State of the art of the extrapolation of simple oxides in the CALPHAD framework

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Extrapolation of simple oxides in the CALPHAD framework

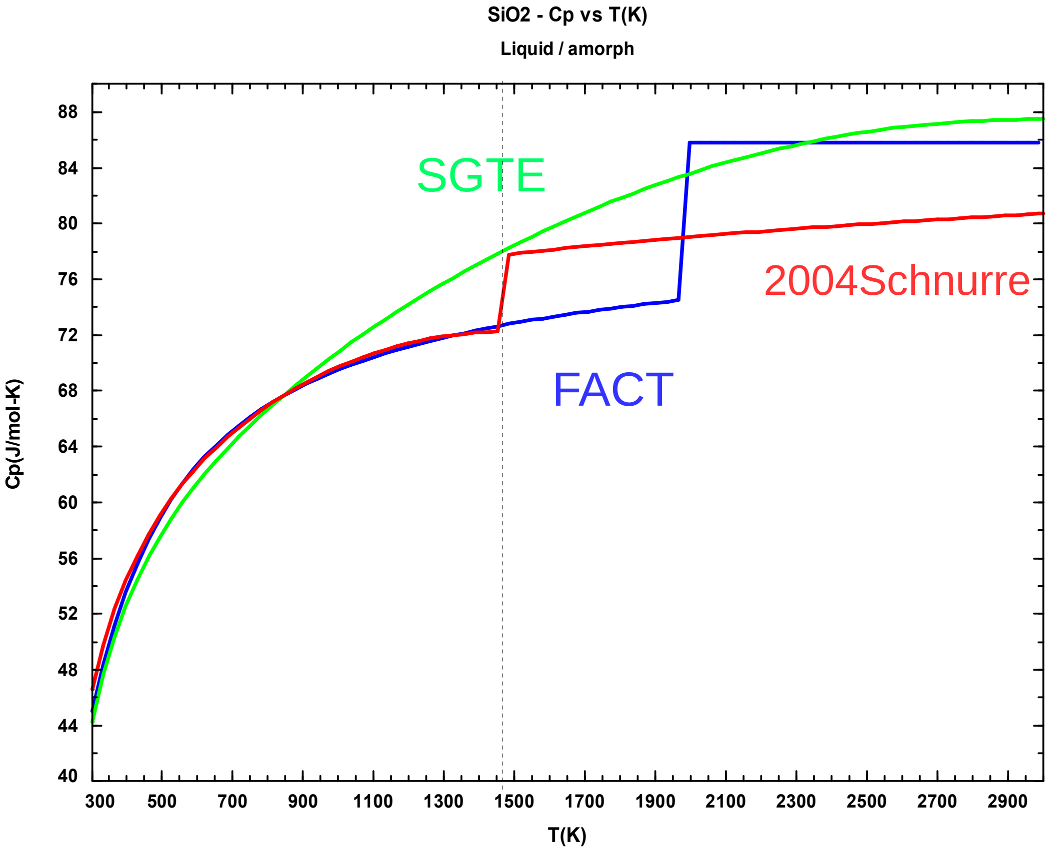
The extrapolation of the Gibbs energy of liquids from high temperature (where experimental data may exist) to room temperature is a key feature in the CALPHAD framework = end members of liquid phase

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 $CaSiO_3$(glass) using SiO_2(glass)
- Al_2O_3 : from $CaAl_2O_4$(glass) & $Ca_{12}Al_{14}O_{33}$(glass) ; $CaAl_2Si_2O_8$(glass)
- MgO : from $CaMgSi_2O_8$(glass)

