



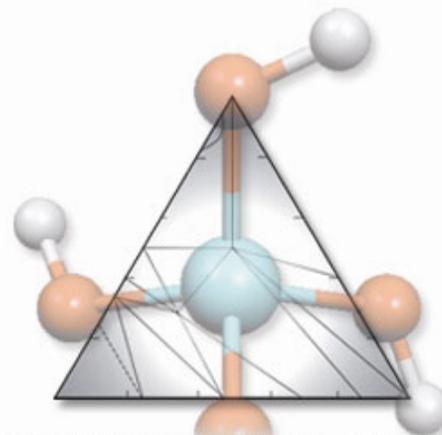
Quantum Chemistry, the Web, and You: Using Computers to Generate a Really Useful Thermodynamic Database

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THERMODYNAMICS RESOURCE



Thermodynamic data are the foundation for understanding any chemically reacting system



- **Why?**

- Chemical equilibrium calculations
- Reverse reaction rates (through microscopy reversibility)
- Rate constants (bond energies)
- Activation energies (transition-state structures, energies)

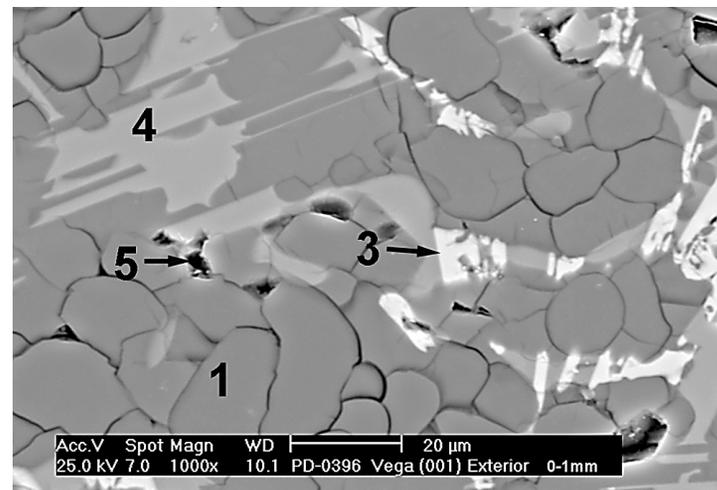
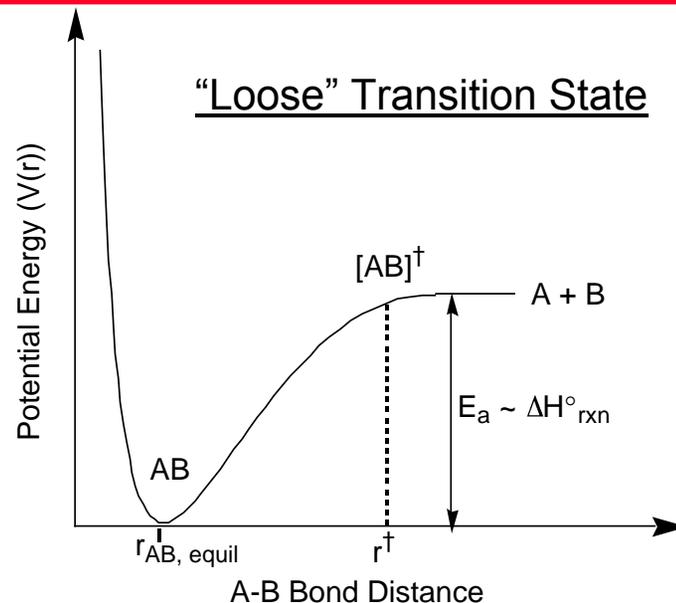
- **What?**

- Heat of formation
- Heat capacity
- Enthalpy
- Entropy

- **Applications:**

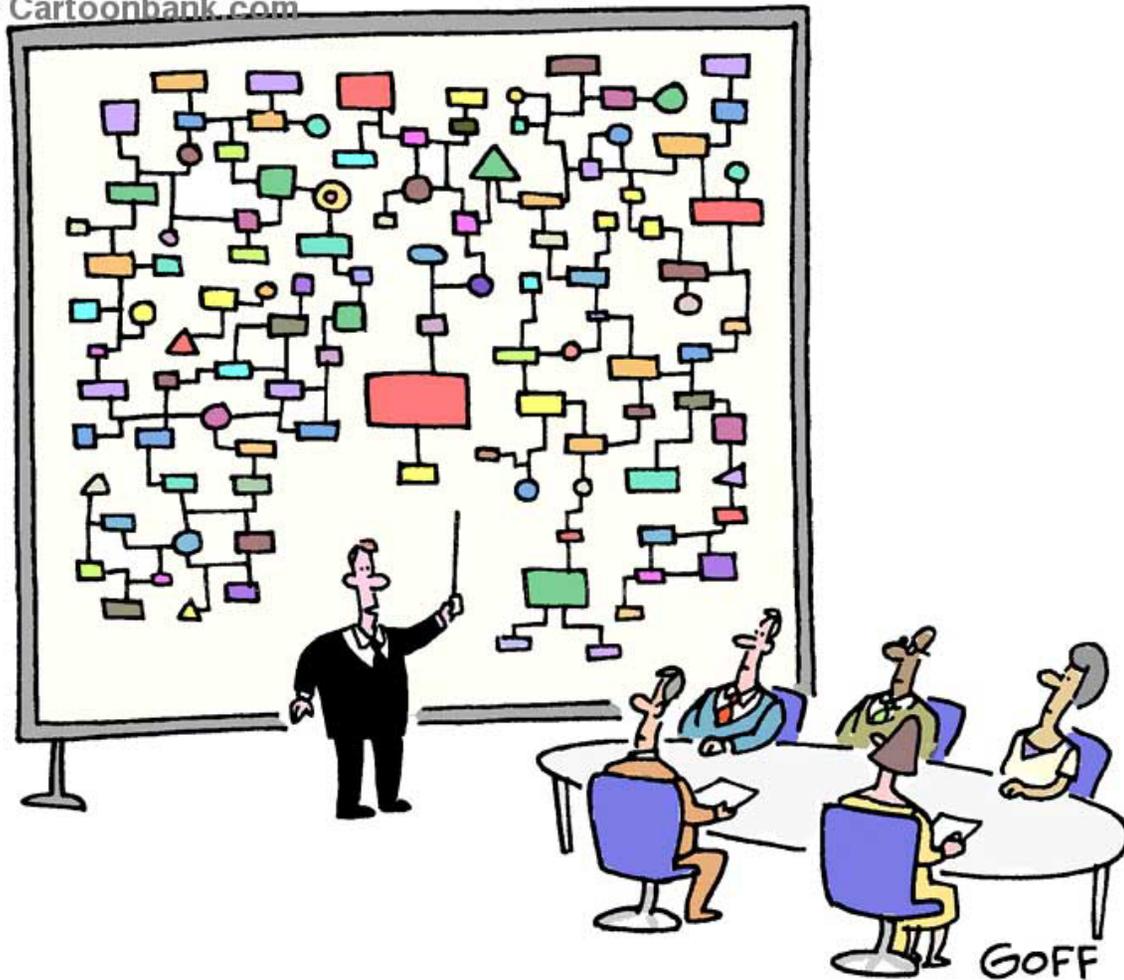
- Corrosion
- Glass manufacturing
- Chemical vapor deposition
- Catalysis
- Combustion

Corrosion of low-density silica refractory by NaOH(g) at high temperature





"We have lots of information technology. We just don't have any information."



