



# Gibbs energy of formation of bismuth(III) oxide

K.T. Jacob\*, Amal K. Mansoor

Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India



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## ABSTRACT

The standard Gibbs energy of formation of  $\text{Bi}_2\text{O}_3$  has been measured using a solid-state cell incorporating yttria-stabilized zirconia as the electrolyte and pure oxygen as the reference electrode. An innovative cell design, with a buffer electrode to absorb the electrochemical flux of oxygen through the electrolyte caused by trace electron/hole conduction, was used to measure the oxygen chemical potential over phase mixture  $\text{Bi} + \text{Bi}_2\text{O}_3$  in the temperature range from 800 to 1473 K. A closed cell was used to avoid possible deviations from equilibrium caused by vaporization of bismuth and oxides of bismuth. The results for  $\alpha\text{-Bi}_2\text{O}_3$  in the temperature range from 800 to 1002 K can be summarized by,

$$\Delta G_f^\circ (\pm 230) / \text{J mol}^{-1} = -584235 + 289.28(T/\text{K})$$

For  $\delta\text{-Bi}_2\text{O}_3$  in the temperature range from 1002 to 1078 K:

$$\Delta G_f^\circ (\pm 230) / \text{J mol}^{-1} = -553669 + 258.77(T/\text{K})$$

The results are discussed in relation to thermodynamic information reported in the literature.

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## 1. Introduction

The Gibbs energy of formation of bismuth(III) oxide has been measured at high temperatures by many investigators using electrochemical cells [1–10]. However, these studies were carried out using open cells and conventional two-compartment cell designs. Because of the relatively high vapor pressures of bismuth and oxides of bismuth [11–13] in equilibrium with  $\text{Bi} + \text{Bi}_2\text{O}_3$  at high temperature as shown in Fig. 1, possible deviation from equilibrium in open cells is a source of concern. Hence, a closed cell was used in this study to avoid problems caused by continuous vaporization. Polarization of electrodes caused by trace hole or electronic conduction in the solid electrolyte and consequent electrochemical permeability the solid electrolyte is a second source of concern. An innovative cell design is developed in this study to deflect this flux to a buffer electrode and avoid electrode polarization. In previous studies air [2,5,8],  $\text{Cu} + \text{Cu}_2\text{O}$  [1,7],  $\text{Ni} + \text{NiO}$  [6] and  $\text{Fe} + \text{Fe}_{1-x}\text{O}$  [3] were used as secondary standards for oxygen chemical potential. The oxygen partial pressure in air is dependent on altitude and weather conditions such as humidity and wind velocity. In this study measurements are made using the primary reference

standard for oxygen,  $\text{O}_2$  gas at 0.1013 MPa. The oxygen electrode is non-polarizable.

The heat capacity of  $\alpha\text{-Bi}_2\text{O}_3$  has been measured in the temperature range from 60 to 298 K by Anderson [14] and from 11 to 50 K by Gorbunov et al. [15]. The results from these two measurements are in reasonably good accord. The standard entropy of  $\alpha\text{-Bi}_2\text{O}_3$  at 298.15 K computed using the low temperature heat capacity data is  $150.0 (\pm 1.6) \text{ J/mol K}$ . Although the early solution calorimetric measurements of the enthalpy of formation of  $\alpha\text{-Bi}_2\text{O}_3$  at 298.15 K by Ditte et al. [16] and Mixter [17] gave discordant results, Mah [18] later provided a reliable value using combustion calorimetry.

## 2. Experimental Aspects

### 2.1. Materials

Bismuth metal and bismuth(III) oxide used in this study were 99.99 mass % pure and were supplied by Apache Chemicals. Spectrochemical analysis of  $\text{Bi}_2\text{O}_3$  showed the major impurities which were Ca (43 mass ppm), Pb (32 mass ppm), Si (12 mass ppm), B (7 mass ppm) and Fe (5 mass ppm). High-purity (99.999 mole%) oxygen gas was dried by passage through columns containing silica gel and magnesium perchlorate. High-purity (99.999 mole%) Ar gas used in this study was also dried the same way. Residual

\* Corresponding author. Fax: +91 8023600472.

