

Stability of High Level Radioactive Waste Forms

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Objective:

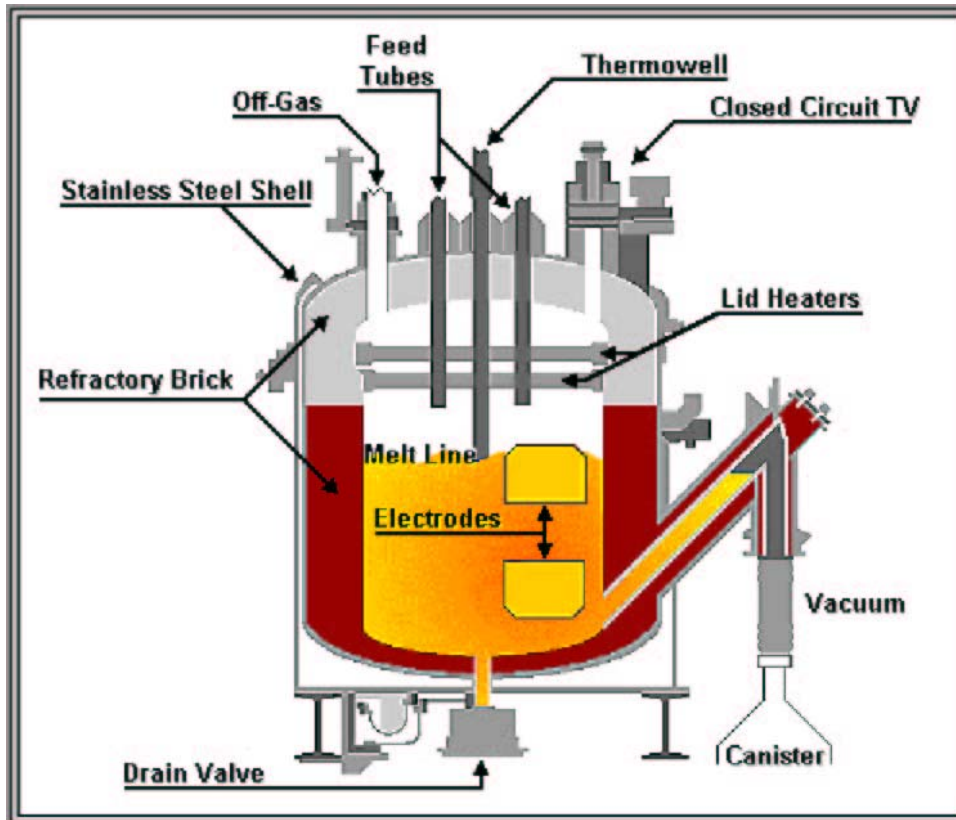
Develop practical models for calculating thermodynamic stabilities of components in complex high level waste glass and spent nuclear fuel.

- Work with large number of components
- Easy to understand and use
- Reliable
- Extrapolatable and interpolatable (T, x_i)

Focus of Studies Related to High-Level Nuclear Waste Glass

- Build database/model to include key components of interest to DOE waste immobilization efforts
- Those components determined to influence loading of major DOE waste streams in glass:
 - Hanford LAW: S/salt formation, Na/durability, P/salt formation
 - Hanford HLW: Cr/eskolaite formation, (Ni, Fe, Cr, Zn)/spinel formation, Zr/zircon formation, Al/nepheline formation, P/salt formation ...
 - DWPF: (Ni, Fe, Cr)/spinel formation, Al/nepheline formation
 - INEEL SBW: S/salt formation, P/salt formation, Na/durability, Al/nepheline formation
 - INEEL Calcine: Zr/zircon and parakeldyshite formation, F/immiscible liquid and crystal formation, Al/nepheloid formation
- Allow incorporation of model accessible to leaching and transport codes

Nuclear Waste Glass Melter



Operating Temperature: 1150°C

Canisters: 3 m x 60 cm, 2300 kg

Wt. % Ranges for Glass Constituents

	Hanford LAW		Hanford HLW		DWPF HLW	
Al ₂ O ₃	2	10	3	15	2.4	5.5
B ₂ O ₃	4	15	4	15	6.8	11.5
CaO	0	7	0	3	0.7	1.3
Cr ₂ O ₃	0	0.5	0	1	0	0.2
Fe ₂ O ₃	0	5	2	15	8.5	12
K ₂ O	0	4	0	2	2.1	2.6
Li ₂ O	0	5	0	6	4.3	5
MgO	0	5	0	1	0	2.1
MnO	-	-	0	7	1.1	2.8
Na ₂ O	5	20	5	20	7.8	15
NiO	-	-	0	3	0.1	1.2
P ₂ O ₅	0	3	0	2	-	-
SiO ₂	30	60	30	60	49.1	55.1
SrO	-	-	0	10	0	0.2
ThO ₂	-	-	0	4	-	-
TiO ₂	0	3	0	2	0.2	0.4
U ₃ O ₈	-	-	0	8	0.8	5
ZnO	0	3	0	4	-	-
ZrO ₂	0	5	0	10	-	-

Complex Oxides Are Difficult To Model Due To Large Number of Interaction Parameters

- Ideal solutions of the end-member oxides give highly inaccurate results
- One of the most successful approaches uses second nearest neighbor interactions to model the oxides, however, it:
 - Requires interaction parameters for every component
 - Interaction terms are expansions and thus have multiple terms both temperature dependent and independent
 - Obtaining the large number of terms requires complex optimization routine

Associate Species Approach Originally Applied by Hastie and Bonnell Simplifies Modeling

- The liquid/glass phase thermochemistry is modeled as an ideal solution of constituent compounds with two non-oxygen atoms present in every species
 - e.g., Soda-alumina glass modeled as ideal solution of $\text{Na}_2\text{O} + \text{AlNaO}_2 + \text{Na}_{2/3}\text{Al}_{4/3}\text{O}_{7/3} + \text{Al}_2\text{O}_3$
- Accurately represents behavior of chemically complex systems
- Predicts activity in metastable equilibrium glass phases
- Logically allows estimation of thermodynamic values values with an accuracy much greater than that required for predicting useful engineering limits on thermodynamic activities in solutions
- Relatively easy for non-specialists in thermochemistry to understand and use

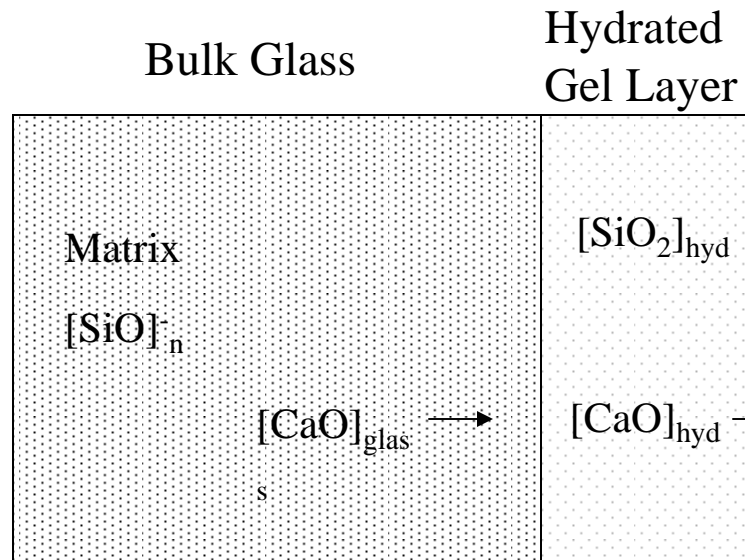
A Modified Associate Species Approach is Necessary To Accommodate Immiscible Liquids

- The presence of two immiscible liquids makes impossible the use of the pure ideal solution
- Positive interaction parameters are therefore utilized in a model that contains two liquid phases with identical constituents
- Free energy minimization routines determine the composition and quantity of each liquid
- Simple manual fitting to the phase diagram yields excellent results

