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.

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The Vaporization of B_2O_3(l) to B_2O_3(g) and B_2O_3(g)

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Vaporize B_2O_3(l) in Reducing Environments

- Applications and need for thermodynamic data
  - Ceramic processing
  - Corrosion of high-temperature ceramics
- Two vaporization routes
  - $B_2O_3(l) = B_2O_3(g)$
  - 2/3 B (or other reductant) + 2/3 $B_2O_3(l) = B_2O_2(g)$
- Approach [1]
  - Ab initio study using quantum chemical composite methods
  - Knudsen effusion mass spectrometry (KEMS) [2]

Previous Studies

- Thermodynamics of B_2O_3(g) well understood, reliable data available
- Questions on 2B(s) + 1/2 $O_2(g) = B_2O_2(g)$; issues with B and B_2O_3(l) rxn

Investigator/method and reaction	$\Delta_f H^o_{298.15}$ kJ/mol—2nd Law	$\Delta_f H^o_{298.15}$ kJ/mol—3rd Law	$\Delta_f H^o_{298.15}$
Ingram (KEMS) [3] 2/3 B + 2/3 $B_2O_3(l) = B_2O_2(g)$	–509.4	–444.1	
Ingram (KEMS) [3] 2/3 B + 2/3 $B_2O_3(g) = B_2O_2(g)$	–455.2	–458.7	
Scheer (Torsion) [4] 2/3 B + 2/3 $B_2O_3(l) = B_2O_2(g)$	–428.6	–462.9	
Rentzepis et al. (Collection) [5] C(s) + $B_2O_3(l) = B_2O_2(g)$ + CO(g)		–466.2	
Searcy and Myers [6] 2MgO(s) + 2B(s) = 2Mg(g) + $B_2O_2(g)$		–458.9	
Nguyen et al. (ab initio) [7] 2B(g, doublet) + 2O(g, triplet) = $B_2O_2(g)$			–457.7

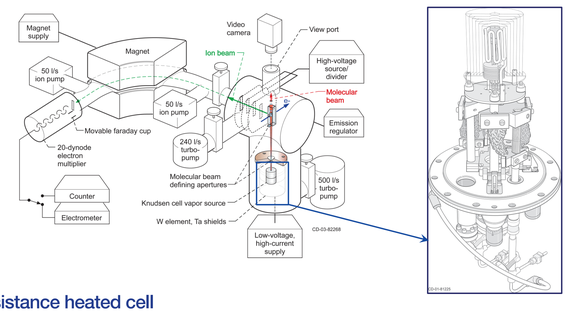
Theoretical Heats of Formation: Quantum Chemistry Composite Methods [8–12]

- Equilibrium geometry and frequencies computed at B3LYP/VTZ+1 level
  - Linear O-B-B-O shape for the B_2O_2(g) and V shape for B_2O_3(g)
- W1BD Method, Gaussian Software [9,10]
  - 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

Species/Reaction	W1BD Enthalpy/kJ mol^{-1}	Nguyen *et al.* (7) Enthalpy/kJ mol^{-1}
$B_2O_2(g)$		
$B_2O_2(g) = 2B(g, doublet) + 2O(g, triplet)$	–479.9 ± 17.2	–457.7
$B_2O_2(g) + 6HF(g) = 2BF_3(g) + 2H_2O(g) + H_2(g)$	–456.7 ± 5.3	
$B_2O_2(g) + 6H_2(g) = 2BH_3(g) + 2H_2O(g) + H_2(g)$	–441.1 ± 14.7	
$B_2O_3(g)$		
$B_2O_3(g) = 2B(g, doublet) + 3O(g, triplet)$	–857.4 ± 17.2	–830.1
$B_2O_3(g) + 6HF(g) = 2BF_3(g) + 3H_2O(g)$	–831.8 ± 5.3	
$B_2O_3(g) + 6H_2(g) = 2BH_3(g) + 3H_2O(g)$	–816.2 ± 14.8	