“And that’s why we need a computer.”

Computational methods are often the only option for obtaining crucial thermodynamic data

DOE Industrial Technologies Program is funding a 5-year effort at Sandia and Oak Ridge National Labs



- Provide a practical thermodynamic resource
 - Gas-phase molecules
 - Condensed phase, esp., variable composition liquids/glasses
- Develop new ab initio methods
- Model condensed-phase oxide systems
- Distribute data using web-based tool



Combustion, Heat treating



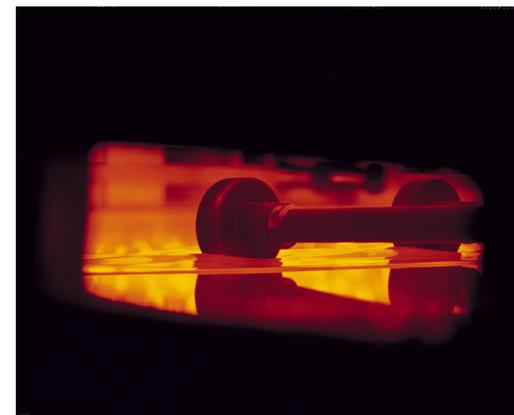
Steel/Metals refining



Glass Manufacturing



Chemicals & Petroleum



Glass coating operations

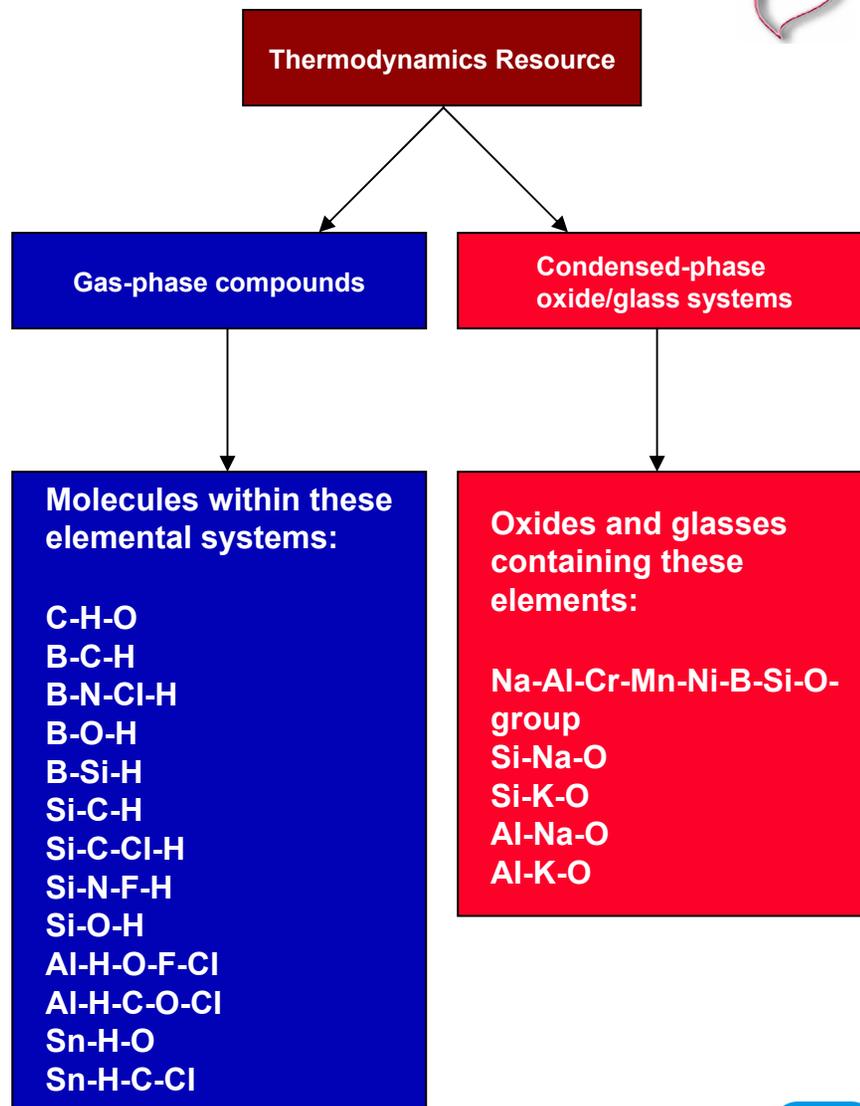
Systems included in the database are selected for their relevance to problems in the DOE/ITP Industries of the Future and through critical assessment of the available data



Thermodynamics Resource is divided into gas-phase data and models of condensed-phase systems



- **Gas phase (Sandia)**
 - Data derived from ab initio quantum chemistry methods
 - Small molecules (typically < 20 atoms)
 - Main-group chemistries
 - Some transition-metal data
- **Condensed phase (ORNL)**
 - Data derived modeling phase diagrams and critical assessments
 - Complex oxide systems
 - Glasses
 - Stoichiometric compounds
- **Both databases are continually updated and expanded**



To calculate gas-phase thermodynamic data several pieces of information are required



Quantity	Required Inputs	Level of Calculation
Heat of formation	<ul style="list-style-type: none">• Electronic energy with electron correlation• Atomic heats of formation (from experiment)	<ul style="list-style-type: none">• High• Electron correlation required:<ul style="list-style-type: none">* Perturbation theory* Coupled Cluster theory* Configuration Interaction
Heat capacity	<ul style="list-style-type: none">• Moments of inertia (molecular structure)• Vibrational frequencies• Barriers for internal rotation	<ul style="list-style-type: none">• Low• Electron correlation optional (HF, DFT, MP2)
Enthalpy, Entropy	Heat capacity	Statistical mechanics



We use the *Bond Additivity Correction (BAC)* suite of methods to predict molecular thermochemistry