To Model A Complex System The First Step Is to Build Up the Model From Constituent Species

- Models for subsystems must be generated
- The models must be checked against established phase equilibria
- For glass, this means using the “solution” model for the liquid phase in calculations and determining if the liquidus (melting points) in the system reflect reality
- FactSage thermochemical software allows us to quickly assess the phase equilibria and determine the “goodness” of the fit

Example of Potential Improvement to Predicted Leaching Rates in Waste Glass Yields Orders of Magnitude Difference in CaO Chemical Activity



Liquid Leachant

The concentration of the leached waste ion is dependent on the activity of [CaO]_{glass}

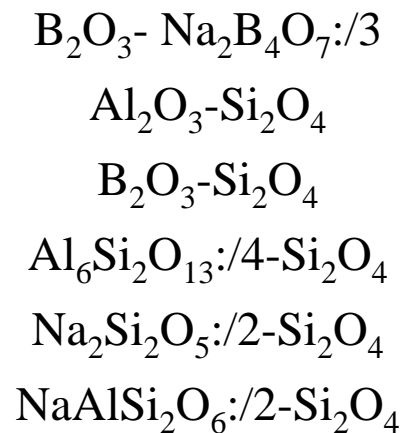
	Concentration CaO in glass	Activity of [CaO] _{glass}	Conc. In Leachant
Ideal Soln. Assumption	1 mol%	0.01	~0.01m
Associates Model	1 mol%	4x10 ⁻⁴³	Dependent on species

An Early Practical Problem That Has Been Addressed Is The Precipitation of Nepheline (NaAlSiO_4) in Specific Waste Glass Formulations

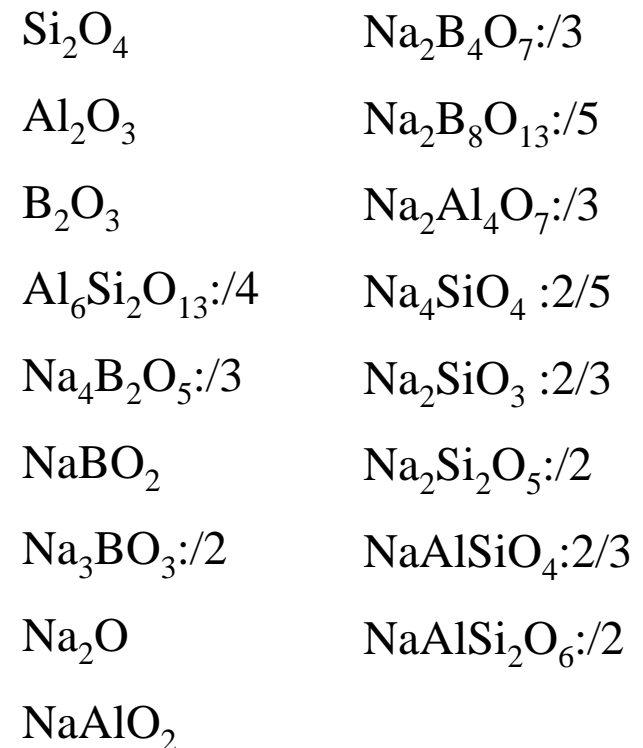
- Addressing the issue of nepheline precipitation is a good example of the utility of the model
- Precipitation of nepheline weakens glass network and adversely affects glass durability (H. Li, et al., 1997)
- Experiment indicates significant effects of other glass formers and modifiers
- Nepheline precipitation therefore limits loading of wastes that are rich in Na_2O and Al_2O_3

Associate Species Model for The $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ System

- The liquid/glass phase thermochemistry is modeled as an ideal solution of constituent compounds with two non-oxygen atoms present in every species
- The paired species below required positive interaction energies to appropriately model the liquid-liquid immiscibilities



Liquid Associate Species for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ system



Computed $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ Ternary Diagram Compares Reasonably With Published Diagram

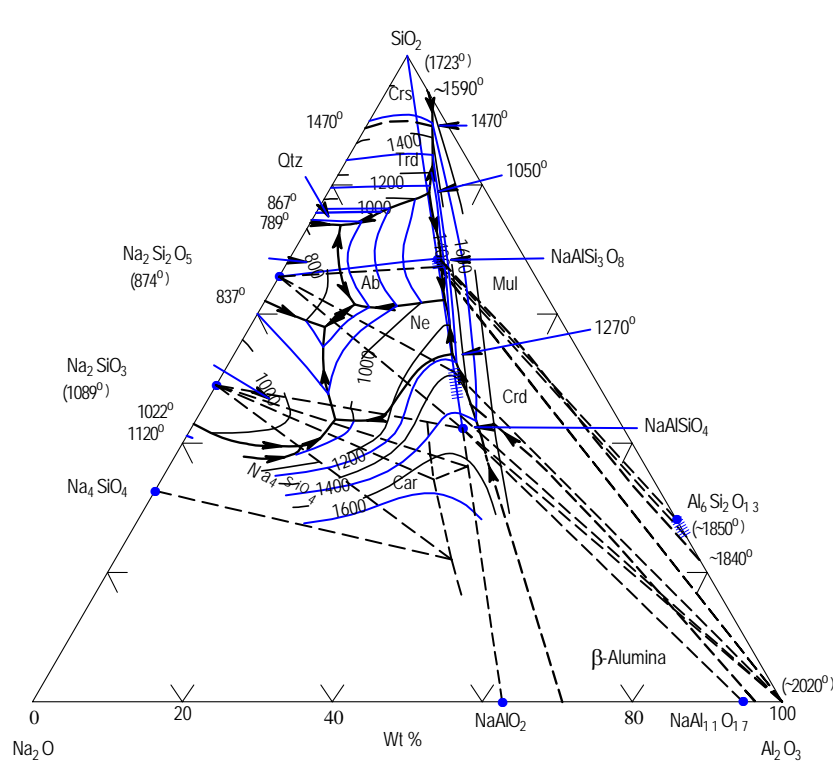
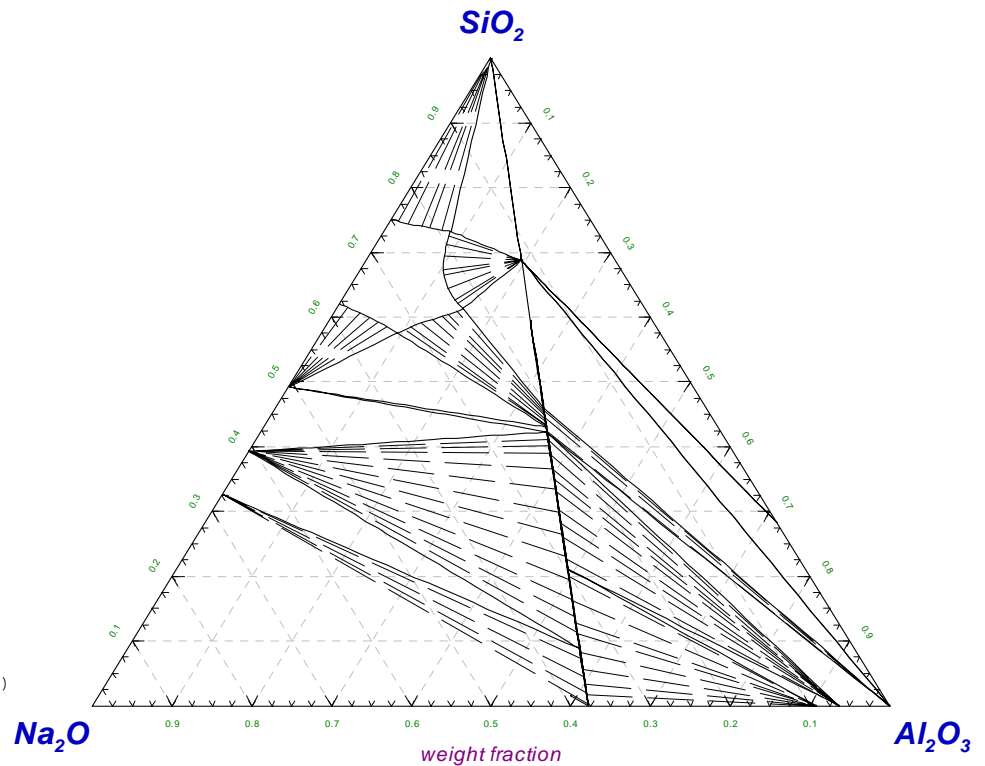
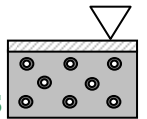