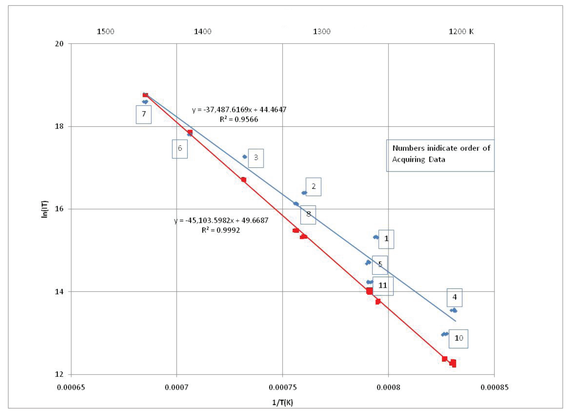
- Spin state is singlet, unless specified. Isogyric reactions (constant spin) preferred.

Glenn Research Center Knudsen Effusion Mass Spectrometer [2]

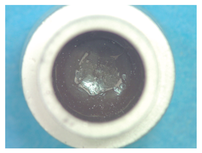


- Resistance heated cell
- Cross axis electron impact ionizer; 90° magnetic sector; and ion counting detector

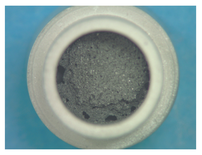
B + B_2O_3 in BN Single Cell 11-1, 2, 3-10



Selection of Proper Reductant for B_2O_3

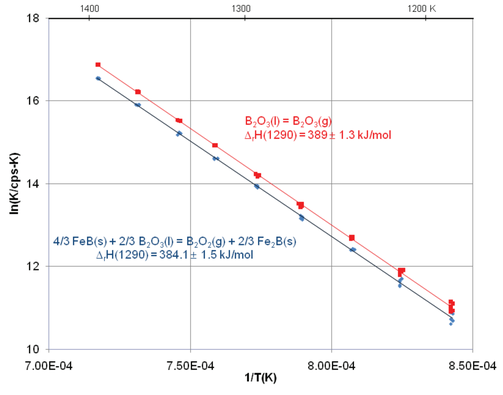


- B + B_2O_3
  - Used by other investigators
  - B_2O_3(l) does not wet B
  - Changing contact area for 2/3 B + 2/3 $B_2O_3(l) = B_2O_2(g)$
  - Led to lack of reproducible B_2O_2(g) vapor pressures



- Use FeB/Fe_2B + B_2O_3
  - Two-phase mixture fixes B activity
  - No changes in mixture—contact area remains constant
  - 4/3 FeB + 2/3 $B_2O_3(l) = B_2O_2(g)$ + 2/3 Fe_2B
  - Gave reproducible vapor pressures

1:1:1 FeB:Fe_2B:B_2O_3 Mixture



Analysis of Data: Determine $\Delta_r H^o_{298.15}$

- 'Σ Plot' method [13,14]

$$\Delta\{-(gef_{298.15})\} - R\ln(I(i)T) = A + B/T$$

$$gef_{298.15} = (G^o_T - H^o_{298.15})/T$$

  - Plot $\Delta\{-(gef_{298.15})\} - R\ln(I(i)T)$ *vs* $1/T$ $\quad Slope = \Delta_r H^o_{298.15}$
- 'Third Law' method [15]
  - $T[\Delta\{-(gef_{298.15})\} - R\ln(K)] = \Delta_r H^o_{298.15}$
  - Obtain $\Delta_r H^o_{298.15}$ for each temperature
- Use experimental Gibbs Energy Functions (gef) [16]—preferred over calculated as determined from measured spectroscopic data

Analysis of Data: Determine $\Delta_f H^o_{298.15}$

- Use heats of formation of other compounds:
  - 4/3 FeB(s) + 2/3 $B_2O_3(l) = B_2O_2(g)$ + 2/3 Fe2B(s)
  - 4/3 B(s) + $O_2(g)$ = 2/3 B_2O_3(l) [16]
  - 4/3 Fe(s) + 4/3 B(s) = 4/3 FeB(s) [17]
  - 2/3 Fe_2B(s) = 4/3 Fe(s) + 2/3 B(s) [17]
  - ---
  - 2 B(s) + $O_2(g) = B_2O_2(g)$
- Total error must include error in each of these heats