- **BAC-MP4**
 - Original BAC method developed in 1980s for main-group compounds
 - Designed to be computationally practical
 - Recently modified to handle 4th-row main group (In, Sn, Sb)
- **New class of BAC methods: *fewer parameters, greater accuracy***
 - BAC-G2 } *High accuracy, broader applicability*
 - BAC-MP2 } *Useful for large molecules*
 - BAC-DFT }
 - BAC-G3 } *Currently under development*
 - BAC-Coupled Cluster }
 - high accuracy
 - useful for highly unsaturated systems
 - “multireference” cases (e.g., diatomics, oxides, transition-metal compounds)
 - determination of reference thermo
- **Statistical mechanics routines to convert *ab initio* results to useful thermochemistry**
 - Scaled vibrational frequencies
 - Hindered rotor corrections



The BAC-MP4 method can provide accurate thermodynamic data for main-group compounds



- Model corrects for systematic errors due to

- Finite basis set size
- Limitations of theory

- MP4(SDTQ)/6-31G(d,p)//HF/6-31G(d)

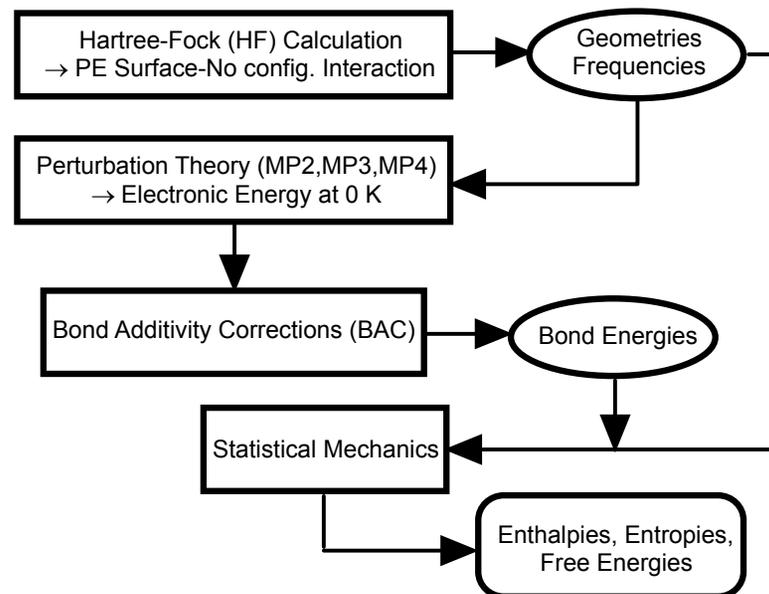
+ Empirical corrections:

$$E_{\text{BAC}}(\mathbf{X}_i - \mathbf{X}_j) = f_{ij} g_{kij}$$

Where:

$$f_{ij} = A_{ij} \exp(-a_{ij} R_{ij})$$

g_{kij} = accounts for nearest-neighbor interactions

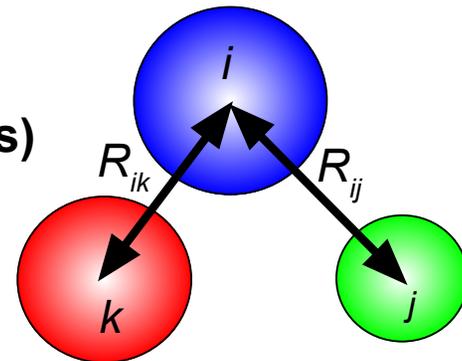


Advantages

- Practical for a wide range of molecules (up to 20 atoms)
- Universal correction factors

Disadvantage

- Accurate reference compounds required to calibrate method



An ad hoc method provides a confidence level for BAC calculations



- Errors in quantum chemistry calculations:
 - Not random
 - Systematic due to limitations of
 - Theory
 - Basis set
 - Reference quantities (e.g., atomic heats of formation)
- **Rate of convergence** provides a measure of relative uncertainty

$$\text{Error(BAC-MP4)} = \{1.0 \text{ kcal mol}^{-1} + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP3}})^2 + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP4SDQ}})^2 + 0.25(E_{\text{BAC}}(\text{spin}_S^2) \text{ or } E_{\text{BAC}}(\text{spin}_{\text{UHF-I}}))^2\}^{1/2}$$

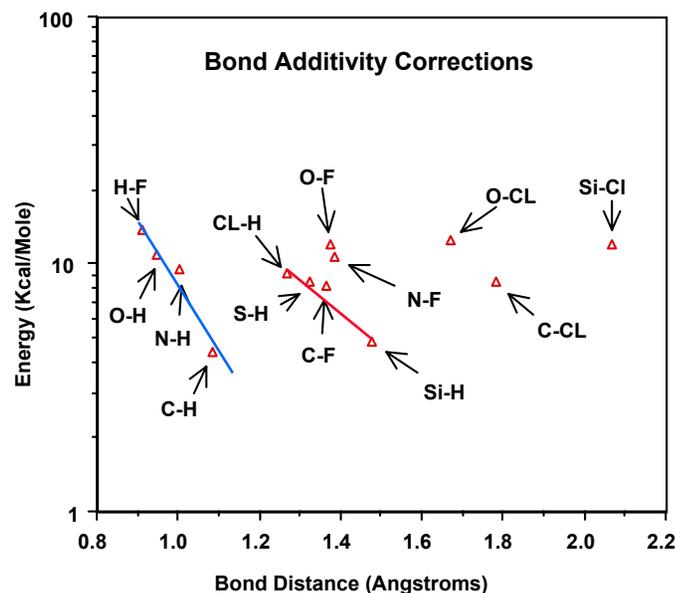
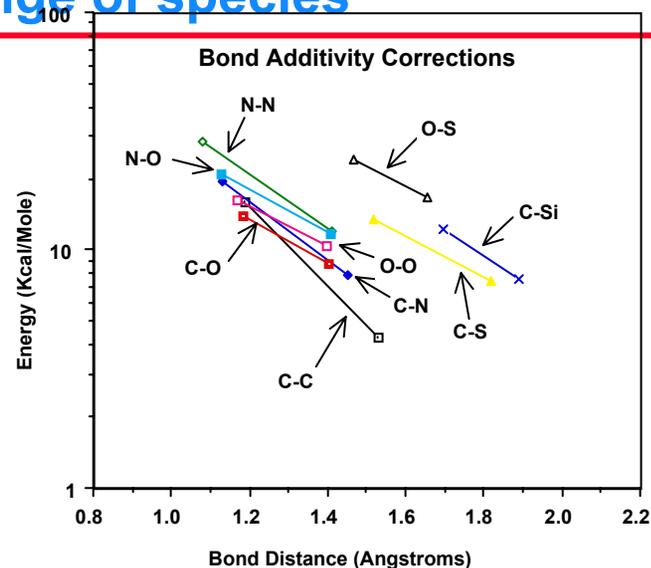
- Additional uncertainty may arise from
 - Spin contamination of the ground state (e.g., $^3\text{CH}_2$)
 - UHF instability (open-shell molecules, e.g., singlet SiH_2)



The BAC method is optimized to achieve the best overall agreement with experiment over a range of species