Fig. 00501—E. F. Osborn and A. Muan,



Computed from associate species model - 900 °C



Partial Experimental and Computed Na_2O - B_2O_3 - SiO_2 Ternary Phase Diagrams Demonstrate Strong Effect of Boria on Liquidus

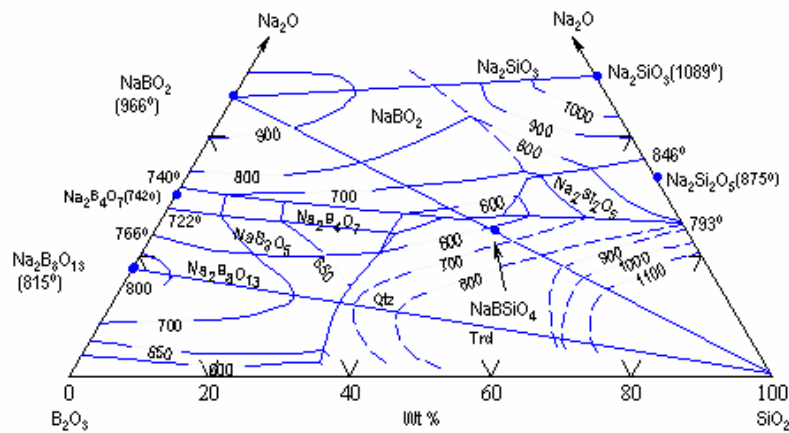
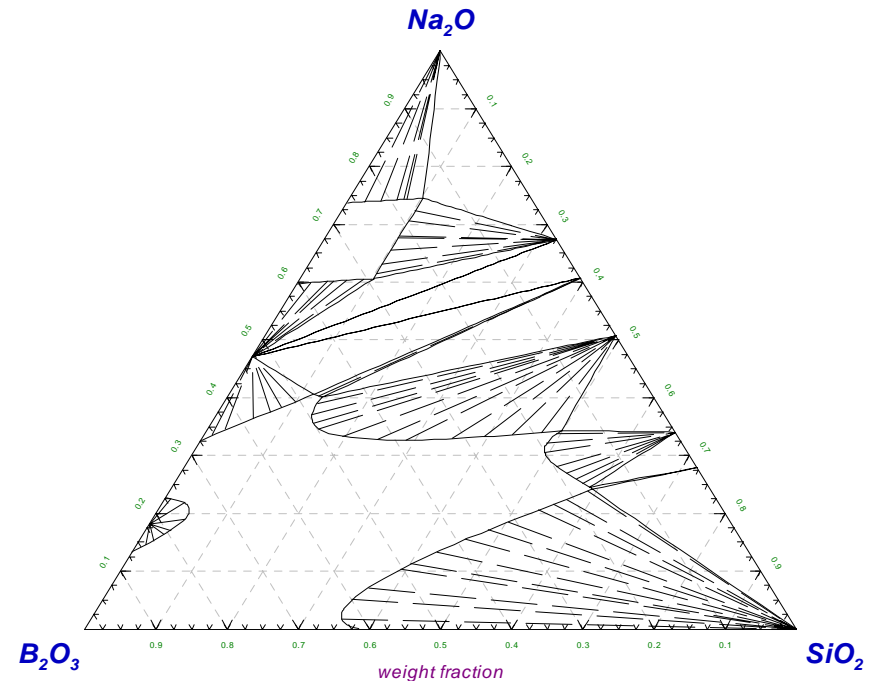


Fig. 00515—G. W. Morey



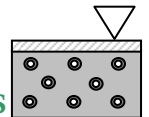
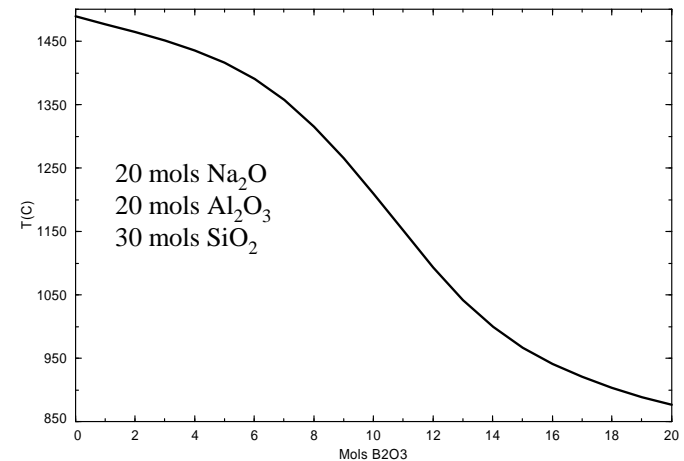
Computed from associate species model - 800 °C

Boria Causes a Sharp Melting Point Depression Near Nepheline

An additional soda-boria species was needed for the liquid model, Na_3BO_3 :/2, and adjustments to the free energies of related species was necessary to obtain good agreement with experiment

Na_2O (Mol %)	Al_2O_3 (Mol %)	B_2O_3 (Mol %)	SiO_2 (Mol %)	Exptl. T_L (°C)	Calc. T_L (°C)
25	25	0	50	1510	1527
16.67	16.67	0	66.67	1124	1096
12.5	12.5	0	75	1085	1117
20	20	20	40	875	874

