The vaporization of B2O3(l) to B2O3(g) and B2O2(g) (Poster)

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The vaporization of B2O3 in a reducing environment leads to formation of both B2O3(g) and B2O2(g). While formation of B2O3(g) is well understood, many questions about the formation of B2O2(g) remain. Previous studies using B(s) + B2O3(l) have led to inconsistent thermodynamic data. In this study, it was found that after heating, B(s) and B2O3(l) appear to separate and variations in contact area likely led to the inconsistent vapor pressures of B2O2(g). To circumvent this problem, an activity of boron is fixed with a two-phase mixture of FeB and Fe2B. Both second and third law enthalpies of formation were measured for B2O2(g) and B2O3(g). From these the enthalpies of formation at 298.15 K are calculated to be -479.9 ± 41.5 kJ/mol for B2O2(g) and -833.4 ± 13.1 kJ/mol for B2O3(g). Ab initio calculations to determine the enthalpies of formation of B2O2(g) and B2O3(g) were conducted using the W1BD composite method and show good agreement with the experimental values.
The Vaporization of B$_2$O$_3$(l) to B$_2$O$_3$(g) and B$_2$O$_3$(g)

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Vaporize B$_2$O$_3$(l) in Reducing Environments
- Applications and need for thermodynamic data
  - Ceramic processing
  - Corrosion of high-temperature ceramics
- Two vaporization routes
  - B$_2$O$_3$(l) = B$_2$O$_3$(g)
  - 2/3 B (or other reductant) + 2/3 B$_2$O$_3$(l) = B$_2$O$_3$(g)
- Approach [1]
  - Ab initio study using quantum chemical composite methods
  - Knudsen effusion mass spectrometry (KEMS) [2]

Previous Studies
- Thermodynamics of B$_2$O$_3$(g) well understood, reliable data available
- Questions on 2B(s) + 1/2O$_2$(g) = B$_2$O$_3$(g); issues with B and B$_2$O$_3$(g) ran

Theoretical Heats of Formation: Quantum Chemistry Composite Methods [8–12]
- Equilibrium geometry and frequencies computed at B3LYP/VTZ+1 level
  - Linear O-B-B-O shape for the B$_2$O$_3$(g) and V shape for B$_2$O$_3$(g)
- W1BD Method, Gaussian Software [9,11]
  - Basis set: aug-cc-VnZ n = D,T, or Q
- Relativistic corrections/spin-orbit coupling effects included
- In the W1BD Modification of the W1 method, Brueckner Doubles used to simplify calculations
- Enthalpies of reaction determined from where all other reactants and products have known enthalpies of formation

Summary of Data for $\Delta H_{298.15}^\circ$ B$_2$O$_3$(g)

Selection of Proper Reductant for B$_2$O$_3$
- B + B$_2$O$_3$
  - Used by other investigators
  - B$_2$O$_3$(g) does not wet B
  - Changing contact area
  - 2/3 B + 2/3 B$_2$O$_3$(g) = B$_2$O$_3$(g)
  - Led to lack of reproducible B$_2$O$_3$(g) vapor pressures

Use FeB/FeB mixture to set B activity, gave more reliable results than B alone

Conclusions
- Theoretical and experimental determination of heat of formation of B$_2$O$_3$(g) and B$_2$O$_3$(g)
- Theoretical: Quantum chemistry composite method
- Experimental: Use FeB/FeB mixture to set B activity, gave more reliable results than B alone
  - For B$_2$O$_3$(g) $\Delta H_{298.15}^\circ = -479.9 \pm 25.7$ kJ/mol
  - For B$_2$O$_3$(g) $\Delta H_{298.15}^\circ = -833.4 \pm 13.1$ kJ/mol

References
10. National Aeronautics and Space Administration, Glenn Research Center, 2011."The Vaporization of B$_2$O$_3$(l) to B$_2$O$_3$(g) and B$_2$O$_3$(g)." 220th Meeting of the Electrochemical Society, High Temperature Corrosion and Materials Chemistry, October 10–11, 2011, Boston, MA.

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