

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 $B_2O_3(l)$ to $B_2O_3(g)$ and $B_2O_3(g)$

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

220th Meeting of the Electrochemical Society,
High Temperature Corrosion and Materials Chemistry, October 10–11, 2011, Boston, MA

Vaporize $B_2O_3(l)$ in Reducing Environments

- Applications and need for thermodynamic data
 - Ceramic processing
 - Corrosion of high-temperature ceramics
- Two vaporization routes
 - $B_2O_3(l) = B_2O_3(g)$
 - $2/3 B \text{ (or other reductant)} + 2/3 B_2O_3(l) = B_2O_3(g)$
- 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 $2B(s) + 1/2 O_2(g) = B_2O_3(g)$; issues with B and $B_2O_3(l)$ rxn

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

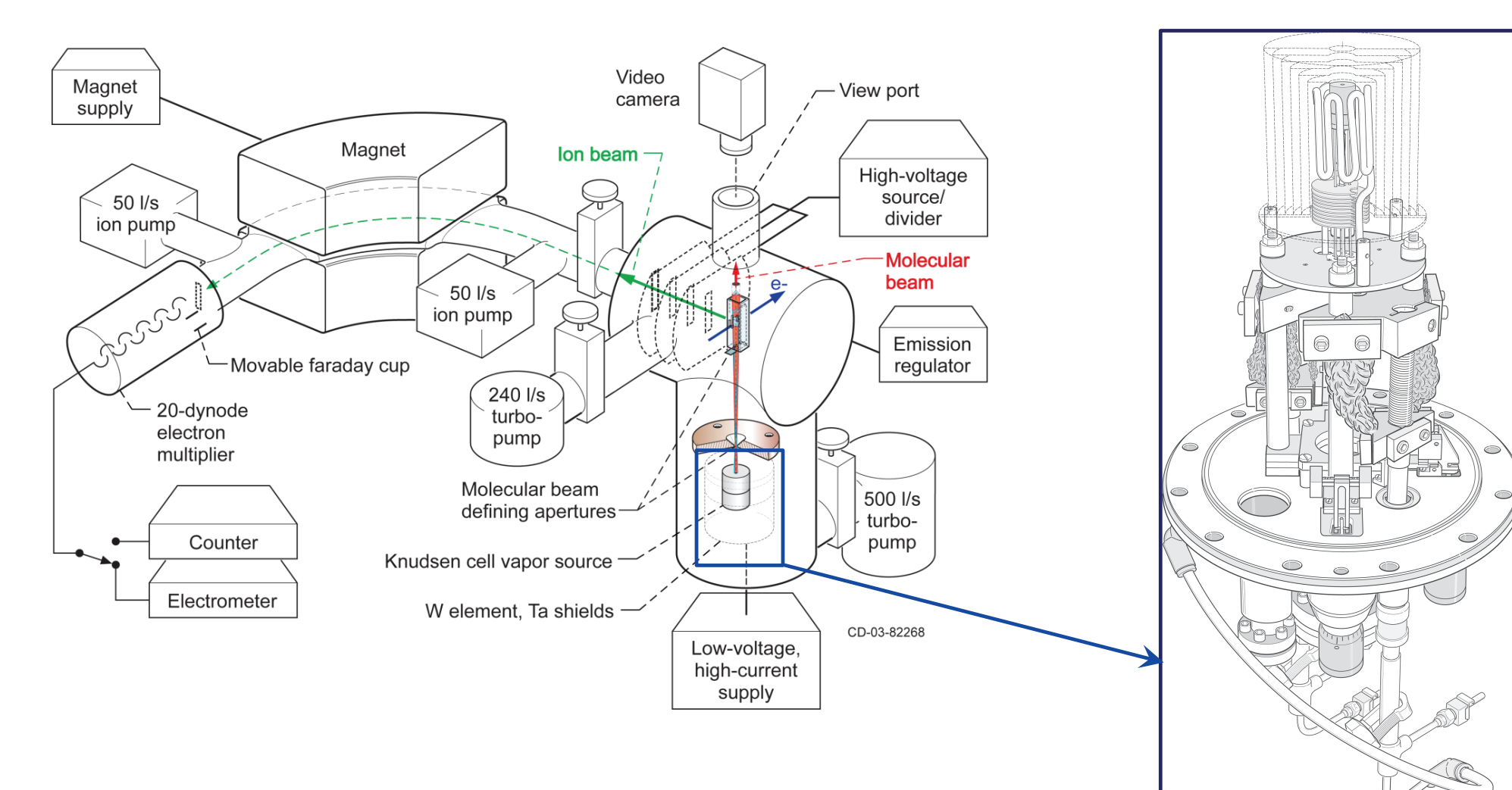
Theoretical Heats of Formation: Quantum Chemistry Composite Methods [8–12]