Liquidus Variability with B_2O_3 Content

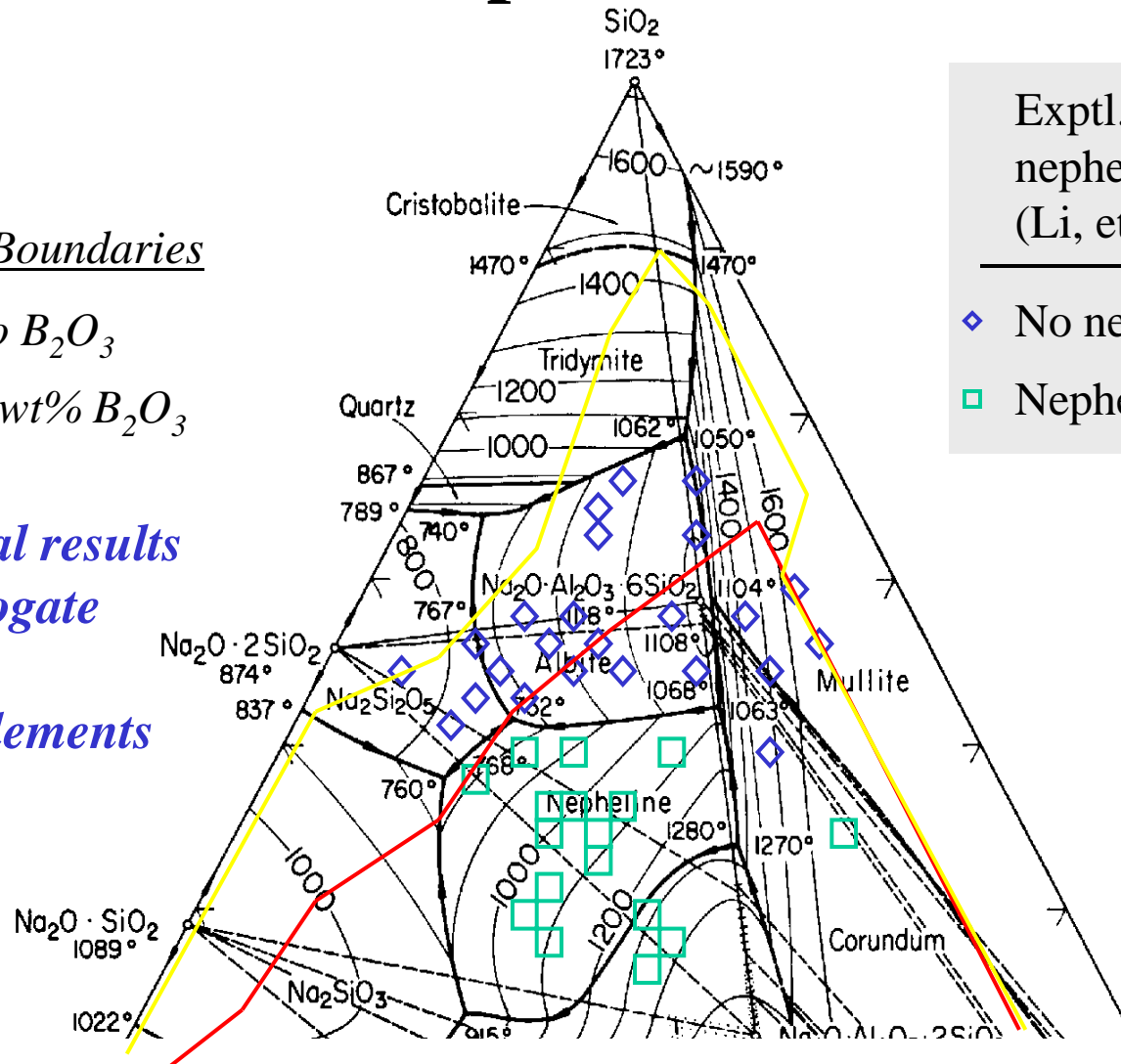


Computed Nepheline-Glass Stability Region Brackets Experimental Results

Computed Boundaries

- No B_2O_3
- 30 wt% B_2O_3

*Experimental results
are for surrogate
HLW with
additional elements*



Exptl. results of
nepheline ppt. expts.
(Li, et al, 1997)

- ◆ No nepheline ppt.
- Nepheline ppt.

Calcium-Containing Systems Were Difficult to Model, But Good Results Were Obtained

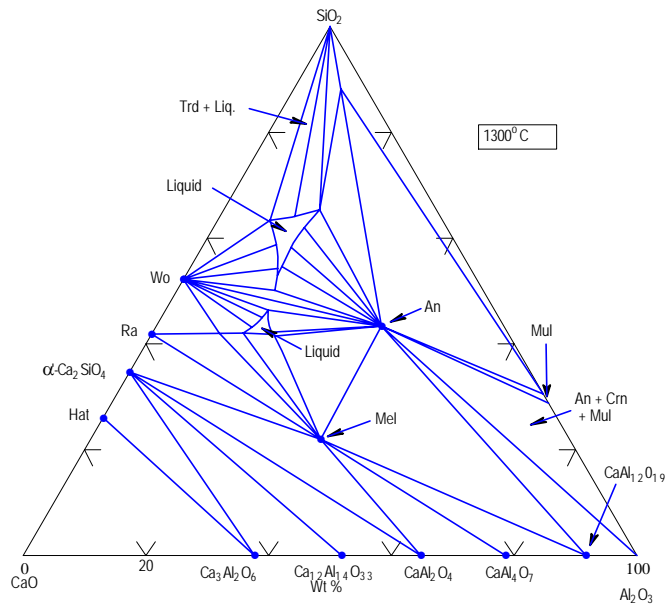
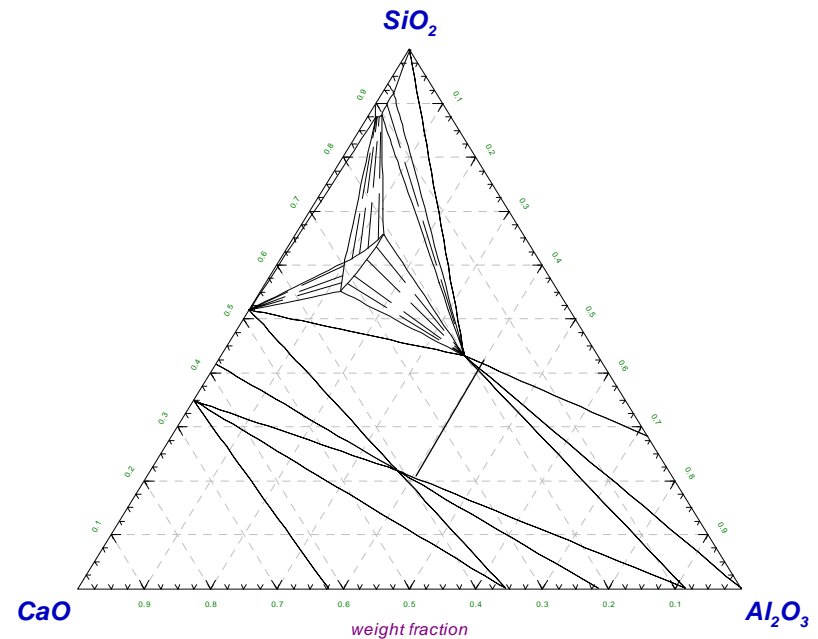


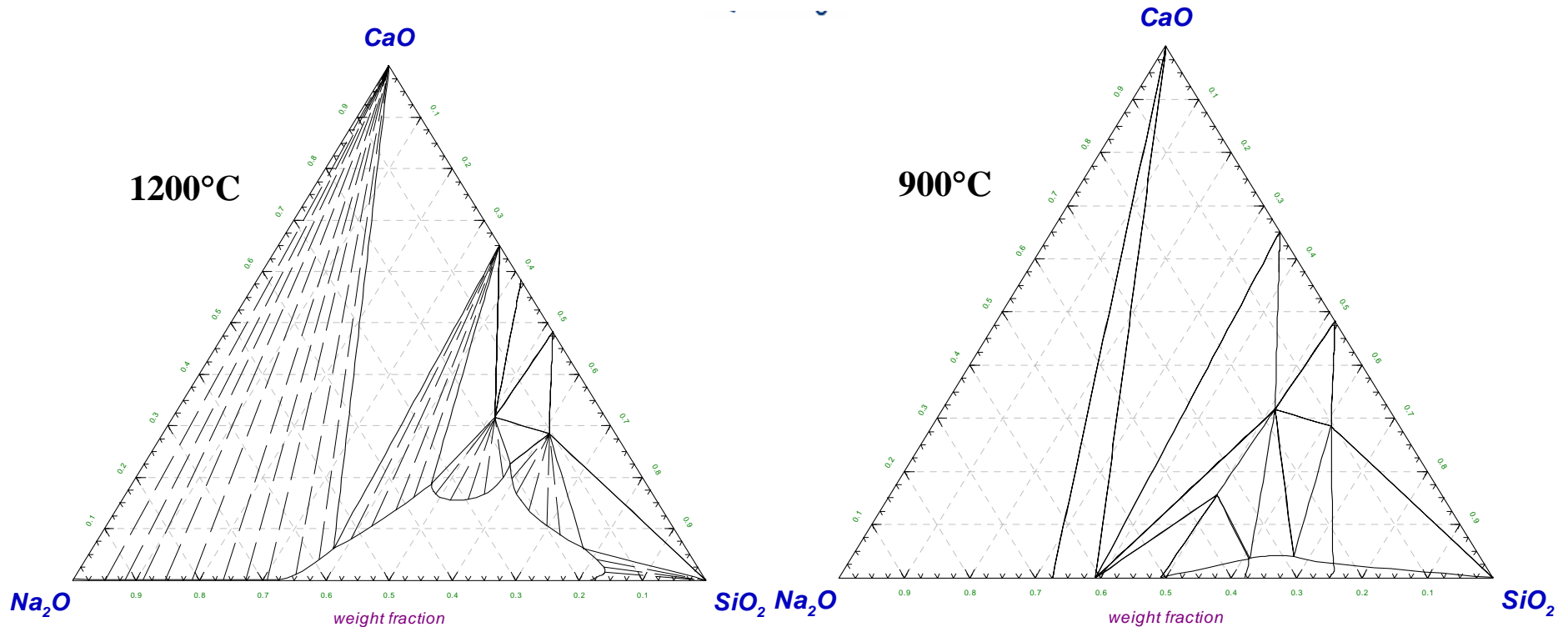
Fig. 10584—R. G. J. Ball, M. A. Mignanelli, T. I. Barry, and J. A. Gisby - 1300 °C