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

SiO2 – liquid



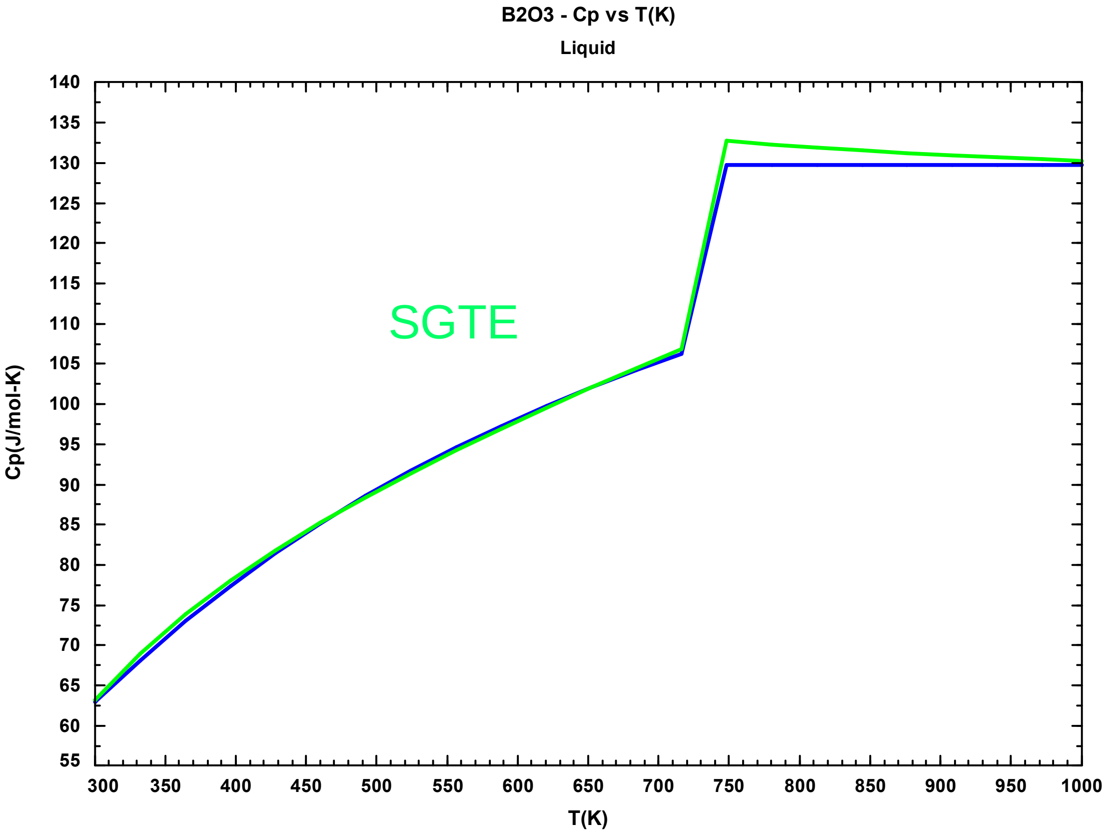
Only Schnurre et al. take into account glass transition