- Equilibrium geometry and frequencies computed at B3LYP/VTZ+1 level
 - Linear O-B-B-O shape for the $B_2O_3(g)$ and V shape for $B_2O_3(l)$
- 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
$B_2O_3(g)$		
$B_2O_3(l) = 2B(g, \text{doublet}) + 2O(g, \text{triplet})$	-479.9 ± 17.2	-457.7
$B_2O_3(g) = 6HF(g) = 2BF_3(g) + 2H_2O(g) + H_2(g)$	-456.7 ± 5.3	
$B_2O_3(g) = 6HI(g) = 2BI_3(g) + 2H_2O(g) + H_2(g)$	-441.1 ± 14.7	
$B_2O_3(g)$		
$B_2O_3(l) = 2B(g, \text{doublet}) + 3O(g, \text{triplet})$	-857.4 ± 17.2	-830.1
$B_2O_3(g) = 6HF(g) = 2BF_3(g) + 3H_2O(g)$	-831.8 ± 5.3	
$B_2O_3(g) = 6HI(g) = 2BI_3(g) + 3H_2O(g)$	-816.2 ± 14.8	

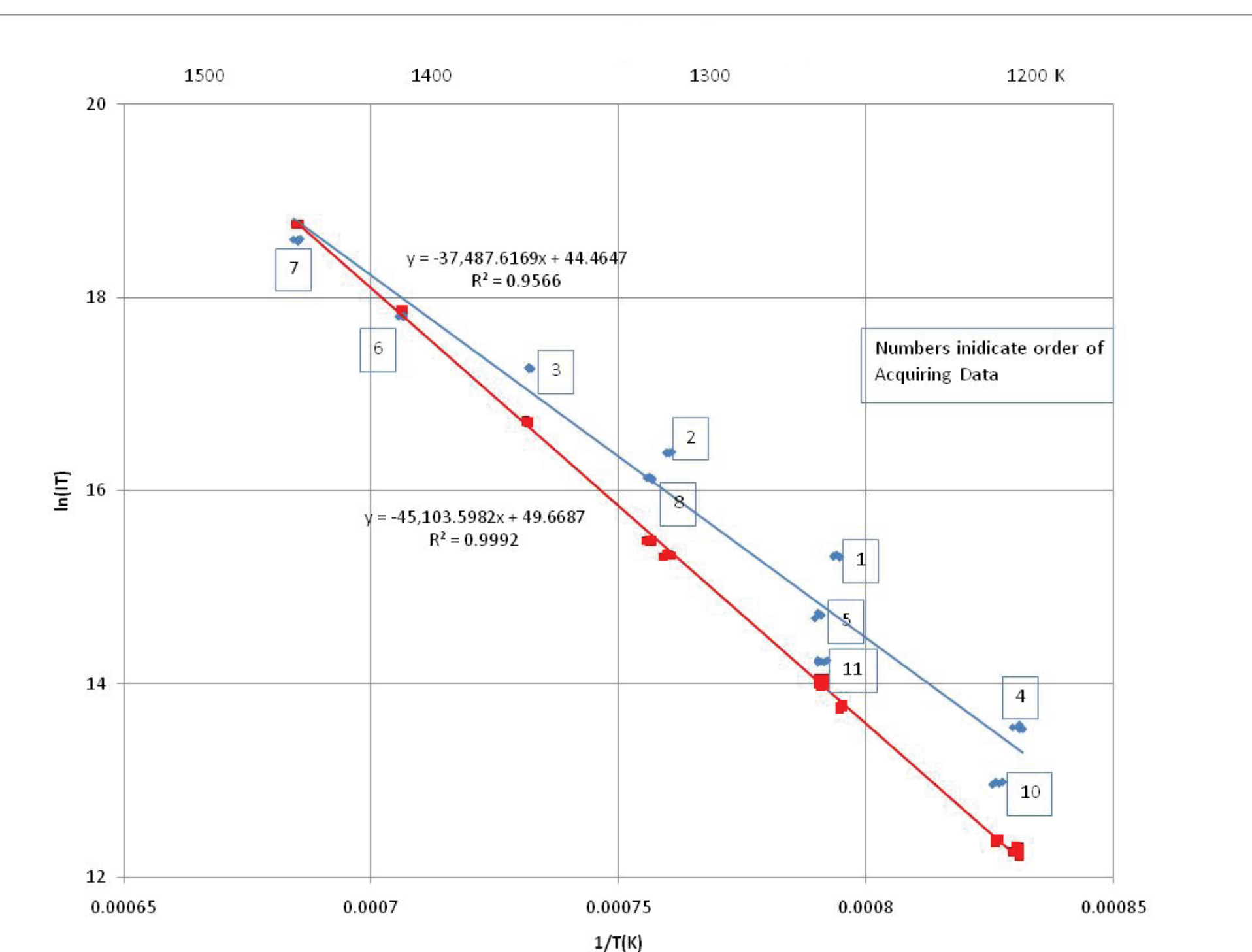
- Spin state is singlet, unless specified. Isogyric reactions (constant spin) preferred.