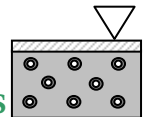
Computed from associate species model - 1300 °C

Associates needed for the liquid/glass include: Ca_2O_2 , $\text{Ca}_3\text{Al}_2\text{O}_6:2/5$, $\text{Ca}_2\text{Al}_2\text{O}_5:/2$, $\text{CaAl}_2\text{O}_4:2/3$, $\text{CaAl}_4\text{O}_7:2/3$, $\text{Ca}_3\text{SiO}_5:/2$, $\text{Ca}_3\text{Si}_2\text{O}_7:2/5$, CaSiO_3 , $\text{Ca}_9\text{Al}_{10}\text{SiO}_{26}:/10$, $\text{CaAl}_2\text{SiO}_6:/2$, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}:/4$, $\text{CaAl}_2\text{Si}_2\text{O}_8:2/5$, $\text{Ca}_2\text{Al}_2\text{Si}_6\text{O}_{17}:/5$

Computed $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ Ternary Phase Diagrams



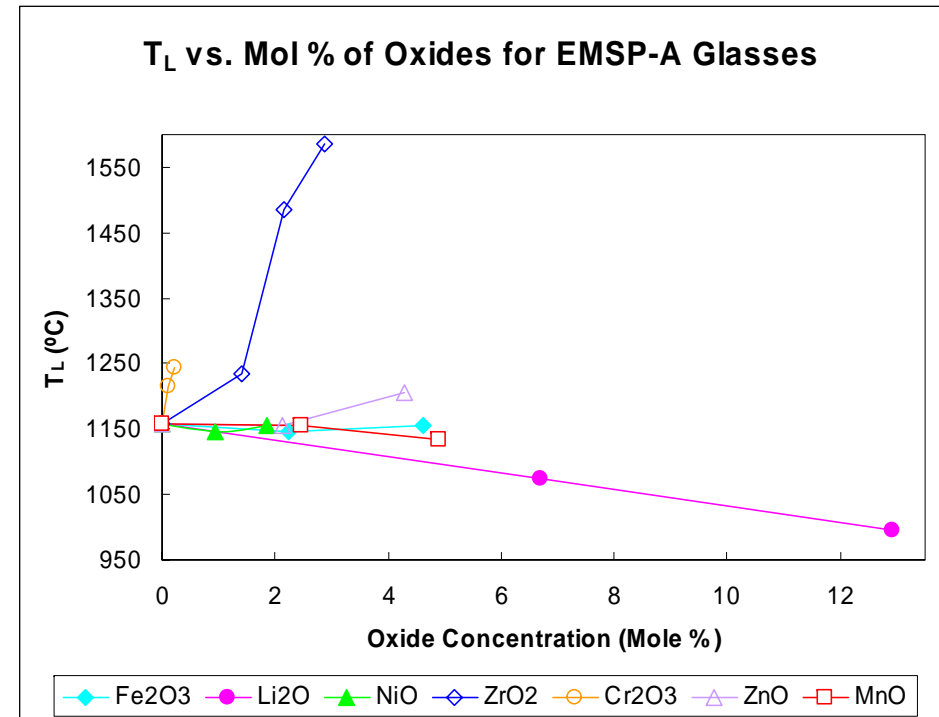
Ternary associates needed for the liquid/glass:



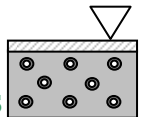
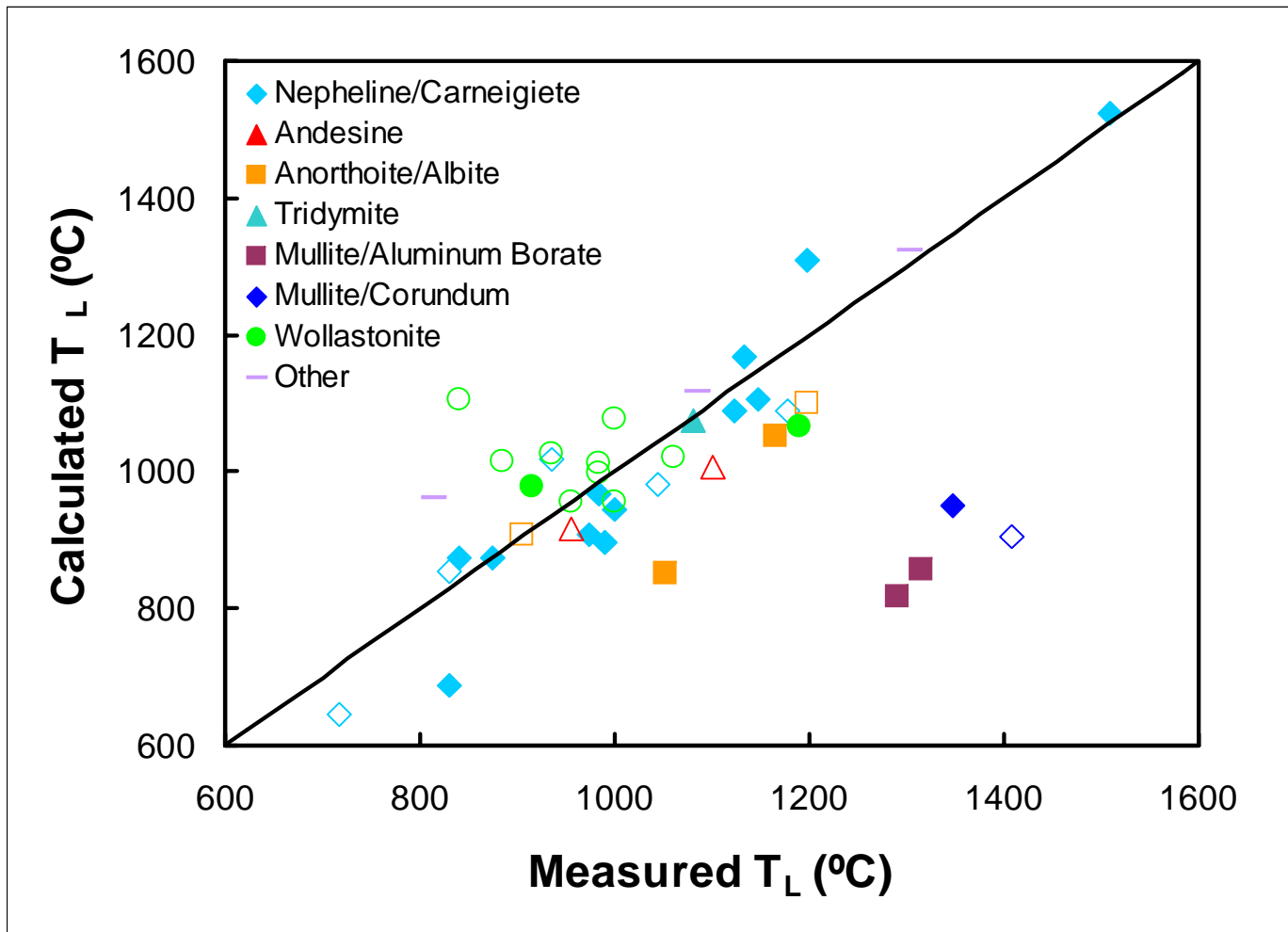
Example of Experimental Liquidus Temperature Measurements Used to Support Modeling

