
Thermodynamics of liquid simple oxides in the CALPHAD framework

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Extrapolation of liquid simple oxides in the CALPHAD framework

The extrapolation of the Gibbs energy of liquids from high temperature (where experimental data may exist) to room temperature is a key feature in the CALPHAD framework = end members of liquid phase

Heat capacities and entropies of pure simple oxides

- SiO_2 , B_2O_3 : experimental data down to 0K for heat capacity
- CaO : may be estimated from $\text{CaSiO}_3(\text{glass})$ using $\text{SiO}_2(\text{glass})$
- Al_2O_3 : from $\text{CaAl}_2\text{O}_4(\text{glass})$ & $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}(\text{glass})$; $\text{CaAl}_2\text{Si}_2\text{O}_8(\text{glass})$
- MgO : from $\text{CaMgSi}_2\text{O}_8(\text{glass})$

With this data, optimize Gibbs energies at high temperature (phase diagram) + heat of mixing / cristallisation in glasses

Thermodynamic models for liquids

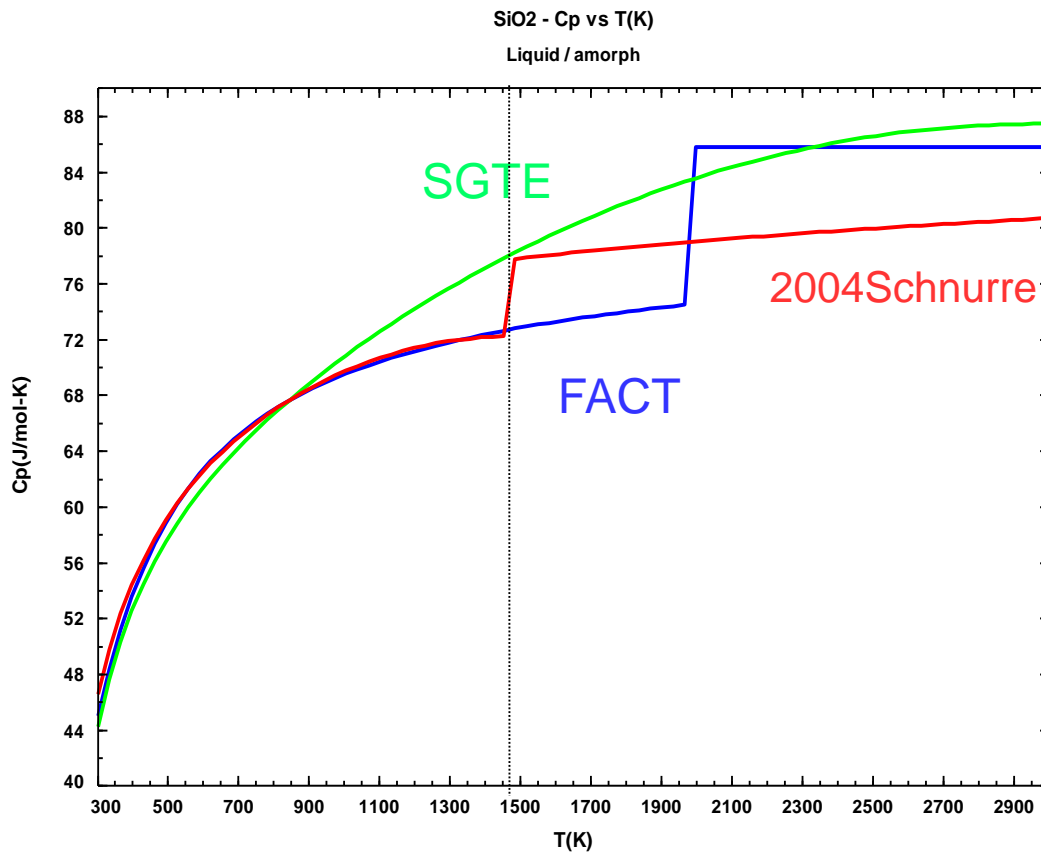
Two-state model

- First proposed by Jon Ågren in 1988
- Assumption : constituents of a liquid phase may be in a solid like (amorphous) or liquid like state
- Gibbs energy is three term function
 - Einstein model for an ideal solid(amorphous) state
$$G = E_0 + 1.5R\theta_e + 3RT \ln(1 - \exp(-\theta_e/T)) - a_1/2T^2 - b_1/20T^5$$
$$E_0: 0K \text{ energy, } \theta_e \text{ Debye temperature, } a_1, b_1 \text{ corrective terms}$$
 - Correction for the Einstein model to fit the experimental data ($A + BT^2$)
 - $-RT \ln(1 + \exp(\Delta G/RT))$, $\Delta G = a_2 + b_2T + c_2T \ln T$ a_2, b_2, c_2 fitting parameters
- Up to now, model used only for metallic systems : Fe, Ag, Cu
- On-going effort to model all solid elements with the Einstein model & liquid elements with two-state model

