Thermochemical and Phase Equilibria Property Prediction for Oxide Glass Systems Based on the Modified Associate Species Approach

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The modified associate species model has proven highly accurate for reproducing phase relations, liquidus surfaces, vapor pressures, and chemical activities of relatively simple glasses. The approach treats the melt and glass as an ideal solution of constituent species, and thus easily accommodates large numbers of elements. The typical nonideality of oxide solutions is treated by including in the solution not only the end-member simple oxides, but, as necessary, binary and ternary oxides liquid species. The interaction energies are in this way incorporated in the complex oxides, allowing accurate *reproduction of the thermodynamics of the binary and ternary oxide systems by an ideal solution containing the species. Models are constructed of the individual relevant binary and ternary oxide systems including all combinations such that the subsystems are appropriately defined. These are tested against known phase equilibria, which are very sensitive to thermodynamic values of the constituents, and to be accurate must reproduce important segments of the phase diagrams. Some adjustment of the thermodynamic values of the binary or ternary oxide liquids may be necessary, and thus they are fit to obtain an accurate model. The “modification” of the associate species model involves the treatment of immiscibility, which requires the use of a solution model with positive interaction energies. The global model for the glass is finally created by including the various species of the subsystems into single solid solution. The result is an accurate representation of the behavior of a complex, multi-component glass.

Computations are performed using commercial thermochemical software, such as ChemSage or the recently introduced FactSage. These codes allow rapid calculation of equilibria and compute and draw phase diagrams. They contain the ideal and non-ideal solution models that can be used in both creating accurate subsystems and in building the global model. Large, assessed databases are coupled to the models and serve as the basis for generating the subsystems. The values in the databases can be modified, and species can be added as needed. The model requires both thermochemical values (heats of formation and transition, heat entropies, and capacities) for individual species and phase equilibria. Where values are not available or suspect, it is often possible to make sufficiently accurate estimations of thermochemical values. The models of the glass systems will consist of interally consistent databases that can be used over a wide range of glass conditions.

In this presentation the most recent modeling results will be presented, with emphasis on particular issues in industrial application. Systems that have been well-modeled, and will be described, include the base glass Na_2O-Al_2O_3-B_2O_3-SiO_2 with the addition of Cr_2O_3 and ZrO_2, among others.

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