Baseline Glass (20% Al₂O₃, 10% B₂O₃, 10% CaO, 20% Na₂O, and 40% SiO₂)

Glass ID#	Fe ₂ O ₃	Li ₂ O	NiO	ZrO ₂	Cr ₂ O ₃	ZnO	MnO
EMSP-A	-	-	-	-	-	-	-
EMSP-A1	4.61	-	-	-	-	-	-
EMSP-A2	2.24	-	-	-	-	-	-
EMSP-A3	-	12.91	-	-	-	-	-
EMSP-A4	-	6.70	-	-	-	-	-
EMSP-A5	-	-	1.86	-	-	-	-
EMSP-A6	-	-	0.93	-	-	-	-
EMSP-A7	-	-	-	2.88	-	-	-
EMSP-A8	-	-	-	1.42	-	-	-
EMSP-A9	-	-	-	-	0.23	-	-
EMSP-A10	-	-	-	-	0.11	-	-
EMSP-A11	-	-	-	-	-	4.29	-
EMSP-A12	-	-	-	-	-	2.14	-
EMSP-A13	-	-	-	-	-	-	4.90
EMSP-A14	-	-	-	-	-	-	2.45
EMSP-A15	-	-	-	2.15	-	-	-

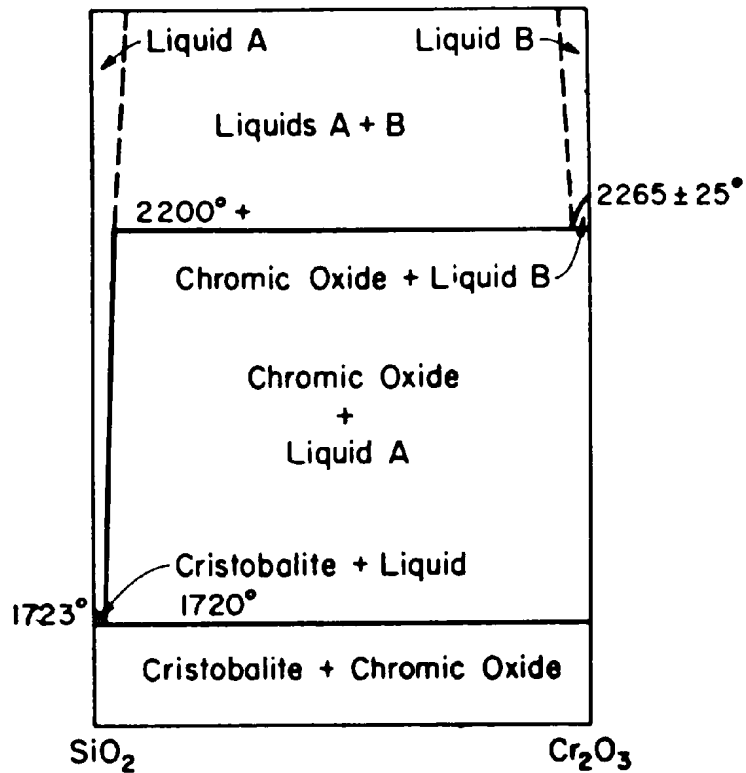


Initial Comparisons of Experimental and Computed Liquidus

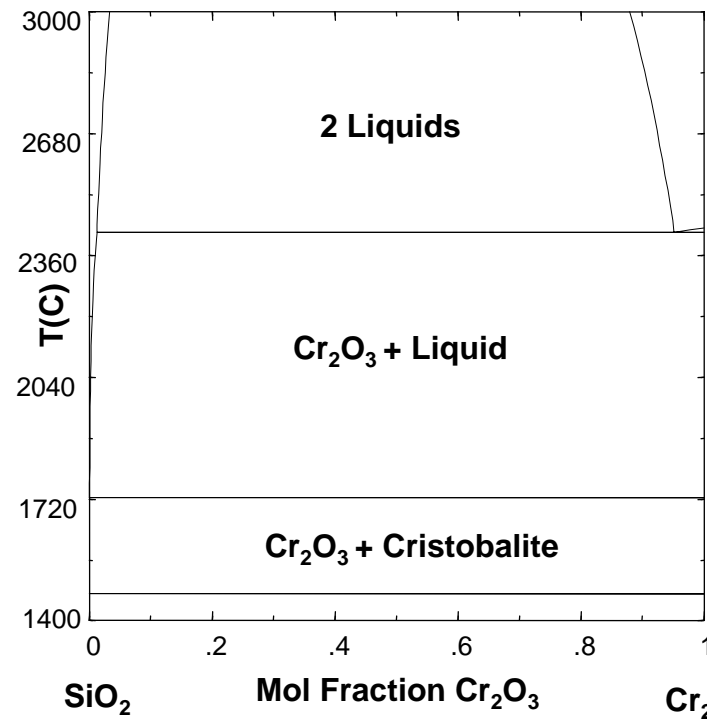


Spinel Formers Are Now Being Addressed: Modified Associate Species Model for the Cr_2O_3 - SiO_2 System

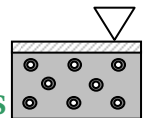
Published (No. 332)