Modified two-state model for oxides

- Proposed by J. Golczewski, H. Seifert & F. Aldinger in 1998
- Developed for amorphous Silicates
- Assumption : constituents are amorphous oxide and structural thermal fluctuations (vacancies)
- Gibbs energy is regular solution
 - Amorphous : Gibbs energy of solid oxide + corrective terms
 - Thermal fluctuation : $60000-RT$
 - Interaction terms : L^0, L^1
- The model is valid not far below T_g and up to T_f

SiO₂ – liquid



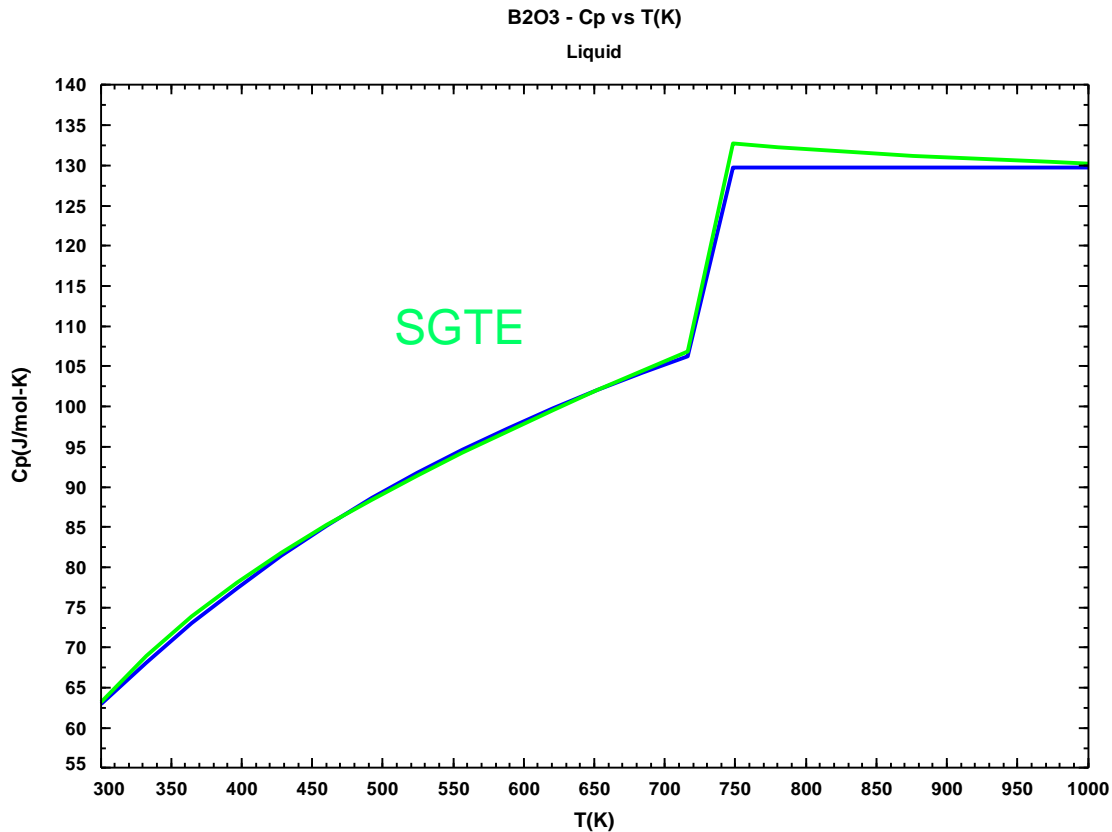
Only Schnurre et al. take into account glass transition

Fact : Solid + liquid at T_{fus}

SGTE : continuous function

	S298K	Cp(298K)
Exp	43.4 43.4	44.06
SGTE	50.3	49.45
FACT	47.6	43.99
2004Schnurre	49.8	46.30