Summary of Data for $\Delta_f H^o_{298.15}$ B_2O_2(g)

Investigator and Technique	Data Points	Average Temperature K	Enthalpy of Reaction 2B(s) + $O_2(g) = B_2O_2(g)$					
			2nd Law kJ/mol	2nd Law kJ/mol	3rd Law kJ/mol	From 2nd Law kJ/mol	From 3rd Law kJ/mol	Tables
Ingram et al. KEMS [3] 2/3B + 2/3$B_2O_3(l) = B_2O_2(g)$	6	1400	302.5 ± 4.2	407.0 ± 7.2	391.5 ± 0.7*	-509.4	-444.1	
Ingram et al. KEMS [3] 2/3B + 2/3$B_2O_3(g) = B_2O_2(g)$	3	1410	103.4 ± 1.0	104.9 ± 1.1	101.4 ± 0.3	-455.2	-458.7	
Scheer—Torsion [4] 2/3B + 2/3$B_2O_3(l) = B_2O_2(g)$	14	1390	382.5 ± 7.2	326.2 ± 4.4	372.7 ± 2.0	-428.6	-462.9	
Rentzepis et al.—Collection [5] $B_2O_3(l)$ +3 C = 3CO + 2B $B_2O_3(l)$ + C = $B_2O_2(g)$ + CO	5						-466.2 ± 6.5	
Searcy and Myers [6] 2MgO + 2B = 2Mg(g) + $B_2O_2(g)$	1	1375					-458.9 ± 16.7	
JANAF [16]								-456.1 ± 8.4
IVTAN [18]								-457.728**
This Study Run 1 4/3 FeB(s) + 2/3 $B_2O_3(l)$ = $B_2O_2(g)$ + 2/3 Fe_2B	8	1284	363.8 ± 2.8	384.9 ± 2.9	411.6 ± 1.6	-498.0	-471.4	
This Study Run 1 4/3 FeB(s) + 2/3 $B_2O_3(g)$ = $B_2O_2(g)$ + 2/3 Fe_2B	8	1284	113.0 ± 2.1	115.6 ± 2.1	125.1 ± 0.8	-489.2	-479.7	
This Study Run 2 4/3 FeB(s) + 2/3 $B_2O_3(l)$ = $B_2O_2(g)$ + 2/3 Fe_2B	6	1280	376.7 ± 1.4	399.0 ± 1.5	413.0 ± 0.9	-484.0	-470.0	
This Study Run 2 4/3 FeB(s) + 2/3 $B_2O_3(g)$ = $B_2O_2(g)$ + 2/3 Fe_2B	6	1280	122.9 ± 1.8	125.6 ± 1.8	125.8 ± 0.5	-479.2	-479.0	
This Study Run 3 4/3 FeB(s) + 2/3 $B_2O_3(l)$ = $B_2O_2(g)$ + 2/3 Fe_2B	9	1290	384.0 ± 1.5	405.5 ± 1.5	414.0 ± 0.7	-477.5	-469.0	
This Study Run 3 4/3 FeB(s) + 2/3 $B_2O_3(g)$ = $B_2O_2(g)$ + 2/3 Fe_2B	9	1290	123.6 ± 1.7	123.7 ± 1.7	126.20 ± 0.6	-481.1	-478.6	

*Ingraham et al. only converted three points to pressure and hence only three points were used for the 3rd Law enthalpy.
**Given class of accuracy is 6-F, which means an uncertainty is ≤40 kJ/mol

Summary of Data for $\Delta_f H^o_{298.15}$ B_2O_3(g)