- Accumulation of error in large molecules (e.g. C_6H_{12}) is also minimized
- Trends allow parameters for poorly characterized bond types to be estimated (e.g., B or P compounds)
- Reference compounds
 - CH_4 , C_2H_2 , H_2CO , CO_2
 - H_2 , H_2O , H_2O_2
 - NH_3 , NO , N_2 , HCN , HNO , NH_2OH
 - O_2
 - CH_3F
 - HF , HO_F
 - BH_3 , BCl_3 , BF_3 , $B(CH_3)_3$
 - $SiCl_4$, SiH_4 , $Si(CH_3)_4$



Examples of BAC-MP4 results: 1st and 2nd row main-group elements



Typical accuracies:

- $\pm 8\text{-}12$ kJ/mol ($\pm 2\text{-}3$ kcal/mol) for closed-shell, hi-valent species (e.g., SiX_4)
- $\pm 9 - 28$ kJ/mol ($\pm 3\text{-}7$ kcal/mol) for:
 - Compounds with a large number of bonds (accumulation of error)
 - Species with UHF instability (e.g., SiH_2 ($^1\text{A}_1$))
 - Species with spin contaminated ground states (e.g., CH_2 ($^3\text{B}_1$))

	ΔH°_{298} (Calc) kJ mol ⁻¹	ΔH°_{298} (Obs) kJ mol ⁻¹		ΔH°_{298} (Calc) kJ mol ⁻¹	ΔH°_{298} (Obs) kJ mol ⁻¹
BHCl ₂	-253.5 ± 4.3	-251 ± 4	SiH ₂ Cl ₂	-311.4 ± 4.6	-320.5 ± 12
BH ₂ Cl	-84.89 ± 4.3	-80.8 ± 20	SiCl ₂	-151.3 ± 15.6	-163.1 ± 10
B(OH) ₃	-1003 ± 8	-1004 ± 20	SiH ₂	271.1 ± 9.2	273.6 ± 5.0
C ₂ H ₄	51.51 ± 4.3	52.3 ± 0.4	SiHF ₃	-1207.6 ± 5.6	-1200.8 ± 20.9
CH ₃	146.0 ± 6.3	146 ± 0.4	Si(OC ₂ H ₅) ₄	-1328	-1315 ± 4
C ₂ H ₅	120.6 ± 6.7	118.5 ± 5.9	HSi(CH ₃) ₃	-163 ± 4	-163.8
NH	364.0 ± 4.6	377 ± 17	H ₂ Si=CH ₂	170.3 ± 10	154.8 ± 20.1
NH ₂	192.9 ± 4.6	190 ± 6	CH ₃ SiCl ₃	-576.6 ± 4.2	-569 ± 11

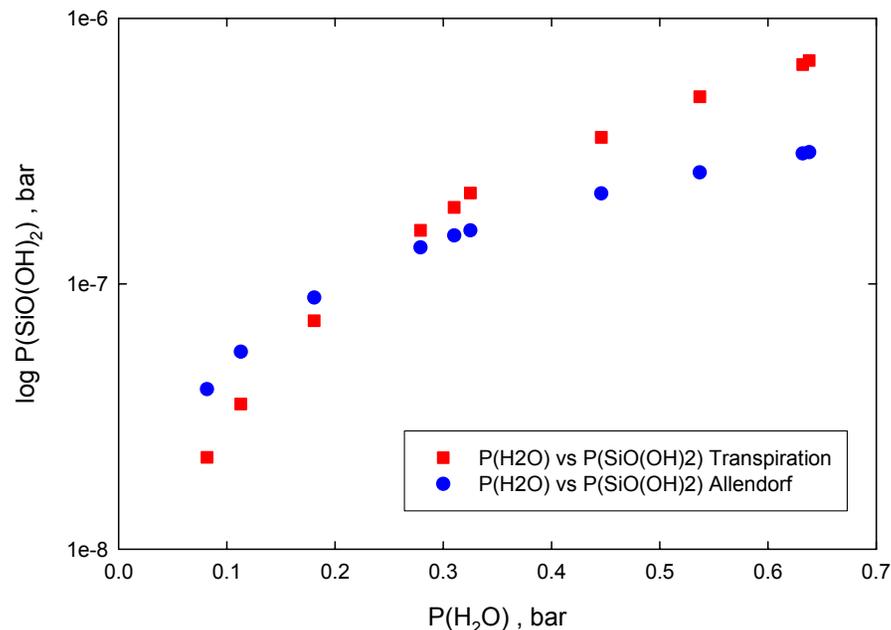


Experimental data are in excellent agreement with BAC predictions for silicon and aluminum hydroxides

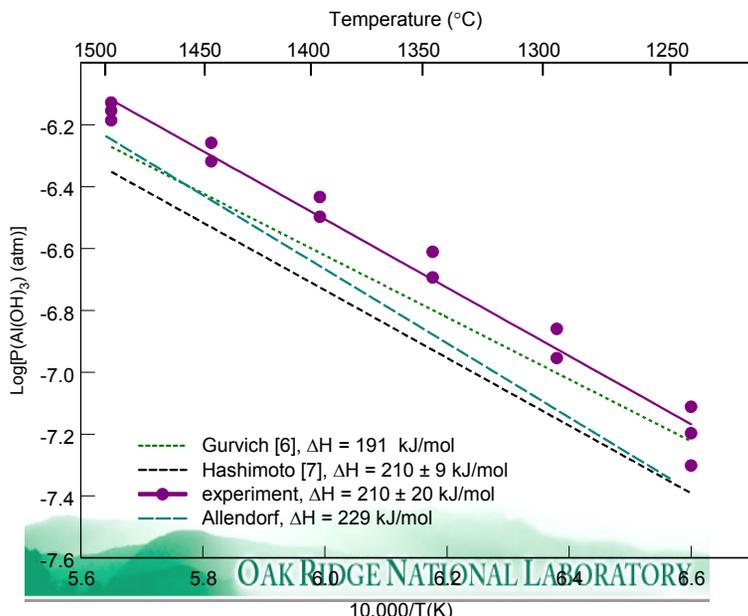


Heat of reaction: $\text{SiO}_2(\text{cr}) + \text{H}_2\text{O}(\text{g}) = \text{Si}(\text{OH})_4(\text{g})$

Study	T(K)	$\Delta_r H^*$
Second law Hashimoto (1992)	1600	56.7 ± 1.7
2nd law Jacobson et al	1200	54.6 ± 2.7
3rd law Jacobson	298.15	58.4 ± 3.6
BAC-MP4	298.15	55.3
Krikorian	298.15	56.5