Glenn Research Center Knudsen Effusion Mass Spectrometer [2]

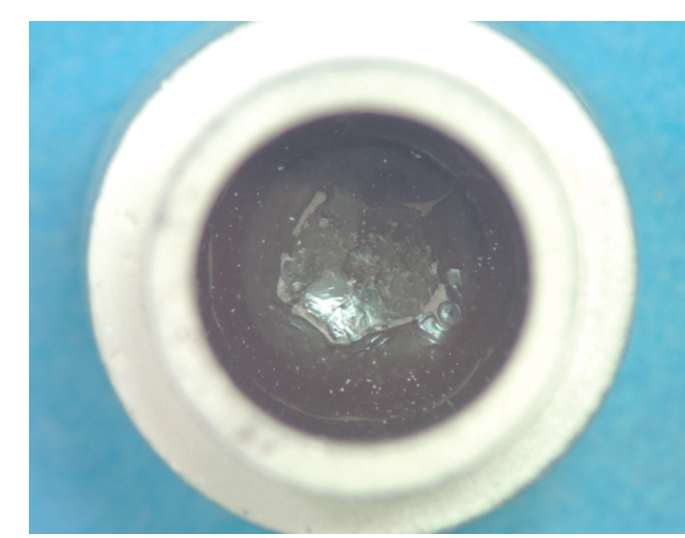


- Resistance heated cell
- Cross axis electron impact ionizer; 90° magnetic sector; and ion counting detector

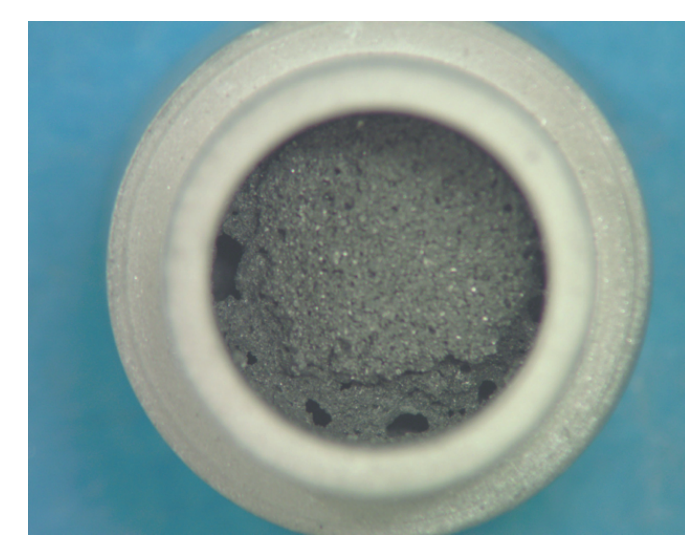
B + B_2O_3 in BN Single Cell 11-1, 2, 3-10