Investigator	Number of Data Points	Average Temperature T	$B_2O_3(l) = B_2O_3(g)$ 2nd Law	2nd Law	3rd Law	2B(s) + 3/2 $O_2(g) = B_2O_3(g)$ From 2nd Law	From 3rd Law	Tables
Hildenbrand—Torsion [19]			302.5 ± 4.2	427.5	417.3	-825.9	-836.0	
Scheer—Torsion [20]	14	1500	364.9 ± 3.8	405.2 ± 3.9	424.2 ± 0.9	-848.2	-829.2	
Shultz et al.—mass spectrometry and weight loss [21]	14			412.1 ± 8.4	415.5 ± 0.1			
JANAF [16]								-836.0 ± 4.2
IVTAN [18]								-835.383*
This Study—B_2O_3 only	11	1320	380.8 ± 1.2	410.7 ± 1.3	429.5 ± 1.2	-842.6	-823.9	
This Study Run 1 FeB/Fe_2B/B_2O_3	8	1270	373.2 ± 1.7	401.7 ± 1.8	428.7 ± 1.7	-851.7	-824.7	
This Study Run 2 FeB/Fe_2B/B_2O_3	6	1225	380.8 ± 1.7	409.9 ± 1.7	430.3 ± 1.3	-843.5	-823.1	
This Study Run 3 FeB/Fe_2B/B_2O_3	9	1290	389.0 ± 1.3	417.9 ± 1.3	430.9 ± 0.8	-835.5	-822.5	

Conclusions

- Theoretical and experimental determination of heat of formation of B_2O_2(g) and B_2O_3(g)
- Theoretical: Quantum chemistry composite method
- Experimental: Use Fe_2B/FeB mixture to set B activity, gave more reliable results than B alone
- For B_2O_2(g) $\Delta_f H^o_{298.15}$ = –479.9 ± 25.7 kJ/mol
- For B_2O_3(g) $\Delta_f H^o_{298.15}$ = –833.4 ± 13.1 kJ/mol

References

1. Jacobson, N. S.; Myers, D. L. J. *Phys. Chem.* **2011**, in press.
2. Copland, E. H.; Jacobson, N. S., NASA/TP—2010-216795.
3. Ingram, M. G.; Porter, R. F.; Chupka, W. A. *J. Chem. Phys.* **1956**, 25, 498.
4. Scheer, M. D. *J. Phys. Chem.* **1958**, 62, 490.
5. Rentzepis, P.; White, D.; Walsh, P. N. *J. Phys. Chem.* **1960**, 64, 1784.
6. Searcy, A.W.; Myers, C. E. *J. of Phys. Chem.* **1957**, 61, 957.
7. Nguyen, M. T.; Matus, M. H.; Vu, T. N.; Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A*, **2009**, 113, 4895.
8. Jensen, F., "Introduction to Computational Chemistry" p164-169, John Wiley and Sons, 1999.
9. Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* 1999, 111, 1843.
10. Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* 2001, 114, 6014.
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T. Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K., Rendell, A., Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision B. 01* **2010**, Wallingford, CT: Gaussian, Inc.
12. http://www.gaussian.com/g_prod/gv_glance.htm. **2009** [cited 2011].
13. Cubicciotti, D. *J. Phys. Chem.* **1966**, 70, 2410.
14. Copland, E. H., NASA Contractor Report 2009-215498.
15. Drowart, J.; Goldfinger, P. *Ang. Chemie-Int. Ed.* **1967**, 6, 581.
16. Chase, M.W. NIST-JANAF Thermochemical Tables. 4th ed. *Journal of Physical and Chemical Reference Data Monograph;* American Chemical Society and American Institute of Physics for the National Institute of Standards and Technology; Washington, D.C., 1998.
17. Barin, I., *Thermochemical Data of Pure Substances* 3rd Edition; VCH; Wieheim, 1995.
18. Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. eds. *Thermodynamic Properties of Individual Substances* 4th ed.; Begell House; New York; 1989.
19. Hildenbrand, D. L.; Hall, W. F.; Potter, N. D. *J. Chem. Phys.* **1963**, 39, 296.
20. Scheer, M. D. *J. Phys. Chem.* **1957**, 61, 1184.
21. Shultz, M. M.; Stolyarova, V. L.; Semenov, G. A. *Fizika i Khimiia Stekla* **1978**, 4, 653.

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