**$\text{SiO}(\text{OH})_2$: BAC-MP4 vs experiment (1673 K).
Jacobson et al. 2003, NASA/GRC**



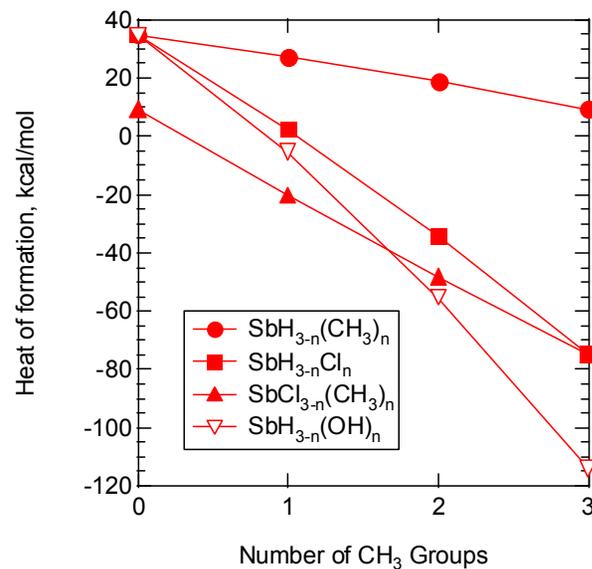
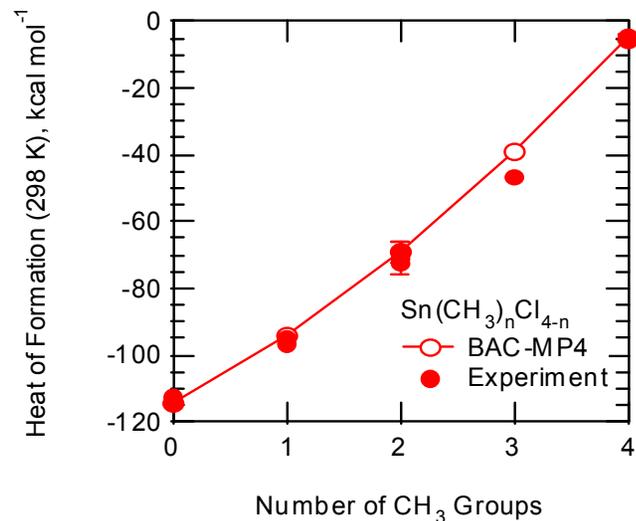
**$\text{Al}(\text{OH})_3$: BAC-G2 vs experiment
Opila et al. 2004, NASA/GRC**



The BAC-MP4 method can now handle 4th-row main-group compounds



- Elements In, Sn, and Sb are not included in the 6-31G(d) basis set
- Relativistic effects are important for compounds of these heavy elements
- Use relativistic effective core potential (ECP) to model the non-valence electrons:
 - $1s^2 2s^2 2p^6 3s^2 3p^6$ in core
 - $3d^{10} 4s^2 4p^n$ in valence
- Data obtained for tin and antimony compounds with these ligands:
 - H, $C_n H_{2n+1}$ (n=1-4), OH, Cl
 - Tin predictions agree well w/ available data (captures “anomeric” effect)
 - Antimony predictions are consistent with other main-group trends



A new class of BAC methods improves the accuracy of ΔH°_f over a broad range of molecules



- Most of the error is concentrated in the predicted ΔH°_f for the atoms
- Bond-wise corrections are generally small

$$E_{BAC\text{-correction}}(total) = \underbrace{\sum_k E_{BAC\text{-atom}}(A_k)}_{\substack{\text{From minimization of BAC-G2} \\ \Delta H^\circ_f \text{ for 143-molecule set}}} + \underbrace{E_{BAC\text{-molecule}}}_{\substack{\text{Spin pairing} \\ \text{a) Electron correlation} \\ \text{b) Spin contamination}}} + \underbrace{\sum_{ij} E_{BAC\text{-bond}}(A_i A_j)}_{\substack{\text{a) Bond} \\ \text{b) Nearest Neighbor}}}$$

- BACs established by optimizing ΔH°_f for main-group compound set
 - BAC-G2 gives best results
 - Halogenated compounds and oxides are the least accurate

Method	Avg. Error kcal/mol	Max. Error kcal/mol
BAC-G2	1.09	2.68
G2 (approx. QCISD(T)/6-311+G(3df,sp) // MP2/6-31G*)	1.74	3.62
BAC-DFT B3LYP/6-311++G(2df,2pd) // B3LYP/6-31G*	1.57	4.04



We are developing methods to treat gas-phase compounds of Cr, Mn, Fe,



- **Cr, Mn, and Fe are common components of both refractories and metal alloys**
- **Corrosion by halides occurs in a number of industrial environments**
- **Thermodynamic data are available in the literature to test and establish methods**
- **Theory is mostly in agreement with the experimental values**
- **Oxides and hydroxides will be treated next**

Compound	Theory	Experiment
MnF	-17.8	-5.2
MnF ₂	-130.1	N/A
MnCl	17.6	15.8± 1.6
MnCl ₂	-62.6	-62.6 ± 1

Compound	Theory	Experiment
FeF	11.9	11.40 ±4.78
FeF ₂	-104.7	-93.10 ±3.39
FeCl	49.8	49.5 ±1.6
FeCl ₂	-33.4	-33.7 ±0.5

	Theory	Experiment
CrF	-5.2	4.57 ± 2.41
CrF ₂	-105.3	-103.23 ± 2.96
CrCl	30.9	31.05±0.65
CrCl ₂	-36.9	-28.11 ± 0.41



