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

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

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 B₂O₃(l) to B₂O₂(g) and B₂O₃(g)

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


Vaporize B₂O₃(l) in Reducing Environments
- Applications and need for thermodynamic data
  - Ceramic processing
  - Corrosion of high-temperature ceramics
- Two vaporization routes
  - B₂O₃(l) = B₂O₂(g)
  - 2B (or other reductant) + 2/3 B₂O₃(l) = B₂O₂(g)
- Approach [1]
  - Ab initio study using quantum chemical composite methods
  - Knudsen effusion mass spectrometry (KEMS) [2]

Previous Studies
- Thermodynamics of B₂O₃(l) well understood, reliable data available
- Questions on 2B(l) + 1/2 O₂(g) = B₂O₂(g); issues with B and B₂O₃(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 B₂O₃(g) and V shape for B₂O₃(l)
- W1BD Method, Gaussian Software [9,10]
  - Basis set: aug-cc-pVnZ n = D,T,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 reagents and products have known enthalpies of formation

Analysis of Data: Determine ΔᵢH°¹⁹⁸.¹⁵
• Use heats of formation of other compounds:
  4/3 FeB(s) + 2/3 B₂O₃(l) = B₂O₂(g) + 2/3 Fe₂B
  2/3 FeB(s) = 4/3 Fe(g) + 2/3 B(l) [17]
- Total error must include error in each of these heats

Summary of Data for ΔᵢH°¹⁹⁸.¹⁵ B₂O₃(g)

Selection of Proper Reductant for B₂O₃
• B + B₂O₃
  - Used by other investigators
  - B₂O₃ does not wet B
  - Changing contact area for
    2/3 B + 2/3 B₂O₃(l) = B₂O₂(g)
  - Led to lack of reproducible B₂O₂(g) vapor pressures
  - Use FeB/Fe to prevent contact—two-phase mixture fixes B activity

Summary of Data for ΔᵢH°¹⁹⁸.¹⁵ B₂O₂(g)

Conclusions
- Theoretical and experimental determination of heat of formation of B₂O₃(g) and B₂O₂(g)
- Theoretical: Quantum chemistry composite method
- Experimental: Use FeB/Fe to prevent contact activity, gave more reliable results than B alone
  - For B₂O₃(g) ΔᵢH°¹⁹⁸.¹⁵ = -479.9 ± 25.7 kJ/mol
  - For B₂O₂(g) ΔᵢH°¹⁹⁸.¹⁵ = -833.4 ± 13.1 kJ/mol

References
3. Ingraham, M. G.; Porter, R. F.; Chupka, W. A.
4. Scheer, M. D.
5. Rentzepis et al.—Collection [5]
7. Cubicciotti, D.
8. Martin, J. M. L.; de Oliveira, G.
9. Martin, J. M. L.; de Oliveira, G.
10. Martin, J. M. L.; de Oliveira, G.
12. Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.
13. Cubicciotti, D.
14. Cubicciotti, D.
15. Barin, I., Cubicciotti, D.
16. Ingham et al. only converted three points to pressure and hence only three points were used for the 3rd Law enthalpy.

Acknowledgments
Helpful discussions with Dr. E. Copland, AT Allena, Monroe, NC, are very much appreciated. OSOR (University of Oklahoma) Director Henry Newman, Sr., Systems Analyst David Allev, and Joshua, Alexander, HPC Application Software Specialist, provided valuable technical expertise. We also thank Dr. C. Rice and M. M. Hale, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK, for assistance with the ab initio calculations. We are also grateful to Dr. Y. Stollemyer, St. Petersburg State University, St. Petersburg, Russia, for many helpful comments. Support from Supersonics Research, Fundamental Aeronautics Program is acknowledged.