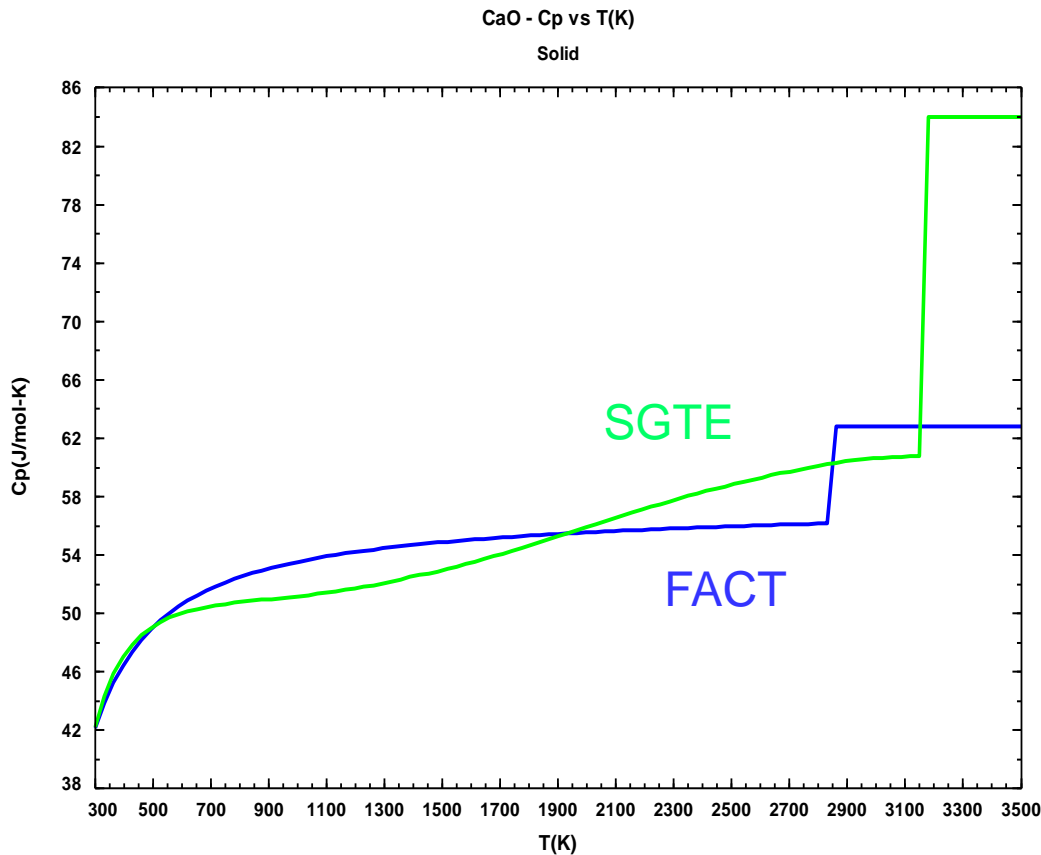
B₂O₃ - liquid



Cp function for FACT and SGTE databases are almost identical, only cp at $T > T_g$ shows some minor difference