Status of gas-phase database



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

- Data now available

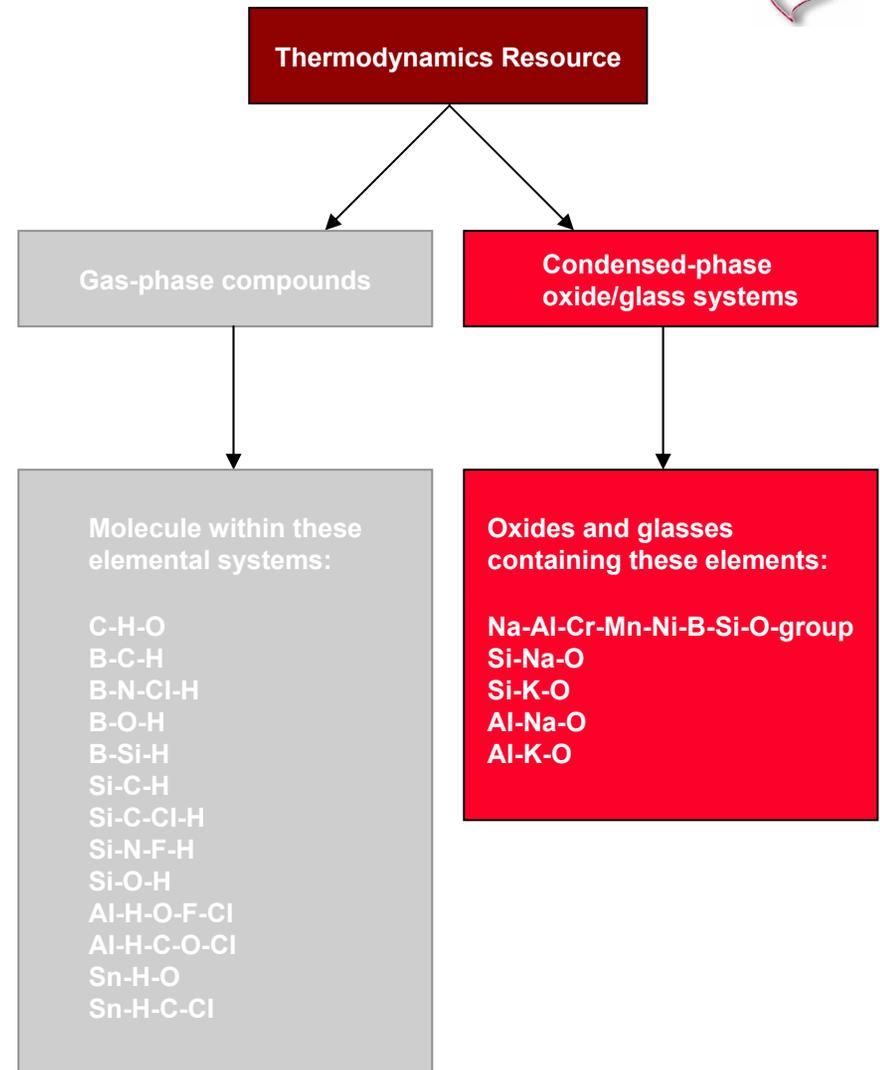
- > 850 compounds on line
- > 400 C-H-O compounds
- 66 Al-H-C-N-O-F-Cl compounds
- > 200 Si-H-C-N-O-F-Cl compounds
- 47 Si-B-H-Cl compounds
- 60 Sn-H-C-Cl compounds
- Ti, Cr, Mn, Fe hydrides, halides, fluorides, hydroxides (projected 9/04)

	Complete		Data available but not yet on web site
	Partially uploaded dataset		New method and data
	Newly added data		Method under development
	Data available elsewhere		New elements for PY4

The condensed-phase *Thermodynamics Resource* provides models of complex oxide thermochemistry



- Provides data relevant to performance of refractories and glasses at high temperature
 - Glass melting
 - Refractory corrosion by water, oxygen, and alkali
 - Nuclear waste glass
 - Slag in combustion systems
- Models available include industrially important refractories:
 - Silica
 - Mullite
 - Chromia
 - Alumina

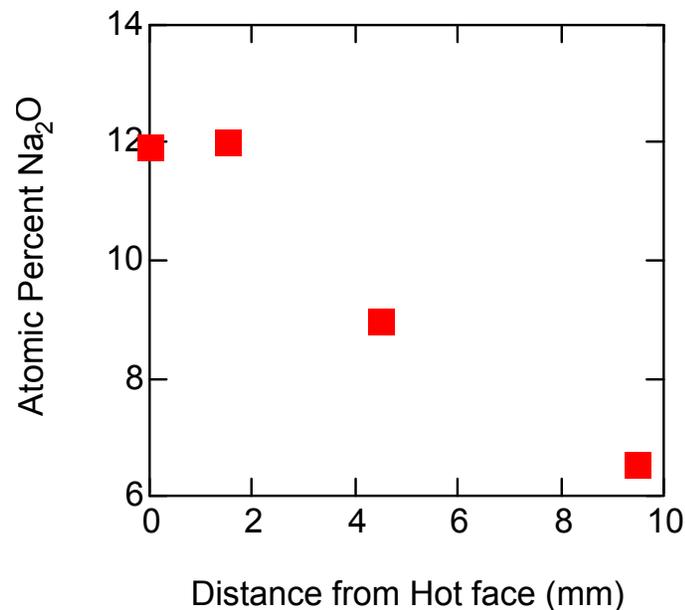
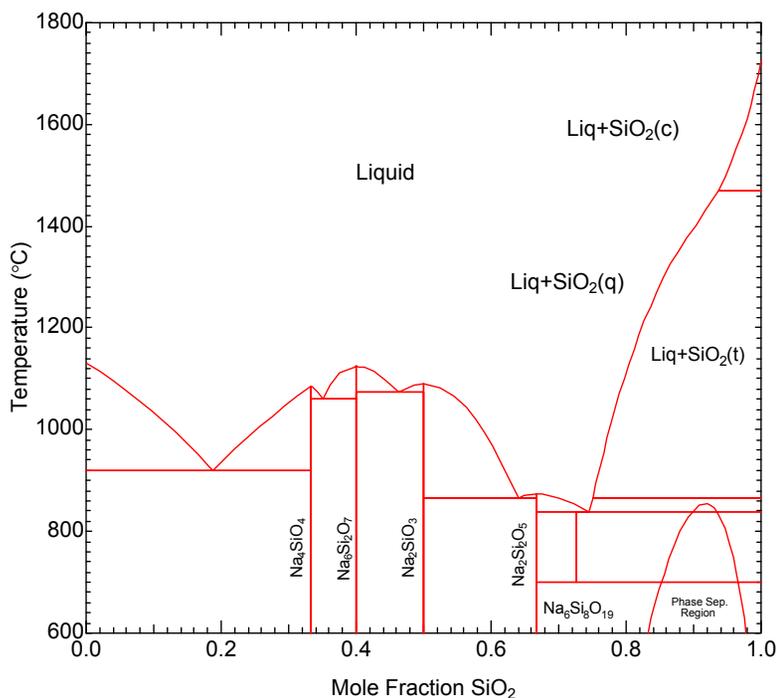
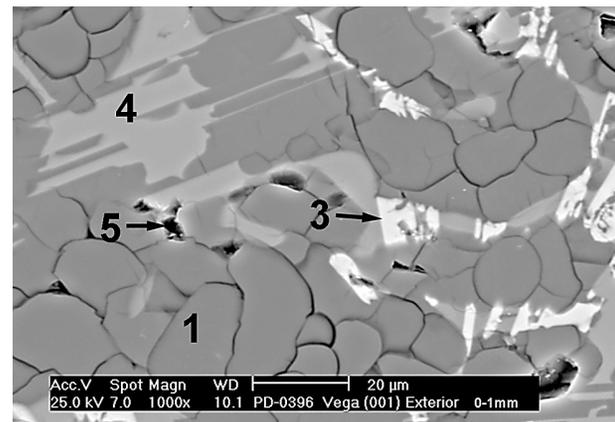


High-temperature oxide equilibria are difficult to model due to non-ideal solution behavior