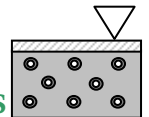
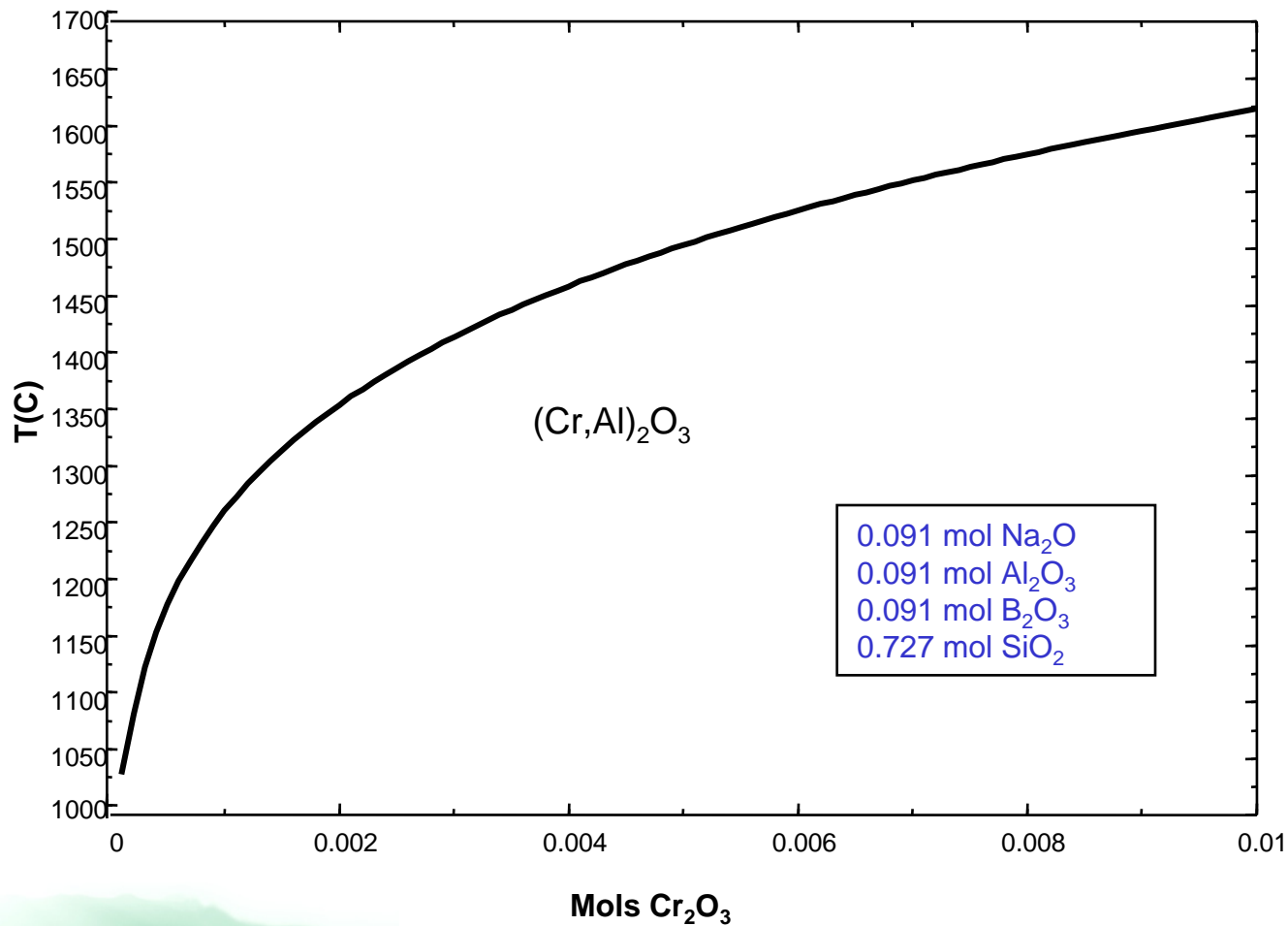
Computed Phase Diagram



For the liquid $G_{\text{ex}} = X(1-X)[100,000 - 5T]$,
where X is the mol fraction of SiO_2

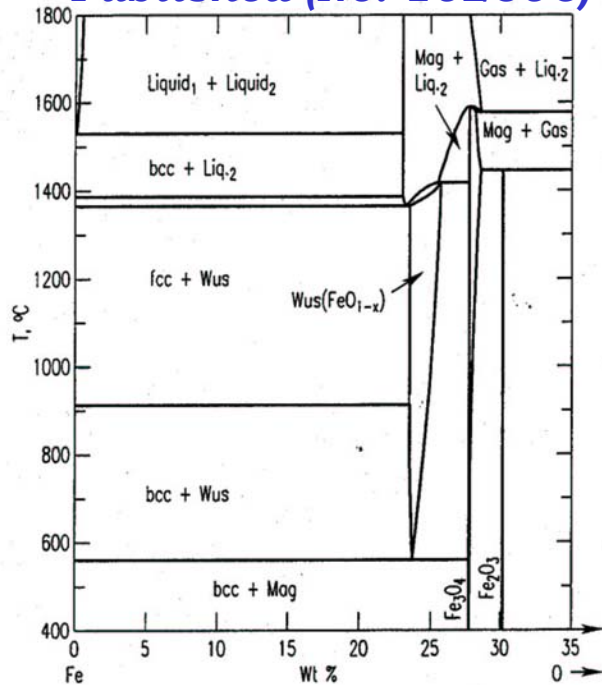


Liquidus Curve for the $\text{Na}_2\text{O}-\text{Cr}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ System as a Function of Cr_2O_3 Content Shows Sensitivity of Liquidus to Chromia



Published (Computed) and Associate Species Model Fe-O Phase Equilibria

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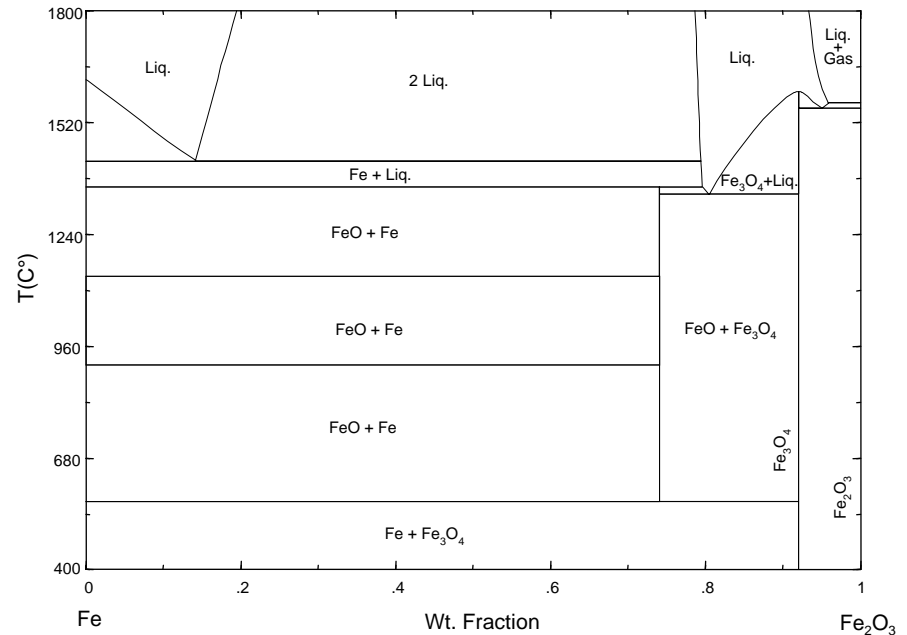


Models

Solid Phases: Compound energy model with ionic constituents

Liquid Phase: Ionic two-sublattice model (required 8 polynomial expansions)

Associate Species Model



Liquid is solution of Fe_2 , Fe_2O_2 , $Fe_3O_4:2/3$, Fe_2O_3

Adj. ΔH_f°	Fe_2O_2	$Fe_3O_4:2/3$	Fe_2O_3
kJ/mol	21	-3.9	97.5

$$G_{xs} = x_i x_j \sum (L_n (x_i - x_j)^{n-1})$$

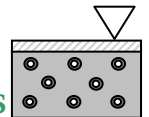
$$\frac{Fe_2 - Fe_2O_2}{L_0=50,000}$$

$$L_1=40,000$$

$$L_2=10,000$$

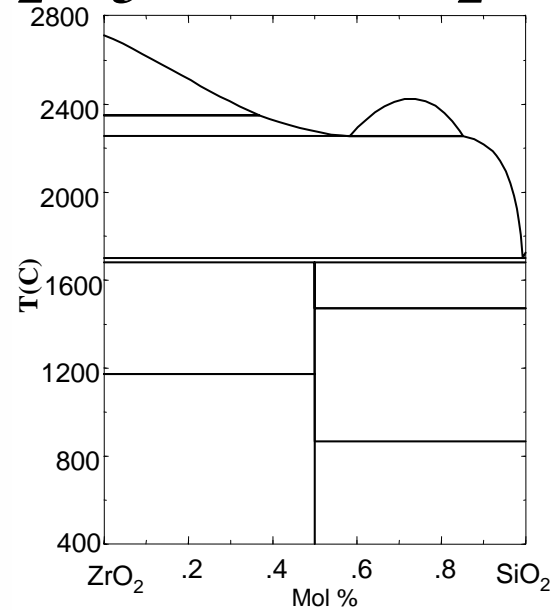
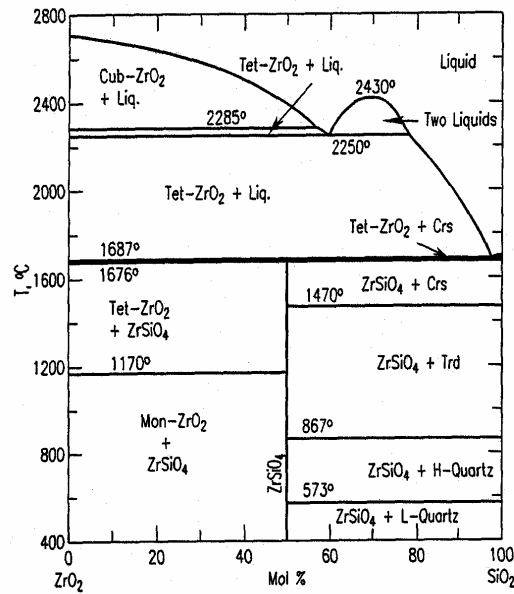
$$\frac{Fe_2 - Fe_3O_4}{L_0=60,000}$$