	S298K	Cp(298K)
Exp	67.4	62.60
SGTE	87.2	62.6
FACT	87.4	62.8

CaO - solid



Different melting points in
FACT & SGTE databases

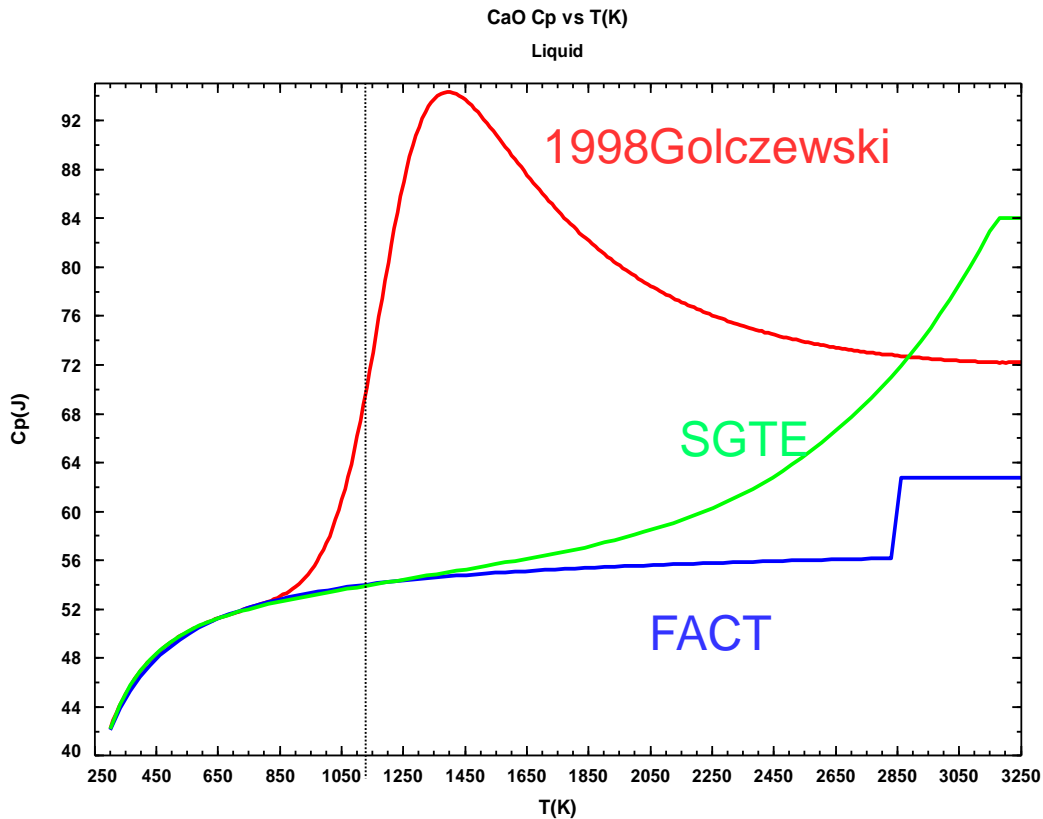
- Fact 2857K

- SGTE 3183K

Different cp functions

Different cp for liquid > T_f

CaO - liquid



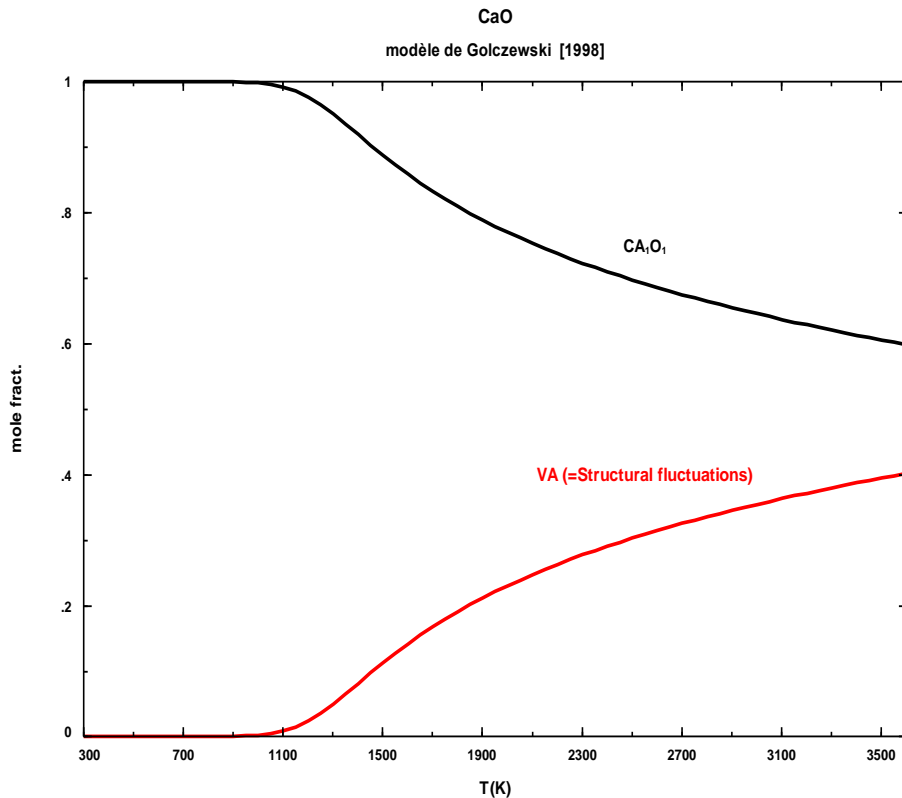
FACT :
solid cp until melting point

SGTE :
broad transition from T_f to low T

1998Golczewski :
Glass temperature included

	S298K	Cp(298K)
Exp	43.8	42.23
SGTE	59.0	42.04
FACT	65.7	42.02

CaO amorphous - 1998Golczewski



Modified two state model with interaction parameter

(CaO,SF)

