The Gibbs Free Energy of Formation of Y$_2$O$_3$

in the Temperature Region 1000—1150 K

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The Gibbs free energy of formation of Y$_2$O$_3$ ($\Delta G^\circ_{\text{Y}_2\text{O}_3}$) has been measured in the temperature region 1000—1150 K, and compared with literature values.$^{1,3}$ The experiments give values for $\Delta G^\circ_{\text{Y}_2\text{O}_3}$ below the values given in the literature.$^{1,3}$

Compilations of the Gibbs free energy of formation of Y$_2$O$_3$,$^{4}$ are based on fairly old measurements. In connection with investigations on the electrolytic deposition of yttrium from fused fluorides containing Y$_2$O$_3$, the Gibbs free energy of formation of Y$_2$O$_3$ has been measured in the temperature region 1000—1150 K by means of a formation cell of the type:

\[
\begin{array}{c|c|c}
\text{Y(s)} & \text{LiF} & X \\
\hline
\text{YF}_3 & (l); \text{Y}_2\text{O}_3(sat) & \text{X}
\end{array}
\]

where X is a C/CO$_2$ ($p=1$ atm), or Pt/O$_2$ ($p=1$ atm) electrode.

EXPERIMENTAL

LiF and YF$_3$ (99.9 %) were used in molar ratio 3:1. The melting point of this mixture is 740 °C.$^{5}$ 5 weight % Y$_2$O$_3$ (99.9 %) was added to the mixture to ensure complete saturation with respect to Y$_2$O$_3$. The solubility of Y$_2$O$_3$ 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 YF$_3$ were weighed out in stoichiometric proportions, and 5 weight % Y$_2$O$_3$ 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 (EMF) 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 cm$^3$/min. No time-dependence of the potentials was found.

The C/CO$_2$ electrode

This electrode has been used by several workers,$^{4-10}$ in the cryolite system. The cell setup in this investigation was:

\[
\begin{array}{c|c|c}
\text{Y(s)} & \text{LiF} & \text{C, CO}_2 (p=1 \text{ atm}) \\
\hline
\text{YF}_3 & (l); \text{Y}_2\text{O}_3(sat) & \text{Y}_2\text{O}_3(sat) + 3/2\text{C(s)} = 2\text{Y(s)} + 3/2\text{CO}_2 \text{ (g, 1 atm)}
\end{array}
\]

with the cell reaction

\[
\text{Y}_2\text{O}_3(sat) + 3/2\text{C(s)} = 2\text{Y(s)} + 3/2\text{CO}_2 \text{ (g, 1 atm)}
\]  

\[
(1)
\]

The EMF of this cell is given by:

\[
E_T = E^\circ_{\text{Y}_2\text{O}_3(sat)} + (RT/2F) \ln \left( [\text{PCO}_2]^{5/2}/a_{\text{Y}_2\text{O}_3(sat)} \right)
\]

\[
(2)
\]

With $p_{\text{CO}_2} = 1$ atm and a saturated solution with respect to Y$_2$O$_3$ ($a_{\text{Y}_2\text{O}_3(sat)} = 1$), eqn. (2) gives $E_T = E^\circ_{\text{Y}_2\text{O}_3(sat)}$, and the Gibbs free energy change of reaction (1), $\Delta G^\circ_{\text{Y}_2\text{O}_3}$, is:

\[
\Delta G^\circ_{\text{Y}_2\text{O}_3} = -6F E^\circ_{\text{Y}_2\text{O}_3(sat)}
\]

\[
(3)
\]
With knowledge of standard Gibbs free energy of formation of CO₂ and \( \Delta G^o_T \) from eqn. (3), the standard Gibbs free energy of formation of \( \text{Y}_2\text{O}_3 \) (\( \Delta G^o_{\text{Y}_2\text{O}_3} \)) can be calculated:

\[
\Delta G^o_{\text{Y}_2\text{O}_3} = \frac{3}{2} \Delta G^o_{\text{CO}_2} - \Delta G^o_T
\]  

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:

\[ E_T = 2.3229 - 4.3890 \times 10^{-4} \times T \]  

The estimated error in the EMF is \( \pm 5 \) mV.