$$\frac{Fe_3O_4:2/3 - Fe_2O_3}{L_0=25,000}$$

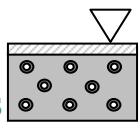
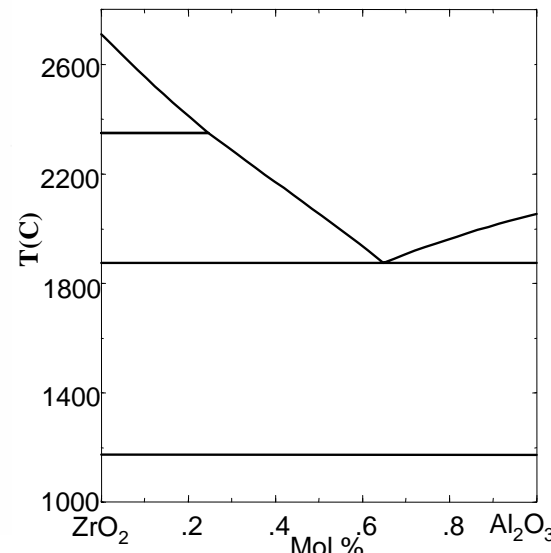
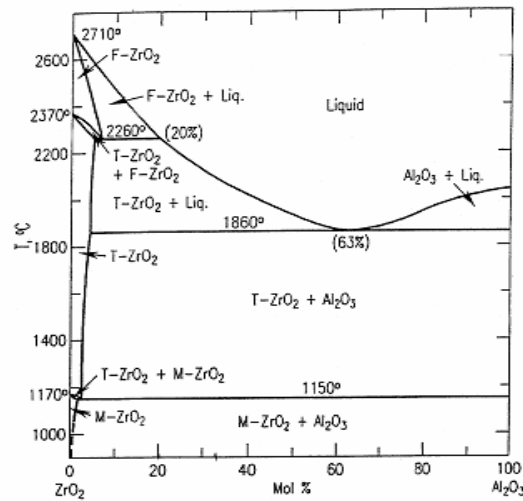


Published and Computed Phase Diagrams for ZrO_2 with Al_2O_3 and SiO_2

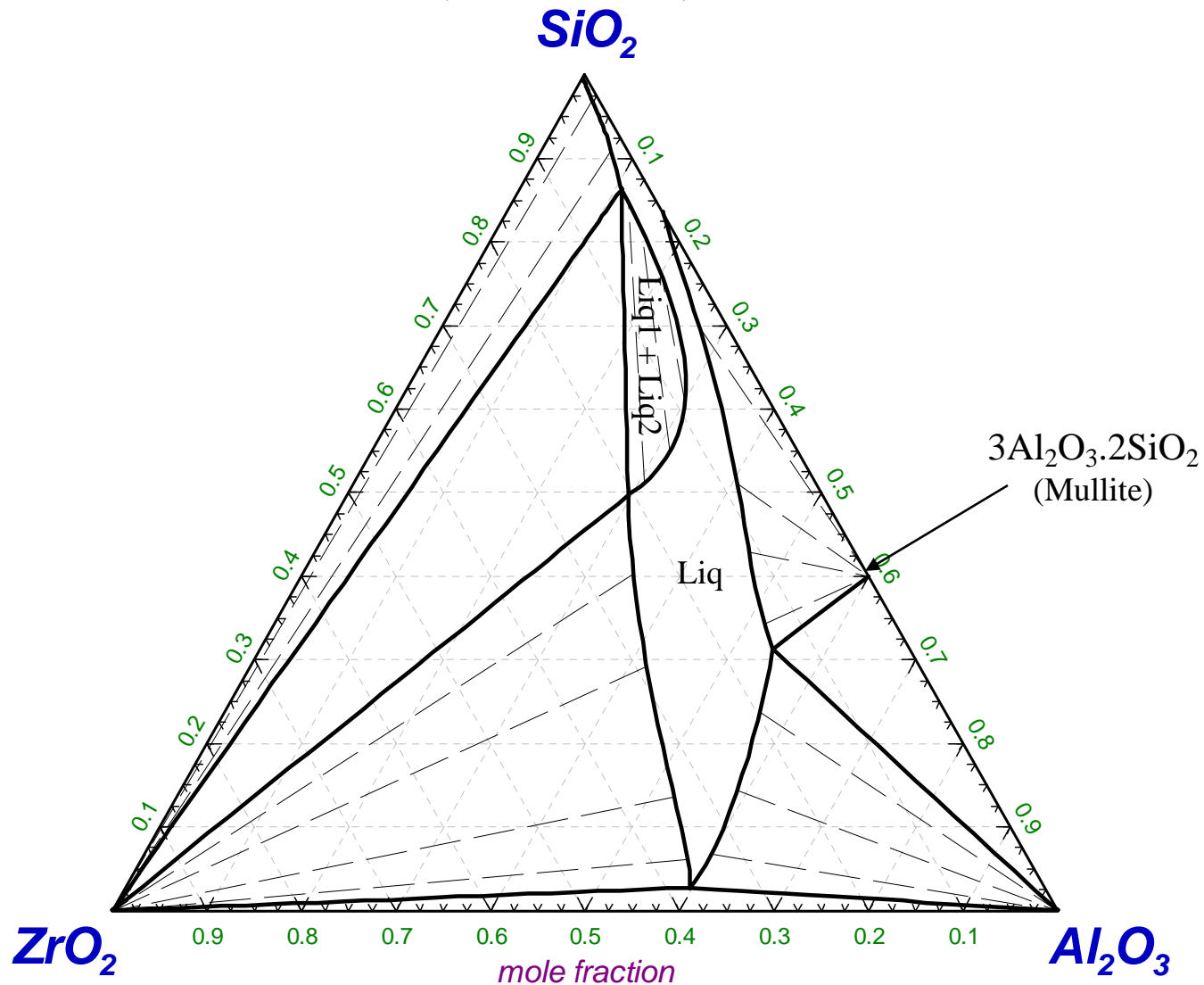
Published



*Computed
assuming
one metal
atom per
species*



Computed $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ Diagram (1850°C)



Summary

- The associate species approach for complex systems is simple, relatively accurate, and highly usable for describing
 - Liquidus surfaces
 - Conditions for crystalline phase formation
 - Chemical activities of glass constituents
- We have developed a base model ($\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$) for waste glass systems that agrees reasonably with published phase diagrams and other thermochemical data
- The computed composition range for precipitation of nepheline shows a wide area for formation of the phase in agreement with experiment
- The example of the effect of chromia content on liquidus temperature demonstrates the strong effect of this constituent, and illustrates the difficulty experienced with chromia content in waste glass fabrication
- ZrO_2 has been modeled with Cr_2O_3 , SiO_2 , and Al_2O_3 by using single metal atom end members.
- The model is currently being extended in to include spinel formers Fe-O, Cr_2O_3 , MnO, and NiO, and to include ZrO_2