SF = « structural fluctuation »

$$G(\text{CaO}) = G_{\text{cryst}} + A + BT$$

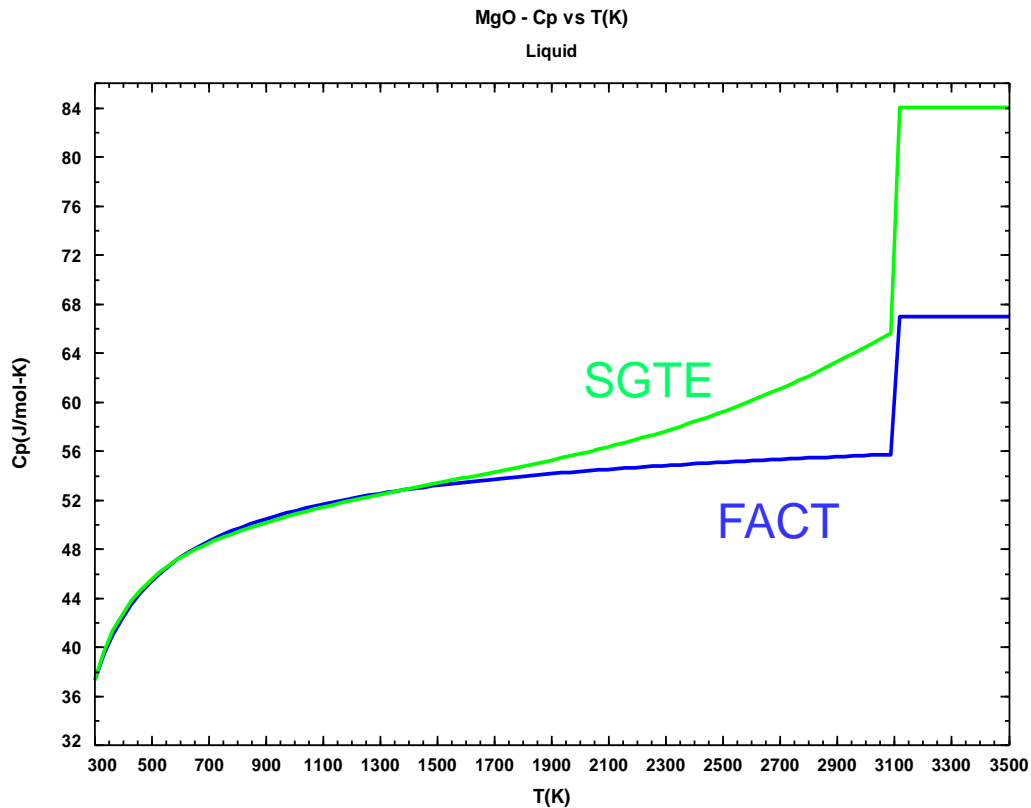
$$G(\text{SF}) = 60000 - RT$$

Interaction :