Selection of Proper Reductant for B_2O_3

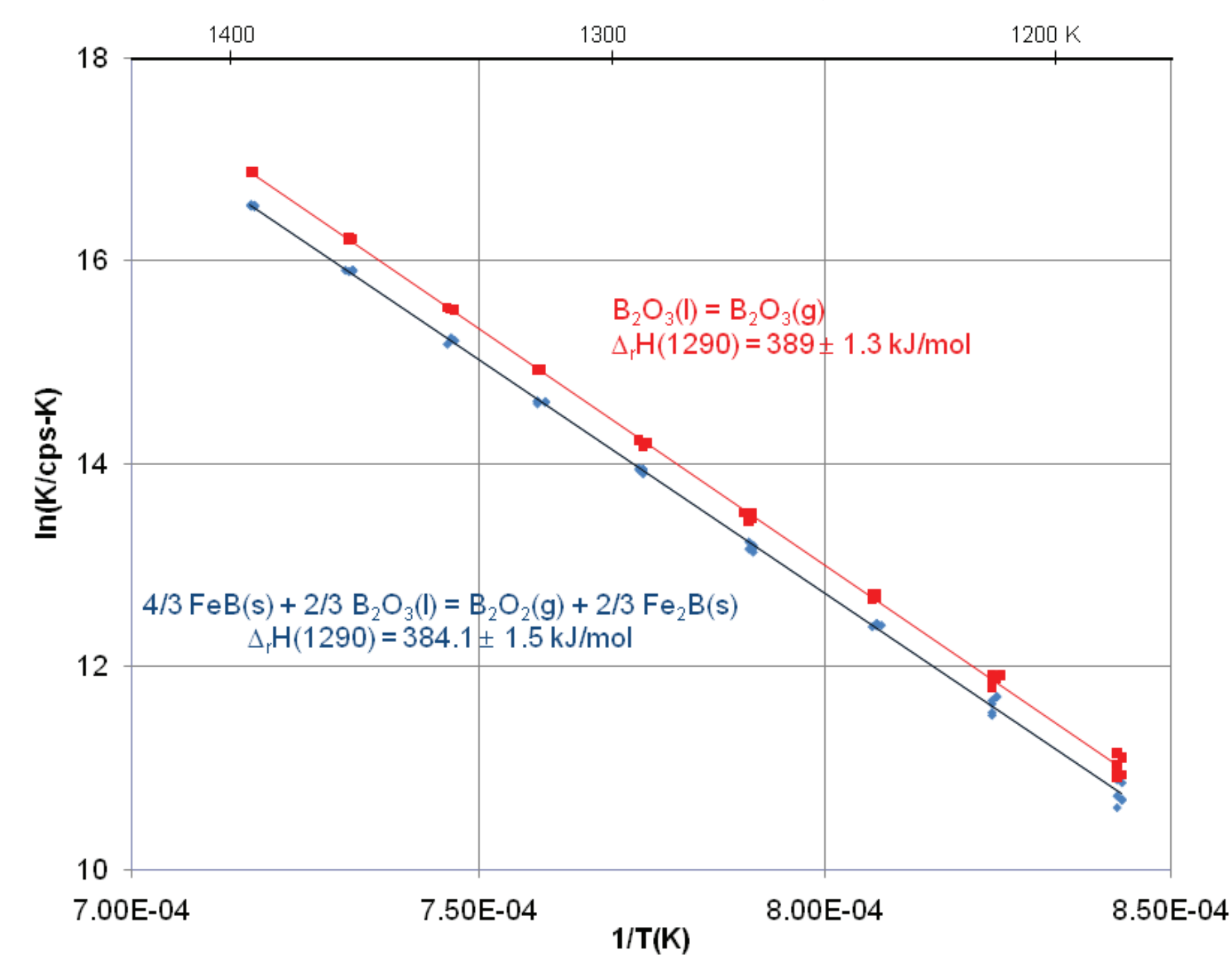


- B + B_2O_3**
 - Used by other investigators
 - $B_2O_3(l)$ does not wet B
 - Changing contact area for $2/3 B + 2/3 B_2O_3(l) = B_2O_3(g)$
 - Led to lack of reproducible $B_2O_3(g)$ vapor pressures