- Ideal solutions of the end-member oxides give highly inaccurate results
- Large number of interaction parameters
- Miscibility gaps can occur
- Practical models are needed to describe these chemical systems

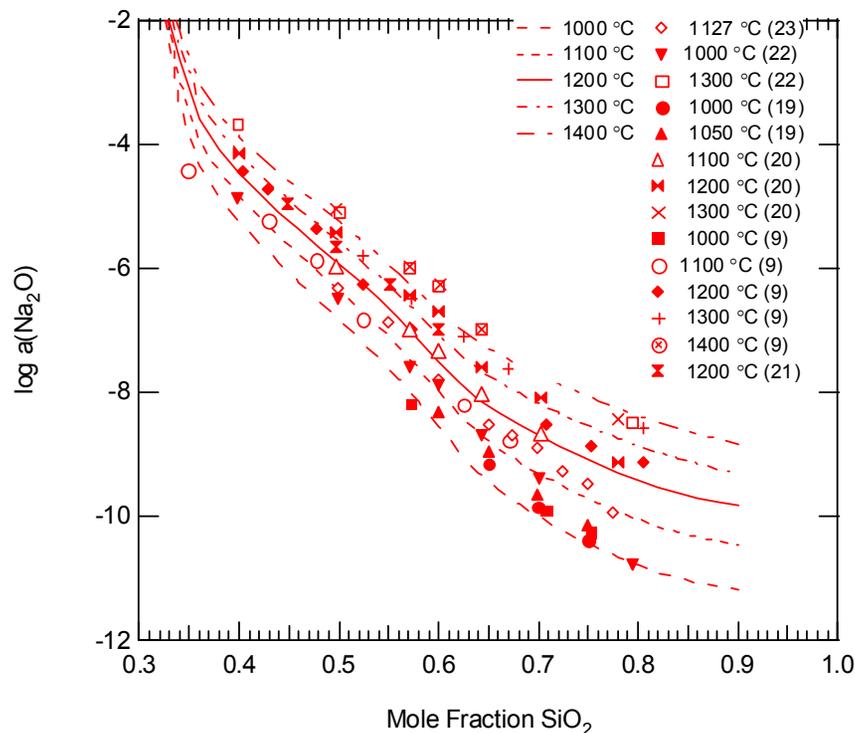
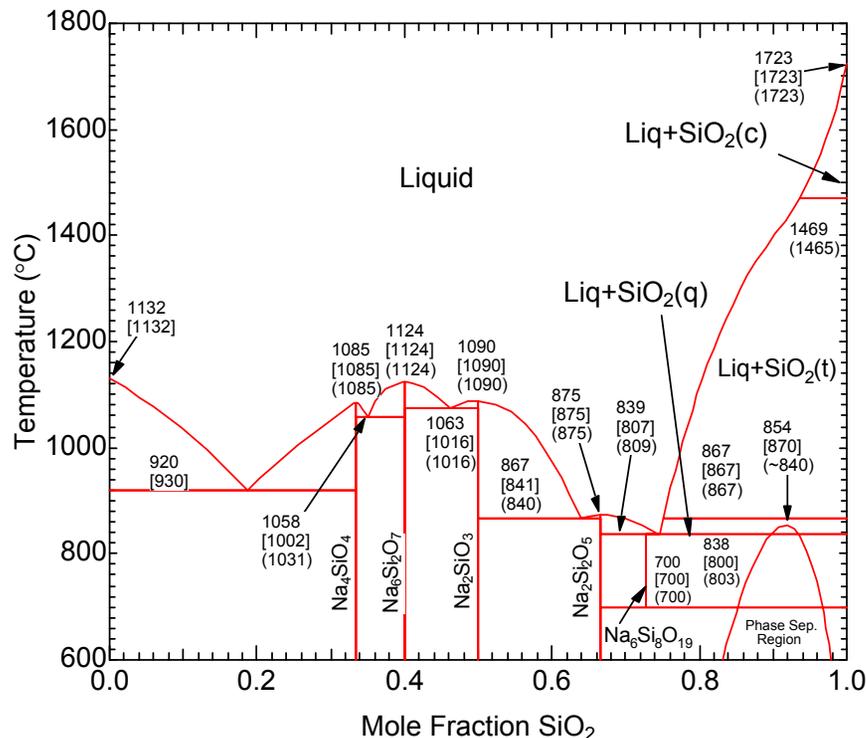
Corrosion of low-density silica refractory by NaOH(g) at high temperature



A very good fit to the phase diagram and measured activities is achieved by the Associate Species Model



Na₂O/SiO₂ system



Values in () are from the literature

“Thermodynamic Analysis of Silica Refractory Corrosion...” M. D. Allendorf, K. E. Spear, *J. Electrochem. Soc.* **148**, B59-B67 (2001)



Current database for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3-\text{MnO}-\text{NiO}-\text{B}_2\text{O}_3-\text{SiO}_2$



Glass/Liquid

Si_2O_4 $\text{NaAlSiO}_4:2/3$
 Al_2O_3 $\text{NaAlSi}_2\text{O}_6:/2$
 B_2O_3 $\text{Al}_2\text{NiO}_4:2/3$
 Cr_2O_3 $\text{Al}_2\text{MnO}_4:2/3$
 Ni_2O_2 $\text{Mn}_2\text{SiO}_4:2/3$
 Mn_2O_2 MnNiO_2
 $\text{Al}_6\text{Si}_2\text{O}_{13}:/4$
 $\text{Na}_4\text{B}_2\text{O}_5:/3$
 NaBO_2
 $\text{Na}_2\text{B}_4\text{O}_7:/3$
 $\text{Na}_2\text{B}_8\text{O}_{13}:/5$
 Na_2O
 NaAlO_2
 $\text{Na}_2\text{Al}_4\text{O}_7:/3$
 $\text{Na}_4\text{SiO}_4:2/5$
 $\text{Na}_2\text{SiO}_3:2/3$
 $\text{Na}_2\text{Si}_2\text{O}_5:/2$

Solution Phases

Mullite:
 $\text{Al}_6\text{B}_{1.33}\text{O}_{11}$
 $\text{Al}_6\text{Si}_2\text{O}_{13}$

 Nepheline:
 NaAlSiO_2
 $\text{NaAlSi}_2\text{O}_6$
 NaAlO_2

 Corundum:
 Al_2O_3
 Cr_2O_3

Crystalline Phases

Al_2O_3 Na_4SiO_4
 B_2O_3 Na_2SiO_3
 SiO_2 (cris) $\text{Na}_2\text{Si}_2\text{O}_5$
 SiO_2 (trid) NaAlO_2
 SiO_2 (quar) $\text{Na}_2\text{Al}_{12}\text{O}_{19}$
 Na_2O $\text{Na}_2\text{Al}_{22}\text{O}_{34}$
 NiO NaAlSiO_4
 Cr_2O_3 NaAlSi_2O
 MnO $\text{NaAlSi}_3\text{O}_8$
 Na_3BO_3 Al_2NiO_4
 $\text{Na}_4\text{B}_2\text{O}_5$ Cr_2NiO_4
 NaBO_2 Ni_2SiO_4
 $\text{Na}_2\text{B}_4\text{O}_7$ Al_2MnO_4
 NaB_3O_5 MnSiO_3
 $\text{Na}_2\text{B}_8\text{O}_{13}$ Mn_2SiO_4
 NaB_5O_8 $\text{Al}_4\text{Mn}_2\text{Si}_5\text{O}_{18}$
 $\text{NaB}_9\text{O}_{14}$ $\text{Al}_4\text{Mn}_3\text{Si}_3\text{O}_{12}$



Today, the web is by far the best – and maybe the most effective – way to distribute information



© Cartoonbank.com



"First of all—you need a Web site."