E-mail addresses: [katob@materials.iisc.ernet.in](mailto:katob@materials.iisc.ernet.in), [ktjacob@hotmail.com](mailto:ktjacob@hotmail.com) (K.T. Jacob), [amalmsnr95@gmail.com](mailto:amalmsnr95@gmail.com) (A.K. Mansoor).

oxygen in Ar gas was removed by passing through copper turnings at 673 K and titanium granules at 1123 K.

## 2.2. Apparatus and procedure

Reversible emf of the solid state electrochemical cell,

Pt, Os, Bi + Bi<sub>2</sub>O<sub>3</sub>/(Y<sub>2</sub>O<sub>3</sub>)ZrO<sub>2</sub>/O<sub>2</sub>(0.1013 MPa), Pt

was measured in the temperature range from 800 to 1473 K. Since calcia-stabilized zirconia (CSZ) used by many previous investigators was found to react with Bi<sub>2</sub>O<sub>3</sub> during long exposures at high temperature, yttria-stabilized zirconia (YSZ) was used in this study as the electrolyte. Pure diatomic oxygen gas at standard pressure (1.013 × 10<sup>5</sup> Pa) was used as the reference electrode, since it is non-polarizable and is the primary reference standard for oxygen potential. The right hand electrode of the cell was positive. There is always a small electrochemical flux of oxygen through the electrolyte from the reference electrode at high oxygen potential to the measuring electrode at low oxygen potential. This flux is caused by the presence of trace electron (or hole) conductivity in the solid electrolyte, facilitating coupled transport of oxygen ions and electrons (or holes). The oxygen flux can cause polarization of the working electrode, but not of the reference electrode. Unlike with air, Ar + O<sub>2</sub> or M + M<sub>x</sub>O<sub>y</sub> mixtures, a concentration gradient cannot be generated at the electrode/electrolyte interface because of the electrochemical flux of oxygen through the electrolyte when pure oxygen at a fixed pressure is used as the electrode. To avoid polarization of the working electrode, a buffer electrode was introduced between the reference and working electrodes to act as a sink for the oxygen flux and prevent it from reaching the working electrode. The three-electrode design is conceptualized in Fig. 2.

The buffer electrode was maintained at the same oxygen potential as the measuring electrode. Since there was no oxygen potential difference between working and buffer electrodes, there was no oxygen flux through YSZ membrane separating the two. Thus, this innovative design prevented the lowering of emf caused by polarization of the working electrode and ensured accurate thermodynamic data. The magnitude of emf loss caused by polarization in conventional two-compartment designs can be obtained by measuring the open circuit potential between the buffer and reference electrodes.

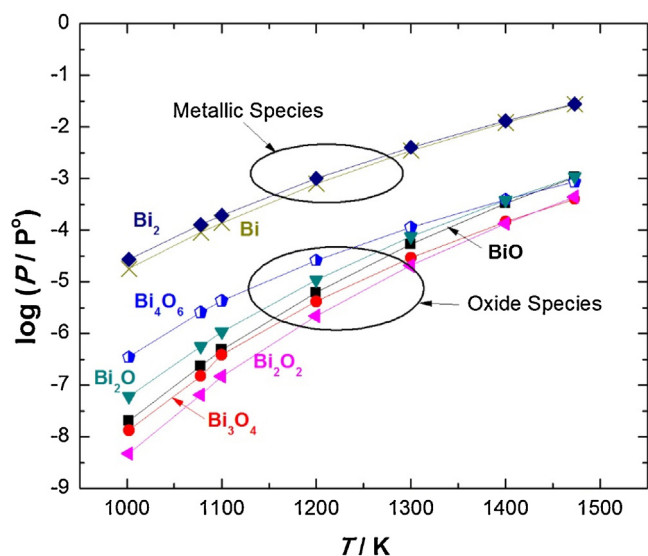


Fig. 1. Vapor pressures of bismuth and oxides of bismuth in equilibrium with Bi + Bi<sub>2</sub>O<sub>3</sub> [11–13].  $P^\circ$  represents the standard atmospheric pressure (0.1013 MPa).