$$L^0 = 22428.4 - 25.72 * T$$

$$L^1 = 43433.0 - 40.57 * T$$

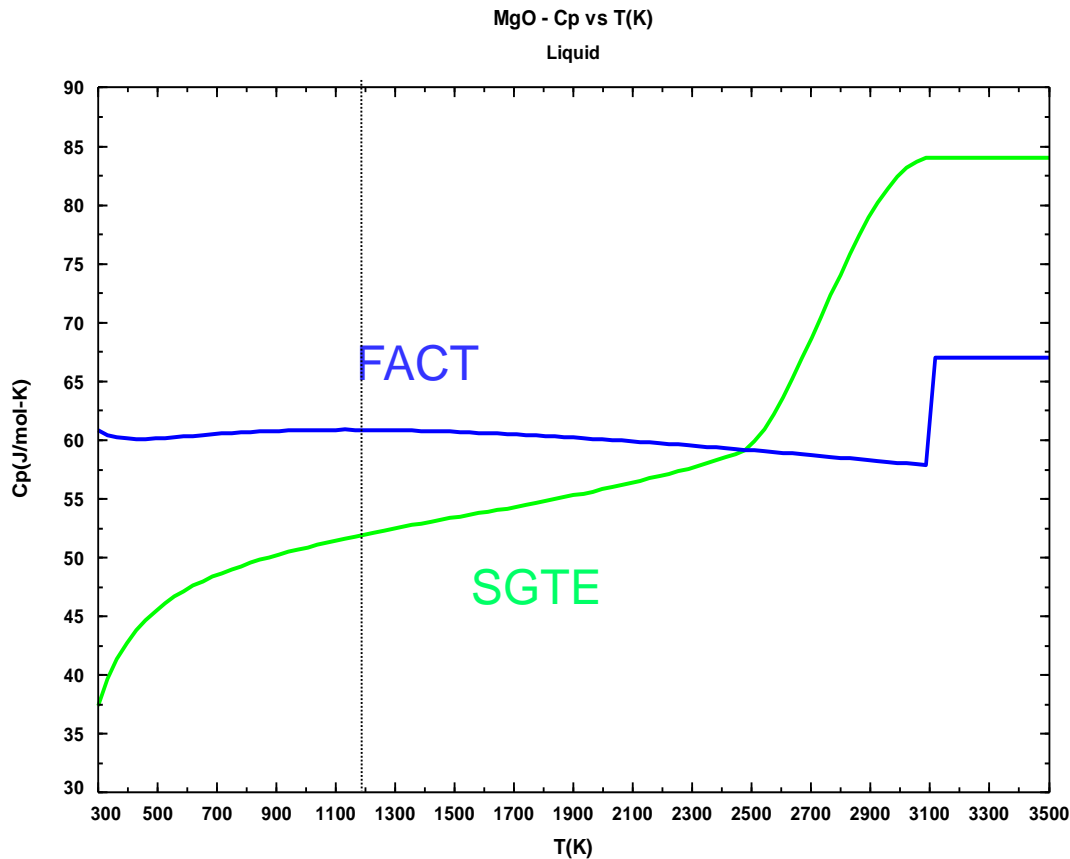
MgO - solid



Identical melting point in both databases

Differences in Cp function and cp for $T > T_f$

MgO - liquid



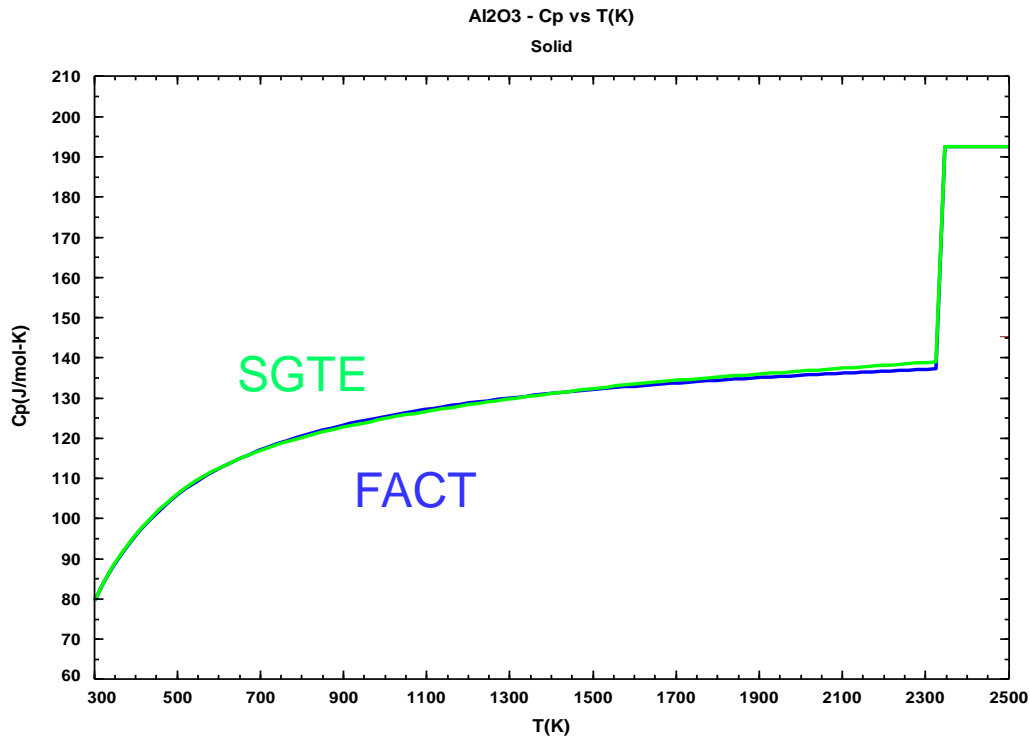
Different Cp extrapolation to RT in both databases.