- Use FeB/Fe₂B + B_2O_3**
 - Two-phase mixture fixes B activity
 - No changes in mixture—contact area remains constant
 - $4/3 FeB + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 Fe_2B$
 - Gave reproducible vapor pressures

1:1:1 FeB:Fe₂B: B_2O_3 Mixture



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

- Use heats of formation of other compounds:
 - $4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 Fe_2B(s)$
 - $4/3 B(s) + O_2(g) = 2/3 B_2O_3(l)$ [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 $\Delta_f H_{298.15}^\circ B_2O_3(g)$

Investigator and Technique	Data Points	Average Temperature K	Enthalpy of Reaction			$2B(s) + O_2(g) = B_2O_2(g)$		Tables
			2 nd Law kJ/mol	3 rd Law kJ/mol	3 rd Law kJ/mol	From 2 nd Law kJ/mol	From 3 rd Law kJ/mol	
Inghram et al. (KEMS) [3] $2/3 B + 2/3 B_2O_3(l) = B_2O_3(g)$	6	1400	302.5 ± 4.2	407.0 ± 7.2	391.5 ± 0.7*	-509.4	-444.1	
Inghram et al. (KEMS) [3] $2/3 B + 2/3 B_2O_3(g) = B_2O_3(g)$	3	1410	103.4 ± 1.0	104.9 ± 1.1	101.4 ± 0.3	-455.2	-458.7	
Scheer—Torsion [4] $2/3 B + 2/3 B_2O_3(l) = B_2O_3(g)$	14	1390	382.5 ± 7.2	358.2 ± 4.4	372.7 ± 2.0	-428.6	-462.9	
Rentzepis et al.—Collection [5] $B_2O_3(l) + C = B_2O_3(g) + CO$	3						-466.2 ± 6.5	
Searcy and Myers [6] $2MgO + 2B = 2Mg + B_2O_3$	1	1375					-458.9 ± 16.7	
JANAF [16]								-456.1 ± 8.4
IVTAN [18]								-457.78**
This Study—Run 1 $4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 Fe_2B$	8	1284	363.8 ± 2.8	383.9 ± 2.9	413.0 ± 1.6	-498.0	-471.4	
This Study—Run 2 $4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 Fe_2B$	6	1280	376.7 ± 1.4	399.0 ± 1.5	413.0 ± 0.9	-484.0	-430.0	
This Study—Run 3 $4/3 FeB(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 Fe_2B$	9	1290	384.0 ± 1.5	405.3 ± 1.5	414.0 ± 0.7	-473.5	-480.0	
This Study—Run 1 $4/3 Fe_2B(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 FeB$	8	1270	373.2 ± 1.7	401.7 ± 1.8	428.7 ± 1.7	-451.7	-424.7	
This Study—Run 2 $4/3 Fe_2B(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 FeB$	6	1225	380.8 ± 1.7	409.9 ± 1.7	430.5 ± 1.3	-443.5	-423.1	
This Study—Run 3 $4/3 Fe_2B(s) + 2/3 B_2O_3(l) = B_2O_3(g) + 2/3 FeB$	9	1290	389.0 ± 1.3	417.9 ± 1.3	430.9 ± 0.6	-435.5	-422.5	

*Inghram 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 $\Delta_f H_{298.15}^\circ B_2O_3(g)$

