Modeling the Limiting Equilibrium Behavior of Chemically Complex Oxide Glass Solutions

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This paper summarizes the research and applications of our thermochemical modeling of glass systems. Our overall goal has been to develop an equilibrium thermodynamic-based model and database that can be used to explain and predict the limiting equilibrium chemistry of glass systems, and to apply the model to technologically important processes. Two specific subgoals are to be able to accurately calculate:

- precipitation temperatures and amounts of specific crystalline phases for a wide range of compositions and temperatures (accurate temperature-composition phase equilibria), and
- thermodynamic activities (accurate Gibbs free energy values) of glass components as a function of temperature and glass composition.

Because we are concerned with chemically complex, multi-component glass systems, it is critical that additions of new components to the database and refinements of data for existing components must be relatively easy and not require a re-evaluations of the entire database. Enlarging and improving the database can then readily occur without major disruptions. Finally, if our model and database are to be useful in developing optimum glass compositions and processing conditions, then modeling predictions must be computationally simple and quick to perform.

We have developed and applied a thermodynamic model and database for glass systems using a liquid solution made up of associate species. This model and database have been successfully used for describing the complex chemistry of commercial glass systems as well as glass used in the storage of high-level nuclear waste (HLW glass). Our modeling calculations are a valuable aid in both the interpretation and prediction of experimental results regarding glass chemistry, and in predicting the limiting chemical behavior of HLW glass in its storage environment. Modeling calculations can also define critical experiments needed to test the predicted behavior. The use of such a model for understanding glass processing and behavior is increasingly valuable as the chemistry of the glass becomes more complex, and as the required specifications on its chemical behavior become more stringent.

The database and modeling discussed in this paper will include components from a base glass system of Na_2O-K_2O-CaO-MgO-Al_2O_3-B_2O_3-SiO_2, and important minor species of FeO_X, SO_Y , and H_2O. We have insured the internal consistency of our thermodynamic data by using a CALPHAD-type of approach in our assessments. Experimental thermodynamic and phase equilibria information are continually being assessed, with thermochemical values being estimated and/or calculated when required data are not experimentally available.

Applications of our database and model to HLW and float glass systems have included

predictions of:

a) precipitation of specific crystalline phases during processing of HLW glass,
b) activities of component species in glass for use in calculating maximum leaching rates in HLW glass,
c) mechanisms for corrosion of refractories in glass melting tanks,
d) limiting soda-lime-silica glass (float glass) chemistry after melting in an air-fired or oxy-fired natural gas combustion environment, and
e) glass - liquid tin interface reactions in a float bath system.

Acknowledgements

Support for this research has included: (1) NSF Industry-University Center for Glass Research (New York State College of Ceramics at Alfred University, Penn State University, and University of Missouri-Rolla), (2) U.S. Department of Energy, Environmental Management Science Program funded by the Office of Environmental Management's Office of Science and Technology, and administered jointly with the Office of Energy Research under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC, and (3) US Department of Energy, Office of Industrial Technologies, Glass Industry of the Future Team: American Air Liquide; BOC Gases; PPG Industries, Inc; Praxair, Inc.; Techneglas; Visteon Automotive Systems.