

1. **Project Name:** **Thermochemical Models and Databases for High-Temperature Materials Processing and Corrosion**
2. **Lead Organizations:** Sandia National Laboratories
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4. **Project Partners:** Advisory Board:
Dr. Ovidu Marin, Air Liquide
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Dr. Randy John, Shell Oil
Ms. Jill Troup, PPG Industries
Dr. David Strickler, Pilkington-LOF
Dr. Amul Gupta, Monafrax
Dr. Dilip Patel, RHI Refractories
Dr. Angel Sanjurjo, SRI International
Dr. Ellen Meeks, Reaction Design
5. **Date Project Initiated and FY of Effort:** Initiated 10/1/2001; currently in Project Year 2
6. **Expected Completion Date:** 9/30/2006
7. **Project Technical Milestones and Schedule:**

Task	Description	Planned Performance Period	Status
1	Thermodynamic Modeling of Critical Condensed-Phase System Componentws	10/1/01 – 9/30/03	Critical subcomponents of model have been successfully modeled
	Inclusion of spinel formers into model	10/01/01 – 9/30/04	In progress
	Inclusion of CaO and MgO into model	10/01/01 – 3/30/05	In progress
	Inclusion of sulfate & phosphate into model	10/01/01 – 9/30/05	
2	High-Temperature Thermochemistry of Gas-Phase Species	10/1/01 – 9/30/06	In progress
	Thermochemistry for main-group compounds (In, Sn, Sb)	10/1/01 – 9/30/02	In progress; anticipated completion date of 6/03
	Basis sets for transition metal compounds	10/1/02 – 9/30/03	in progress
	Transition-metal thermochem.: 1st row	10/1/03 – 9/30/04	
	Transition-metal thermochem.: 2nd row	10/1/04 – 9/30/05	
	Transition-metal thermochem.: 3rd row	10/1/05 – 9/30/06	

3	Database Development	10/1/01 – 9/30/06	In progress
	Prototype web site complete	4/30/02	Completed and open to public 8/31/02
	3D molecular structure visualizer	10/1/03 – 9/30/04	Completed 8/02
	FACT/ChemSage fitting software	4/1/02 – 9/30/03	In progress
	Import first half of BAC database	10/1/04 – 9/30/05	Approx. 50% of this imported to date
	Import critical condensed phase base model	10/1/01 – 9/30/03	Completed
	Import model including spinel formers	10/1/01 – 9/30/04	In progress
	Import remaining condensed phase constituents	10/1/01 – 9/30/06	
	Import second half of BAC database	10/1/05 – 9/30/06	

8. Past Project Milestones and Accomplishments: The objective of this project is to provide thermochemical data and models for an important set of materials – refractories and glasses. Such data are the basis for determining the potential for chemical interactions among materials and are essential for predicting stability and corrosion.

Task 1 Thermodynamic modeling of condensed-phase systems

- A subcontract was placed with Prof. Karl Spear (Penn State University) to supply thermochemical data for the Si-Ca-(Na or K)-O condensed-phase, which is important for predicting corrosion of ceramics in black-liquor gasification facilities and glass furnaces.
- The models for the liquid phases of the spinel forming oxides of chromium, nickel, and manganese among themselves and with the base system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ were modeled and an integrated model containing all the components was produced. The addition of these constituents will allow accurate modeling of many refractories which have binder phases containing these oxides.

Task 2 Prediction of high-temperature thermochemistry of gas-phase species

- Using the enhanced funding received this year, a Ph.D. level quantum chemist was hired at 50% time to aggressively develop new computational methods needed to predict thermochemistry for deep main-group and transition-metal compounds.
- A new computational method based on coupled-cluster theory was developed for compounds of tin, indium, antimony. Such compounds are of great importance to the glass industry as they are used to alter the properties of the glass (optical, photonic, electronic...) or used as coatings on the glass.
- An article describing the new method for calculating Sn thermochemistry was submitted to and accepted by *J. Phys. Chem. A*.

Task 3 Database development

Rapid and accurate dissemination of the data produced by this project requires electronic means of communication. Building a database on a web site is clearly the method of choice today. A major portion of the activities in this project to date involved the design and launching of a new web site tailored to provide a clear and useful display of the data in a format that is readily accessed by potential users in industry.

