The vaporization of $\text{B}_2\text{O}_3(\ell)$ to $\text{B}_2\text{O}_3(g)$ and $\text{B}_2\text{O}_2(g)$ (Poster)

Nathan Jacobson and Dwight Myers (East Central University, Ada, OK)

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

Nathan Jacobson, NASA Glenn Research Center, Cleveland, OH 44135
Dwight Myers, East Central University, Ada, OK 74820


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(g) + 1/2 O$_2$(g) = B$_2$O$_2$(g); issues with B and B$_2$O$_3$(l) rxn
- Basis set: aug-cc-VnZ n = D, T, or Q
- 2O$_2$(g) and V shape for B$_2$O$_3$(g)

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

Glenn Research Center Knudsen Effusion Mass Spectrometer [2]

- Resistance heated cell
- Cross axis electron impact ionizer; 90° magnetic sector, and ion counting detector

Analysis of Data: Determine $\Delta_f^o H_{298.15}$

- Use heats of formation of other compounds:
  - 4/3 FeB(s) + 2/3 B$_2$O$_3$(g) = B$_2$O$_3$(g) + 2/3 Fe$_2$B(d)
  - 4/3 FeB(s) + 2/3 B$_2$O$_3$(g) [16]
  - 4/3 FeB(s) + 4/3 B(s) = 4/3 Fe$_2$B(s) [17]
- 2/3 FeB(s) = 4/3 Fe(s) + 2/3 B(s) [17]

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

Summary of Data for $\Delta_f^o H_{298.15}$ B$_2$O(g)

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/FeB mixture to set B activity, gave more reliable results than B alone
- For B$_2$O$_3$(g) $\Delta_f^o H_{298.15} = -479.9 \pm 25.7$ kJ/mol
- For B$_2$O$_3$(g) $\Delta_f^o H_{298.15} = -833.4 \pm 13.1$ kJ/mol

References

3. Scheer, M. D.