Investigator	Number of Data Points	Average Temperature T	$B_2O_3(l) = B_2O_3(g)$			$2B(s) + 3/2 O_2(g) = B_2O_3(g)$		Tables
			2 nd Law	2 nd Law	3 rd Law	From 2 nd Law	From 3 rd Law	
Hildenbrand—Torsion [19]			302.5 ± 4.2	427.5	417.3	-825.9	-836.0	
Scheer—Torsion [20]	14	1500	364.9 ± 3.8	402.6 ± 3.9	424.2 ± 0.9	-442.2	-429.2	
Shube et al.—mass spectrometry and weight loss [21]	14			412.1 ± 8.4	415.5 ± 0.1			
JANAF [16]								-456.0 ± 4.2
IVTAN [18]								-453.38**
This Study— B_2O_3 only	11	1320	380.8 ± 1.2	410.7 ± 1.3	429.5 ± 1.2	-442.6	-423.9	
This Study—Run 1 $Fe_2B_3B_2O_3$	8	1270	373.2 ± 1.7	401.7 ± 1.8	428.7 ± 1.7	-451.7	-424.7	
This Study—Run 2 $Fe_2B_3B_2O_3$	6	1225	380.8 ± 1.7	409.9 ± 1.7	430.5 ± 1.3	-443.5	-423.1	
This Study—Run 3 $Fe_2B_3B_2O_3$	9	1290	389.0 ± 1.3	417.9 ± 1.3	430.9 ± 0.6	-435.5	-422.5	

Conclusions

- Theoretical and experimental determination of heat of formation of $B_2O_3(g)$ and $B_2O_3(l)$
- Theoretical: Quantum chemistry composite method
- Experimental: Use Fe₂B/FeB mixture to set B activity, gave more reliable results than B alone
- For $B_2O_3(g)$ $\Delta_f H_{298.15}^\circ = -479.9 \pm 25.7$ kJ/mol
- For $B_2O_3(l)$ $\Delta_f H_{298.15}^\circ = -833.4 \pm 13.1$ kJ/mol

References

- Jacobson, N. S.; Myers, D. L. *J. Phys. Chem.* **2011**, in press.
- Copland, E. H.; Jacobson, N. S. *NASA/TN-2010-216795*.
- Inghram, M. G.; Pitzer, R. F.; Chupka, W. A. *J. Chem. Phys.* **1956**, *25*, 498.
- Scheer, M. D. *J. Phys. Chem.* **1958**, *62*, 400.
- Rentzepis, P.; White, D.; Walsh, P. N. *J. Phys. Chem.* **1960**, *64*, 1784.
- Searcy, A. W.; Myers, C. E. *J. Phys. Chem.* **1967**, *61*, 957.
- Nguyen, M. T.; Mattau, M. H.; Vu, T. N.; Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2009**, *113*, 4895.
- Jensen, F. "Introduction to Computational Chemistry" p164-169, John Wiley and Sons, 1999.
- Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.
- Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, *114*, 8014.
- 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, M.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Blizov, 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.; Kudrin, 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.; Comperti, 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.
- <http://www.nist.gov/pml/chemistry/csd/csd.cfm>, 2009 [cited 2011].
- Cubicciotti, D. *J. Phys. Chem.* **1966**, *70*, 2410.
- Copland, E. H. *NASA Contractor Report 2009-215498*.
- Drowart, J.; Goldfinger, P. *Ang. Chemie-Int. Ed.* **1967**, *6*, 581.
- 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.
- Barin, I. *Thermochemical Data of Pure Substances 3rd Edition*; VCH: Weinheim, 1995.
- Gurvich, L. V.; Veys, I. V.; Alcock, C. B. eds. *Thermodynamic Properties of Individual Substances 4th ed.*; Begell House: New York; 1989.
- Hildenbrand, D. L.; Hall, W. F.; Pitzer, N. D. *J. Chem. Phys.* **1963**, *39*, 296.
- Scheer, M. D. *J. Phys. Chem.* **1957**, *61*, 1184.
- Shultz, M. M.; Stolyarova, V. L.; Semenov, G. A. *Fizika i Khimiya Stekla* **1978**, *4*, 653.

Acknowledgments

Deliberate discussions with Dr. E. Copland, AT1 Allvac, Monroe, NC, are very much appreciated. OSCAR (University of Oklahoma) Director Henry Neeman, Sr., Systems Analyst David Akin, and Joshua Alexander, HPC Application Software Specialist, provided valuable technical expertise. We also thank Dr. C. Rice and Mr. M. Halye, Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK, for assistance with the ab initio calculations. We are also grateful to Dr. Valentina Stolyarova, St. Petersburg State University, St. Petersburg, Russia, for many helpful comments. Support from Supersonics Research, Fundamental Aeronautics Program is appreciated.