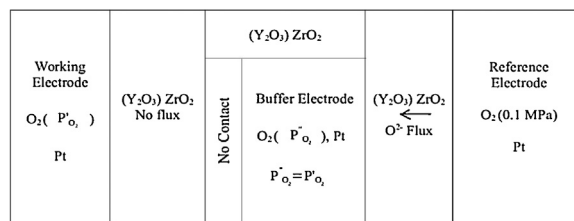


Fig. 2. Three-electrode design of the electrochemical cell to prevent polarization of the working electrode.

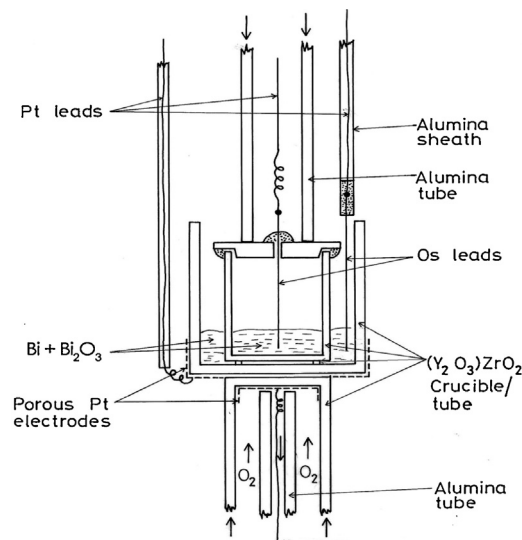


Fig. 3. Schematic diagram of the apparatus used for emf measurements.

A schematic of the cell assembly is displayed in Fig. 3. Oxygen reference electrode was fabricated inside a long inverted impervious tube of yttria-stabilized zirconia (YSZ) containing 12 mole percent Y<sub>2</sub>O<sub>3</sub>. Inside of the tube near the closed end was platinumized. The thin layer of Pt was spherodized by heat treatment. A Pt mesh was pressed against the platinumized surface by an alumina tube. A Pt wire (0.25 mm diameter) welded to the Pt mesh provided electrical connection for measurement of emf. The reference electrode was mounted inside an alumina tube (not shown in the figure) and fixed to a water-cooled brass head attached to the bottom of the alumina tube. The brass-head closing the bottom of the alumina tube had provisions for gas inlet/outlet and thermocouple leads. Pure oxygen gas was flowed through the YSZ tube at a flow rate of 1.5 ml/s. The pressure of oxygen gas in the tube was electronically controlled at 0.1013(0.0006) MPa and remained constant during experiment independent of ambient conditions.

The measuring electrode consisted of an equimolar mixture of bismuth and bismuth(III) oxide (~30 g) contained inside an YSZ crucible. The crucible was closed with an YSZ lid with a small orifice in the center. Osmium (99.9 mass % pure) wire passing through this orifice made contact with the mixture of bismuth and bismuth(III) oxide. The orifice and the gap between the lid and crucible were closed with alumina cement. The Os wire was attached to a Pt lead in the constant temperature zone of the furnace. Hence, there was no thermoelectric contribution to the emf. The YSZ crucible housing the working electrode was placed inside a larger YSZ crucible containing Bi + Bi<sub>2</sub>O<sub>3</sub> which functioned as the buffer electrode. The twin crucible assembly was placed over the inverted YSZ tube as shown in Fig. 3. The cell assembly was pressed together by an alumina tube spring loaded at the top. Electric leads were provided for measuring the oxygen potential of the buffer electrode. This allowed assessment of the error that was caused by

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