Cp vs T in FACT almost constant

CP vs T in SGTE with broad transition below Tf

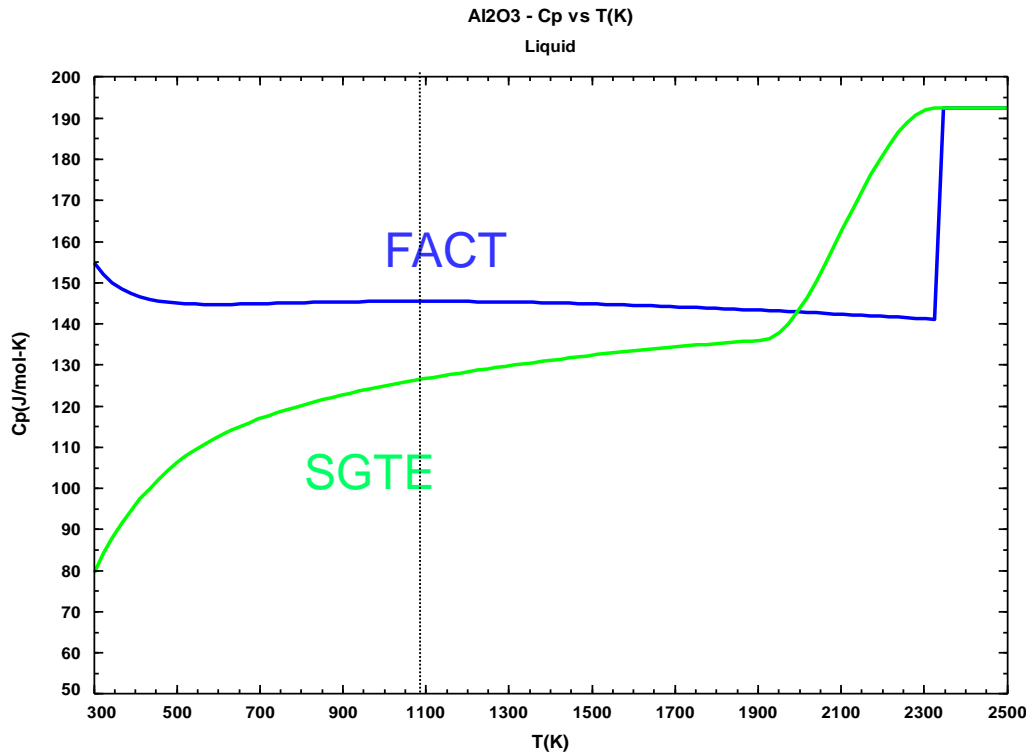
	S298K	Cp(298K)
Exp	30.6 30.7	38.24
SGTE	49.5	37.22
FACT	27.0	60.81