- The web site was launched for public and includes gas-phase and condensed-phase data. This completes a major Task 3 milestone.
- Numerous enhancements of the web site were implemented, including:

- A 3D viewer (major milestone completed *two years ahead of schedule*)
- Error estimates on gas-phase data
- An access counter on the main page
- "Shopping cart" for accumulating data prior to download to the user's computer
- 339 gas-phase species in the C-H-N-O system were included in the initial opening of the web site. These data are essential for modeling materials stability in virtually any high-temperature combustion environment.
- 66 molecules in the Al-H-C-O-F-Cl system were added to the database. These species are directly relevant to the stability and corrosion of alumina, which is key component of many refractories.
- The Na₂O-Al₂O₃-Cr₂O₃-MnO-NiO-B₂O₃-SiO₂ condensed phase system database was assembled and is now provided in the web site.
- Procedures for uploading data to the web site were documented
- A subcontract was placed to retain the services of the web manager, who left Sandia to become self employed.
- A survey was sent to members of the industry advisory board and numerous productive comments were received

9. Planned Future Milestones:

Task 1 Thermodynamic modeling of condensed-phase systems

- Complete the condensed phase model, including Ca, Mg, Fe and Zr constituents, which are key components of many commercial glasses and refractories.
- Integrate sulfate and phosphate constituents into condensed phase model. Sulfates and phosphates are found in many glasses, and are volatilized corrodants or corrosion products.

Task 2 Prediction of high-temperature thermochemistry of gas-phase species

- Complete calculations of thermochemistry for gas-phase main-group compounds, providing data for indium, tin, and antimony compounds.
- Complete a method for predicting the thermochemistry the most important first-row transition metal elements. In particular, we plan to focus on compounds of titanium, chromium, manganese, and iron.
- Publish as much of the new data for the main-group species as possible in reviewed scientific journals.

Task 3 Database development

- Add the ability to obtain temperature-dependent fits in forms useful for modeling programs other than CHEMKIN, such as FACTSage. The ability to directly use these software packages with the databases developed in this program will allow industrial users to directly model their chemical systems without the difficulty of data gathering and assessment, and without having to retain experts for development of an interface between database and chemical/finite element computational software.
- Supplement the existing web site with thermochemical data for approximately 230 silicon-containing species, 120 boron-containing species, and 75 tin-containing species. Data for higher hydrocarbon species (> C₆) will be uploaded as well.

10. Issues/Barriers

Calculation of thermochemical data for main-group oxygen compounds involving tin and other important elements deep in the periodic table proved to be impossible with standard methods. Thus, a new, more powerful, computational method had to be developed. This was done successfully during the past year and results will be displayed on the web site during the next project year. (We anticipate that accurate prediction of transition-metal thermochemistry will prove equally difficult and expect to spend the majority of the coming project year developing the methods needed to address compounds containing titanium, chromium, manganese, and iron.) The ability to include these elements in the database is important to the glass industry because they are additives/dopants that alter glass properties, or are used in glass coatings to produce higher value products. No significant deviations from the original scope or budget are expected, however.

Difficulties have arisen in the condensed phase model development as to the appropriate "standard" stoichiometry to assume for oxide liquid species. The resolution of this issue may require some reassessment of already completed models to produce more accurate and even simpler models based on a relaxed stoichiometric requirement. Any gain in simplification and accuracy of the associate species model will make understanding and using it for predicting glass melting temperatures and chemical compatibility more likely. This should be accomplished within the original schedule and budget.

11. Intended Market and Commercialization Plans/Progress

Thermochemical data for gas-phase and condensed compounds are essential for predicting the thermal and chemical stability of materials used in high-temperature and/or corrosive industrial environments. Thus, such data are expected to be of wide interest to companies involved in glass melting, chemicals production, metals refining, and pulp/paper processing. The product of this research is the data obtained from high-level computations, which is the only practical means today of obtaining this information. These data are being made freely available through an interactive web site. To alert potential users to this resource, we have widely advertised it through both electronic and print-media. For example, the site was written up in Sandia *Combustion Research News*, a publication mailed to over 1600 subscribers in industry, academia, and government. In addition, one of the companies participating on our industrial advisory board (Reaction Design) is providing a link from their web site to ours. Additional publicity activities will occur this year. In particular, we plan to alert major technical societies involved in materials research, so that they can announce it in their member magazines and provide links to it through their web sites. The Materials Research Society, The Electrochemical Society, American Ceramic Society, and the American Institute of Chemical Engineers are among those who will be contacted.

12. Patents, publications, presentations

I. M. B. Nielsen, C. L. Janssen, M. D. Allendorf "Ab initio predictions for thermochemical parameters for tin-oxygen compounds," accepted for publication in *J. Phys. Chem. A.*, 2003.