The database has been on line since August 2002

<http://www.ca.sandia.gov/HiTempThermo/index.html>

Thermodynamic Properties

[Privacy & Security](#)

Site Links: [MP4] C1H4 [CH4]

[HiTempThermo Home](#) [Additional Data](#) [Find another molecule](#)

[Gas-Phase Data](#) **CHEMKIN Coefficients:** ([Explanation](#)) (Copy/Paste into your favorite text editor.)

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Basis Sets: $\Delta H_f^\circ(298) \pm \text{Error_Estimate} = -17.9 \text{ kcal/mol}$
 $S^\circ(298) = 44.44 \text{ cal/mol-K}$

[EMSL Gaussian Basis Sets](#) ΔG° at the following temperatures (kcal/mol):

300K	600K	1000K	1500K	2000K	2500K
-12.2	-5.6	4.4	17.5	30.6	43.5

Databases: [NIST Kinetics](#) **Comments:** Reference: C. F. Melius, unpublished data.



Future activities



- Links to DOE/OS-funded database collaboratory
- Collaboration with NASA/Glenn Research Center (experimental measurements of gas-phase transition-metal thermochemistry)
- Theory development for transition-metal compounds
- Expansion of main-group species and updating with BAC-G2 values
- Use of *Thermodynamics Resource* as a tool for teaching thermodynamics and modeling



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- **Karl Spear (Materials Science & Engineering, Penn State University)**
- **Nathan Jacobsen, Elizabeth Opila (NASA/Glenn Research Center)**
- **Funding:**

US/DOE Industrial Technologies Program
Industrial Materials for the Future Program



BAC-CCSD(T) results for compounds of heavy elements are in good agreement with the (limited) data



- **BAC parameters obtained by optimizing fit for a 70-molecule set (elements H, C, O, Cl, Ti, Sn)**
- **Heats of formation for tin compounds**
 - Best –available experimental data
 - Hi-level theory
 - CCSD(T)/triple- and quadruple zeta correlation-consistent basis sets
 - Large-core pseudopotential
 - Isogyric reactions
 - Extrapolation to infinite basis set
- **Titanium halides and small oxides**
 - Experimental data available for all compounds examined

Compound	ΔH_f° (kcal/mol)	Error*
SnO	3.4	-1.8**
SnO ₂	10.1	0.7†
H ₂ SnO	33.6	1.3†
H ₃ SnOH	-23.6	-0.4†
SnCl ₂	-47.9	0.6**
SnCl ₄	-115.1	-0.8**
SnH ₄	36.3	0.3**

Compound	ΔH_f° (kcal/mol)	Error*
TiCl	47.2	1.9**
TiCl ₂	-47.3	-0.3**
TiCl ₃	-120.7	-1.9**
TiCl ₄	-182.2	0.2**
TiO	12.2	-0.8**
TiO ₂	-72.3	0.7**

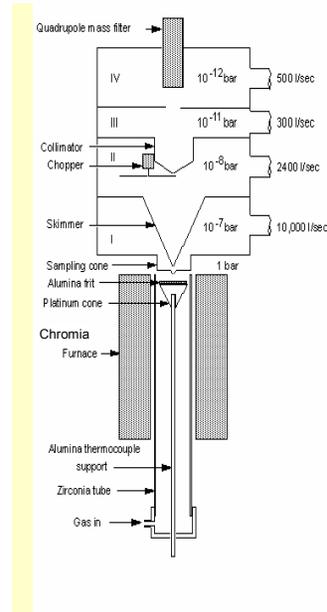
*Estimate (kcal/mol) from best available experiment (**) or theory (†)



Volatile chromium species play a key role in the high-temperature performance of Cr-containing materials



- Cr_2O_3 is volatile in high-temperature water vapor environments:
$$\frac{1}{2} \text{Cr}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \frac{3}{4} \text{O}_2(\text{g}) \rightarrow \text{CrO}_2(\text{OH})_2(\text{g})$$
- Volatility leads to reduced lifetime for Cr-base materials and contamination of system with Cr_2O_3 . Applications include:
 - Chrome-containing refractories
 - Chrome-plated tubing
 - Chromium-containing alloys
- Strategy:
 - Measure volatility using transpiration technique
 - Use Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to quantify concentration of Cr-containing species
 - Determine enthalpy and entropy of volatilization reaction



These experiments will lead to thermodynamic data that can be compared with theory to validate computational methods for transition metals



Associate Species approach simplifies modeling



- **Developed by Hastie and Bonnell (NIST) to model slags**
- **Expanded by Spear (Penn State) and Besmann (ORNL) to model nuclear waste glass**
- **Liquid/glass-phase thermochemistry**
 - **Modeled as an ideal solution of constituent compounds with constant number of non-oxygen atoms in every species**
 - **Miscibility gaps modeled using positive interaction terms**
 - **Free energy minimization routines (e.g., in FactSage or ChemSage) determine the composition and quantity of each liquid**
 - **Simple manual fitting to the phase diagram yields excellent results**



The Associate Species approach simplifies modeling of processes such as alkali corrosion



- **Example: Solutions of SiO_2 with Na_2O are non-ideal:**
 - Raoult's law cannot be used to predict equilibrium vapor pressures:
$$P_i \neq P_{\text{total}} \cdot X_i$$
- **Associate “chemical species”**
 - account for negative free energies due to non-ideal mixing of liquid SiO_2 with M_2O
 - e.g. in the $\text{Na}_2\text{O}/\text{SiO}_2$ system:
 Na_2O , $(2/5)\text{Na}_4\text{SiO}_4$, $(2/3)\text{Na}_2\text{SiO}_3$, $(1/2)\text{Na}_2\text{Si}_2\text{O}_5$, Si_2O_4
 - Positive regular solution model simulates immiscibility gaps
- **Thermodynamic data optimized to achieve best overall agreement with most accurate data for:**
 - each phase
 - phase diagram
 - measured activities for Na_2O and K_2O dissolved in liquid silica

