Thermodynamic Optimization of the $CaO-B_2O_3-SiO_2$ system

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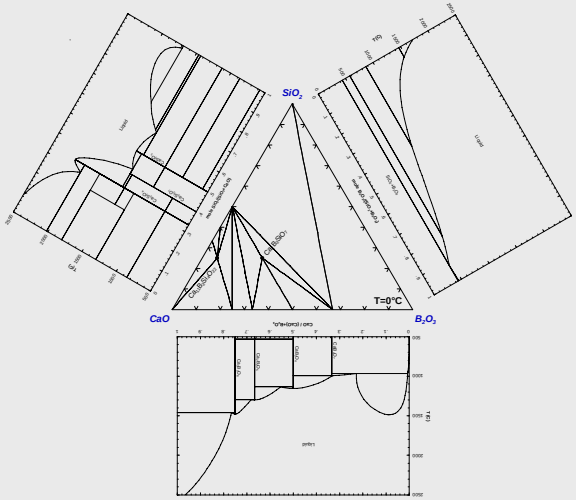
Abstract

B_2O_3 is a main constituent of the large and important family of borate- and borosilicate glasses. The outstanding properties of these glasses are their resistance to thermal shock and their chemical durability. They find widespread application as laboratory glasses for the chemical industry and are also used for high intensity lighting and heat resistant ovenware. They are better known under the brand names Pyrex® (Corning) and Duran® (Schott).

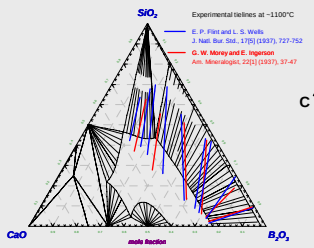
We are currently developing a quantitative thermodynamic description of multicomponent B_2O_3-containing liquids using the Modified Quasichemical Model for short-range ordering through critical evaluation of all available thermodynamic and phase equilibrium data. The thermodynamic descriptions show quite many interesting features such as stable and metastable miscibility gaps and excess heat capacities that are a challenge to model.

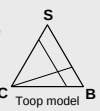
Here we present the recently optimized binary system $CaO-B_2O_3$ and show some results on extrapolating to the $SiO_2-B_2O_3$-CaO system. The measured excess heat capacity of the liquid phase in the $CaO-B_2O_3$ system was optimized using interaction parameters that are nonlinear with respect to temperature. All optimized binary systems agree well with all the selected sets of experimental data. Upon extrapolation of the thermodynamic properties of the liquid phase into the multicomponent systems we find that the model chosen has a profound influence on the quality of the extrapolation. Choosing a symmetric Kohler- or Muggianu model invariably leads to very poor predictions of the ternary systems, since CaO and MgO are chemically similar but are very different than both SiO_2 and B_2O_3. The use of an asymmetric Toop model is therefore mandatory for meaningful extrapolations. The majority of experimental data in the multicomponent systems are liquidus data. The general features of the experimental liquidus surface are reproduced reasonably well with no ternary terms in the liquid model. The agreement can be further improved somewhat by including optimized ternary interaction parameters.

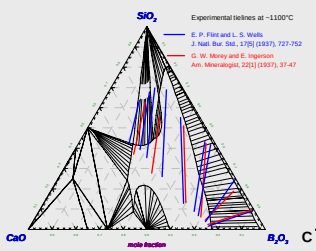
Overview

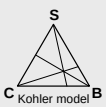


Extrapolation Methods





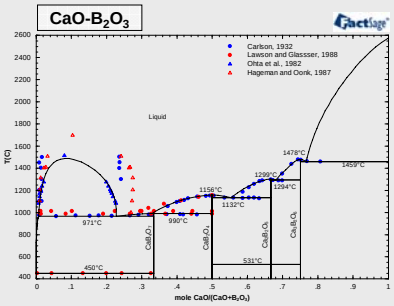


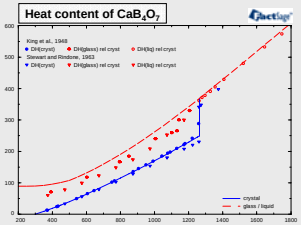


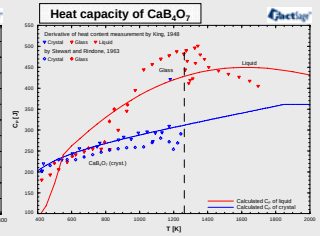
Calculated isothermal sections at 1100°C with no ternary interaction parameters.

Extrapolation using the Toop model (top) predicts the experimentally determined miscibility gap reasonably well. The symmetric Kohler model (bottom) fails to give a reasonable prediction of the ternary system.

The binary $CaO-B_2O_3$ system







The biggest challenge in modeling the binary $CaO-B_2O_3$ system is to reproduce the large excess heat capacity that manifests itself in the significantly steeper slope of the heat content measurements of the liquid compared to the solid phase. The origin of this excess heat capacity is rooted in structural changes taking place in the borate liquid on increasing temperature. In this work we model this effect by introducing temperature dependent interaction parameters for the liquid phase.

The ternary $CaO-B_2O_3-SiO_2$ system