Database of Thermodynamic Data for Industrial Applications Now On-Line

The modeling of glass and refractory systems will allow both optimal selection of compatible materials as well as interpretation of failure mechanisms in glass production and the use of refractories in many applications. The ability to model glass melting temperatures, crystal precipitation in glasses, and the effect of composition on chemical behavior are critical to increasing throughput, decreasing energy use, and extending facility life. Prediction of refractory lifetimes as well as understanding their suitability for a particular industrial application requires accurate thermodynamic data, most of which are not available in standard databases. The lack of significant experimental efforts means that computational methods based on quantum-chemistry techniques are the only recourse for obtaining this vital data. Activities under this task are directed toward predicting thermodynamic data for compounds of particular relevance to the glass, pulp/paper, chemicals, and metals refining industries, where refractories are extensively used.

A new on-line database designed to provide thermochemistry for gas- and condensed-phase species relevant to a wide range of high-temperature processes is now available at: www.ca.sandia.gov/HiTempThermo/index.html. The database is produced jointly by Sandia National Laboratories and Oak Ridge National Laboratory. This dynamic source of thermochemical data provides essential information for scientists and engineers seeking to simulate high-temperature processes using equilibrium codes, computational fluid dynamics, and other models of high-temperature chemical processes.

The thermodynamic and other molecular properties found in the gas-phase portion of the database are all obtained from Bond Additivity Correction (BAC) calculations, a class of quantum-chemistry based methods developed at Sandia. Predicted heats of formation from this method are typically accurate to $\pm 12 \text{ kJ mol}^{-1}$. The current gas-phase database includes approximately 400 compounds in the C-H-O-N-Al system. Data for compounds containing boron and silicon will be added in the near future. The values available allow us of the CHEMKIN modeling of reacting flows. A free 3D molecular viewing software package, MOLEKEL, is available to assist the user. New computational methods are being developed as part of the project to provide data relevant to other high-temperature systems of industrial interest.

For condensed phases, the modified associate species model is used, which has proven highly accurate for reproducing phase relations, liquidus surfaces, vapor pressures, and chemical activities of glasses and slags. This approach treats the melt and glass as an ideal solution of constituent species and thus easily accommodates large numbers of elements. The most recent modeling results emphasize thermodynamic issues relevant to a broad range of industrial applications involving refractories. Systems modeled to date include the base glass $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ with the addition of Cr_2O_3 , MnO , NiO , and ZrO_2 .

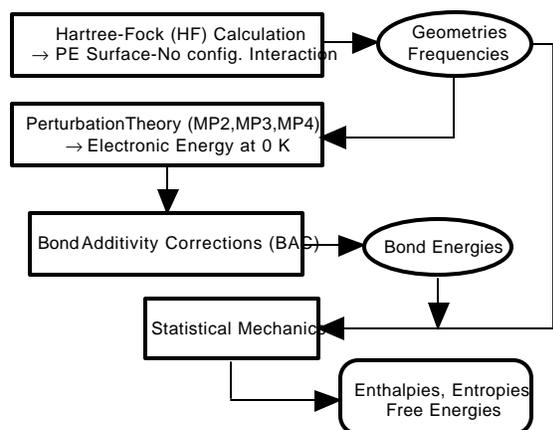


Figure 1. Schematic of the BAC-MP4 method used to calculate gas-phase thermochemistry. Molecular geometries and frequencies, used to calculate heat capacities and entropies, are obtained using Hartree-Fock theory. The electronic energy, from which heats of formation are derived, is obtained from Møller-Plesset perturbation theory.

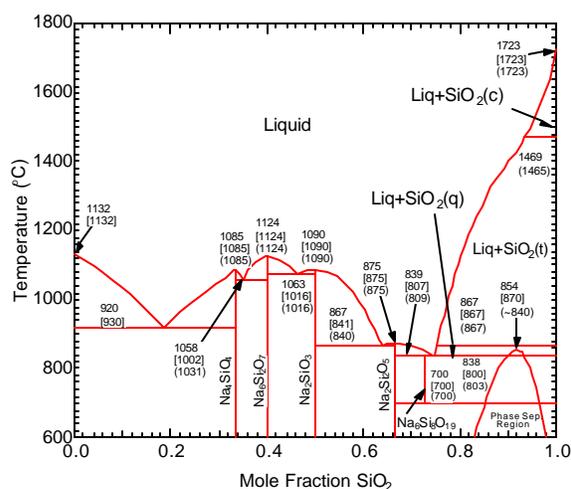


Figure 2. Phase diagram for the $\text{Na}_2\text{O}-\text{SiO}_2$ system calculated by the modified associate species model, showing calculated liquidus, eutectic temperatures, etc. Numbers in brackets and parenthesis are literature values corresponding to these temperatures.