Al₂O₃ - solid



Cp functions in FACT and SGTE databases are identical

Al₂O₃- liquid



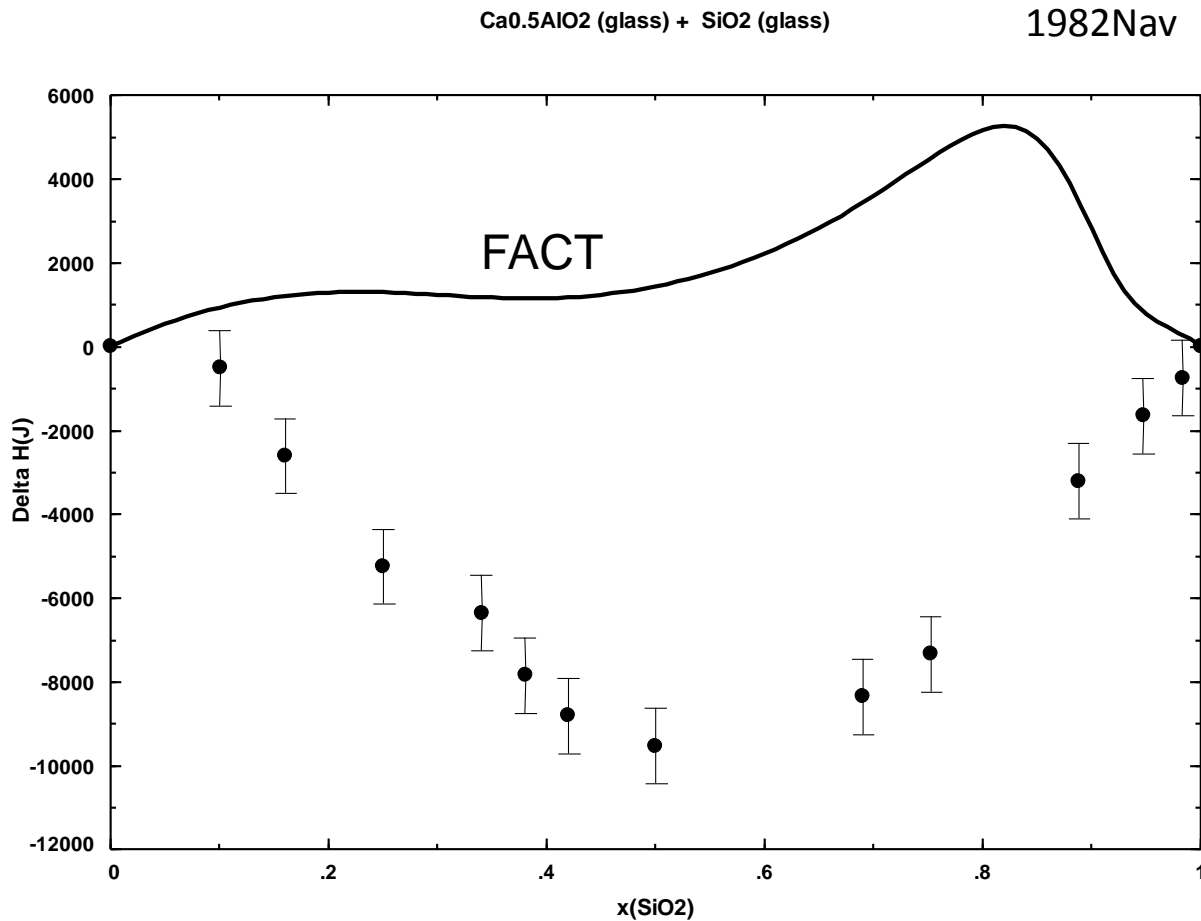
Different Cp extrapolation to RT in both databases.

Cp vs T in FACT almost constant

Cp vs T in SGTE with broad transition below Tf

	S298K	Cp(298K)
Exp	69.5 69.1	79.89
SGTE	93.4	79.02
FACT	43.6	155.06

Heat of mixing $\text{Ca}_{0.5}\text{AlO}_2 - \text{SiO}_2$



Vitrification CaAl_2O_4

Exp :
25682 J/mol

Calc (FACT) :
19598 J/mol

Heat of vitrification for selected compounds

	Vitrification (985K)		Fusion	
	exp	calc (FACT)	exp	
NaAlSi ₃ O ₈ (Albite)	51890	59440	65350	67659
CaAl ₂ Si ₂ O ₈ (Anorthite)	77755	156063	133648	160555
CaMgSi ₂ O ₆ (Diopside)	85600	128158	129704	129568

Comparison of standard entropies of selected compounds

	S298K – glass		S298K – crystal	
	exp	calc	exp	calc
SiO ₂	43.3	50.3	41.4	41.5
CaSiO ₃ - PW	86.2	117.0 112.0	87.2	86.9
CaSiO ₃ - W			81.7	79.8 82.0
CaMgSi ₂ O ₆ (Diopside)	159.9	202.7	142.0	142.5
MgSiO ₃	74.1	74.1 79.5	66.3	66.6
CaAl ₂ Si ₂ O ₈ (anorthite)	198.7	233.3	199.3	200.2
Mg ₂ Al ₄ Si ₅ O ₁₃ (Cordierite)	414.5	427.2	407.1	418.0

Conclusions

- The heat capacities of pure liquid oxides are not well described in the FACT and SGTE databases. This leads to considerable errors in higher order systems.
- The optimized standard entropies in the thermodynamic databases for selected glasses differ considerably from the experimental ones
- The glass transition is not correctly modeled, even for $\text{SiO}_2(\text{glass})$ for which experimental data exists
- The experimental heats of mixing in glasses, as measured by solution calorimetry, has apparently not been taken into account in the modelings.
- There are scarce attempts in the literature to improve the data (2004Schnurre, 1998Golczewski)