The Pt/O₂ (\( p = 1 \) atm) electrode cell set-up was:

\[
\text{Y(s)} \mid \text{LiF(l); Y}_2\text{O}_3(\text{sat}) \mid \text{Pt, O}_2 (p = 1 \text{ atm})
\]

with the cell reaction:

\[
\text{Y}_2\text{O}_3 (\text{sat}) = 2\text{Y(s)} + 3/2 \text{O}_2 (g, 1 \text{ atm})
\]  

A saturated solution with respect to \( \text{Y}_2\text{O}_3 \) (i.e. \( \alpha_{\text{Y}_2\text{O}_3} = 1 \)) and an \( \text{O}_2 \)-pressure of 1 atm, give \( E_T = E^o_T \), and the standard Gibbs free energy of formation of \( \text{Y}_2\text{O}_3 \) can be calculated directly from the measured EMF:

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\text{Reference} & \text{Temp.} & \text{Measured} & \text{Lit. value} \\
\text{electrode (X)} & \text{K} & \text{\( \Delta G^o \), kJ} & \text{\( \Delta G^o \), kJ} \\
\hline
\text{Pt/O}_2 & 1000 & -1707.5 & -1594.9(1) \\
\text{C/CO}_2 & 1000 & -1685.3 & -1636.7(2) \\
\text{Pt/O}_2 & 1050 & -1692.4 & -1584.4(1) \\
\text{C/CO}_2 & 1050 & -1672.7 & -1623.7(2) \\
\text{Pt/O}_2 & 1100 & -1677.3 & -1569.8(1) \\
\text{C/CO}_2 & 1100 & -1660.6 & -1611.2(2) \\
\text{Pt/O}_2 & 1150 & -1661.8 & -1551.0(1) \\
\text{C/CO}_2 & 1150 & -1648.0 & -1598.2(2) \\
\hline
\end{tabular}
\end{table}

**Fig. 1.** Cell used for the EMF measurements.

**Fig. 2.** EMF as function of \( T \) with the C/CO₂ (\( p = 1 \) atm) electrode.

**Fig. 3.** EMF as function of \( T \) with the Pt/O₂ (\( p = 1 \) atm) electrode.

**Gibbs Free Energy of Formation**

\[
E_T = 2.3229 - 4.3890 \times 10^{-4} \times T
\]  

The estimated error in the EMF is \( \pm 5 \) mV.
\[ \Delta G^{\circ}_{\text{Y}_{2}\text{O}_{3}} = -6FE^{\circ}_T \]  

(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 \((E_V, V) - T \) dependence is:

\[ E_T = 3.4725 - 5.2450 \times 10^{-4} \times T \]  

(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 \( \text{Y}_3\text{O}_5 \) 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 \( \text{Y}_3\text{O}_5 \) below the values found in the literature. The result indicates that the accepted value\(^1\) for the Gibbs free energy of formation of \( \text{Y}_3\text{O}_5 \) is too high in the temperature region 1000–1150 K. At 1000 K, the discrepancy is \(-101.5 \text{ kJ} \) compared with Wicks and Block’s\(^1\) values, and \(-58.7 \text{ kJ} \) compared with the calculated values from Kubaschewski, Evans and Alcock.\(^2\) At 1150 K, the discrepancy is \(-103.9 \text{ kJ} \) and \(-56.7 \text{ kJ} \), respectively. In both cases, the mean value from the measurements with the \( \text{Pt/O}_2 \) \((p = 1 \text{ atm})\) and \( \text{CO/CO}_2 \) \((p = 1 \text{ atm})\) reference electrodes is used.

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REFERENCES


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