gibbs free energy of formation of Y_2O_3 is too high in the temperature region 1000 – 1150 K. At 1000 K, the discrepancy is –101.5 kJ compared with Wicks and Block's¹ values, and –59.7 kJ compared with the calculated values from Kubaschewski, Evans and Alcock.² At 1150 K, the discrepancy is –103.9 kJ and –56.7 kJ, respectively. In both cases, the mean value from the measurements with the Pt/ O_2 (*p* = 1 atm) and C/ CO_2 (*p* = 1 atm) reference electrodes is used.

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