Fact : Solid + liquid at Tfus

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

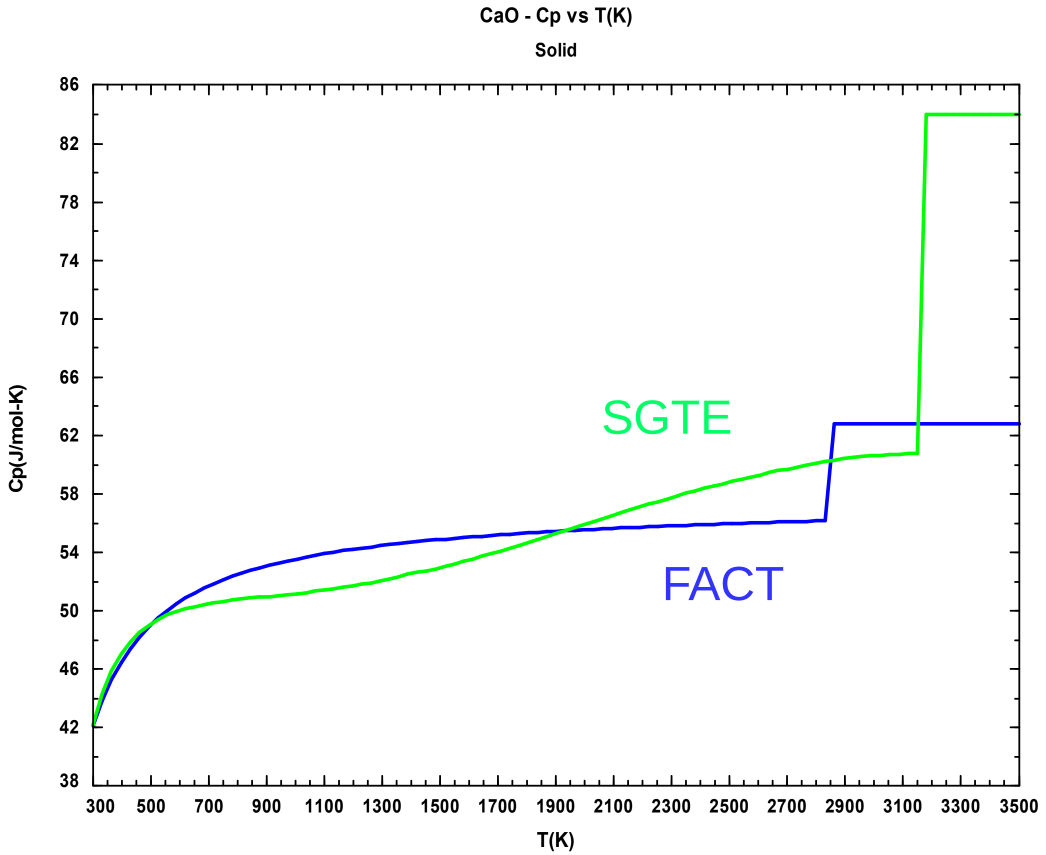
B2O3 - liquid



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

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

CaO solid

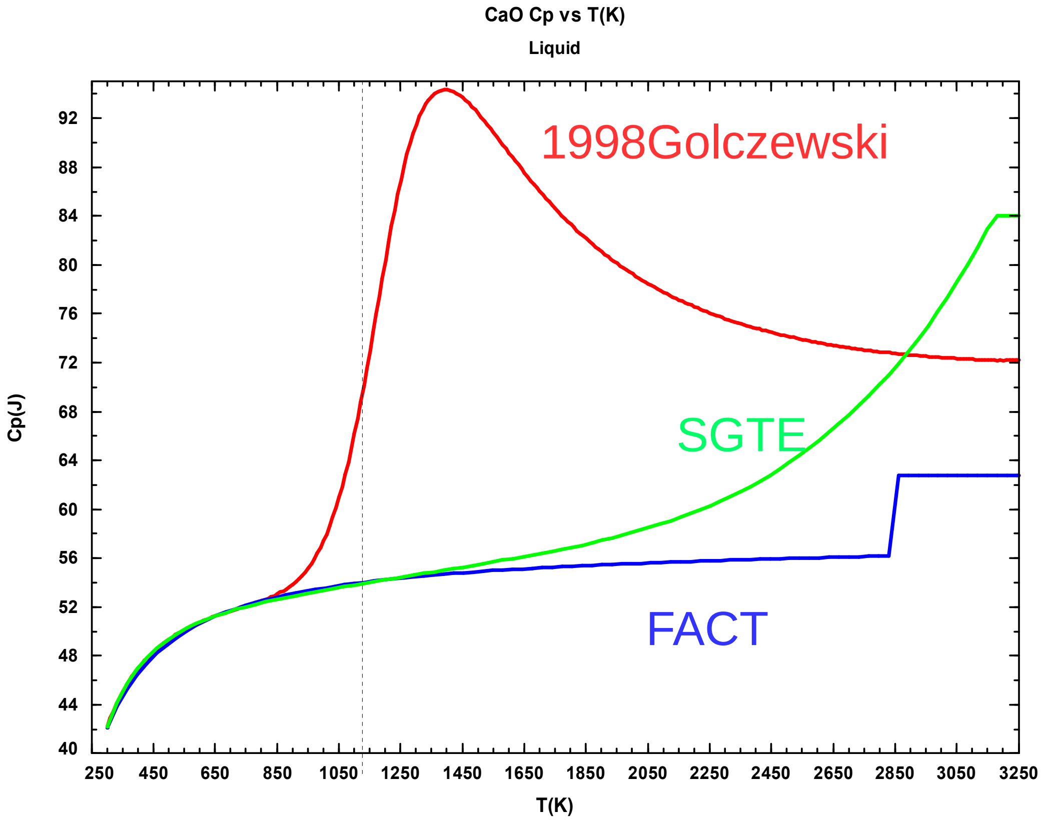


Different melting points in FACT & SGTE databases
- Fact 2857K
- SGTE 3183K

Different cp functions

Different cp for liquid > Tf

CaO - liquid



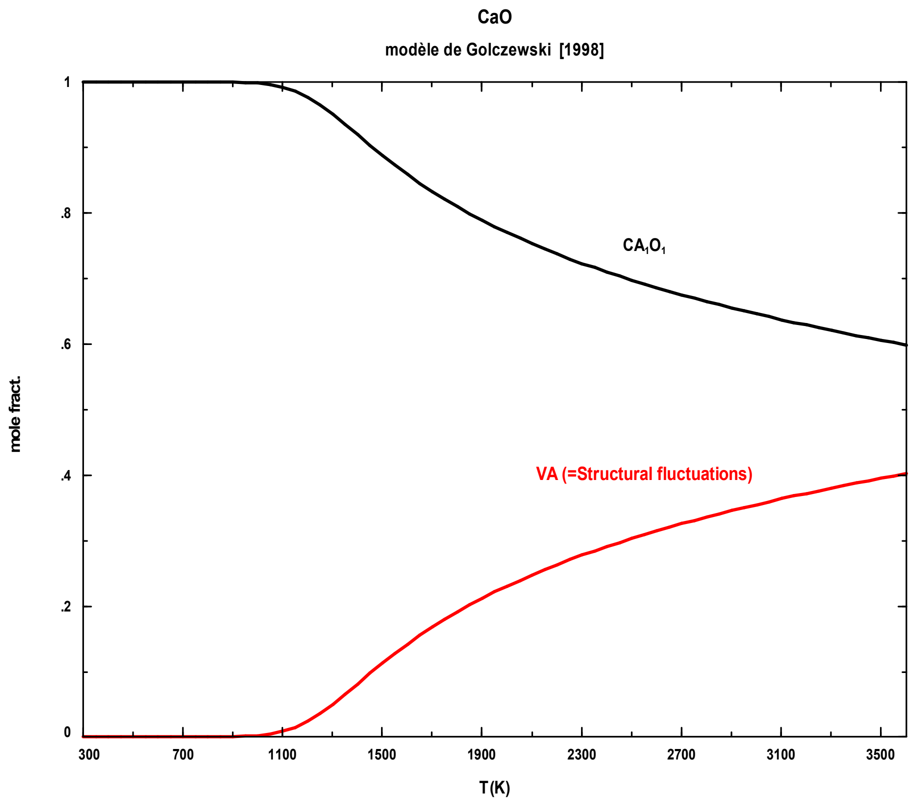
FACT :
solid cp until melting point

SGTE :
broad transition from Tfus 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



Bragg-Williams type model

(CaO,SF)

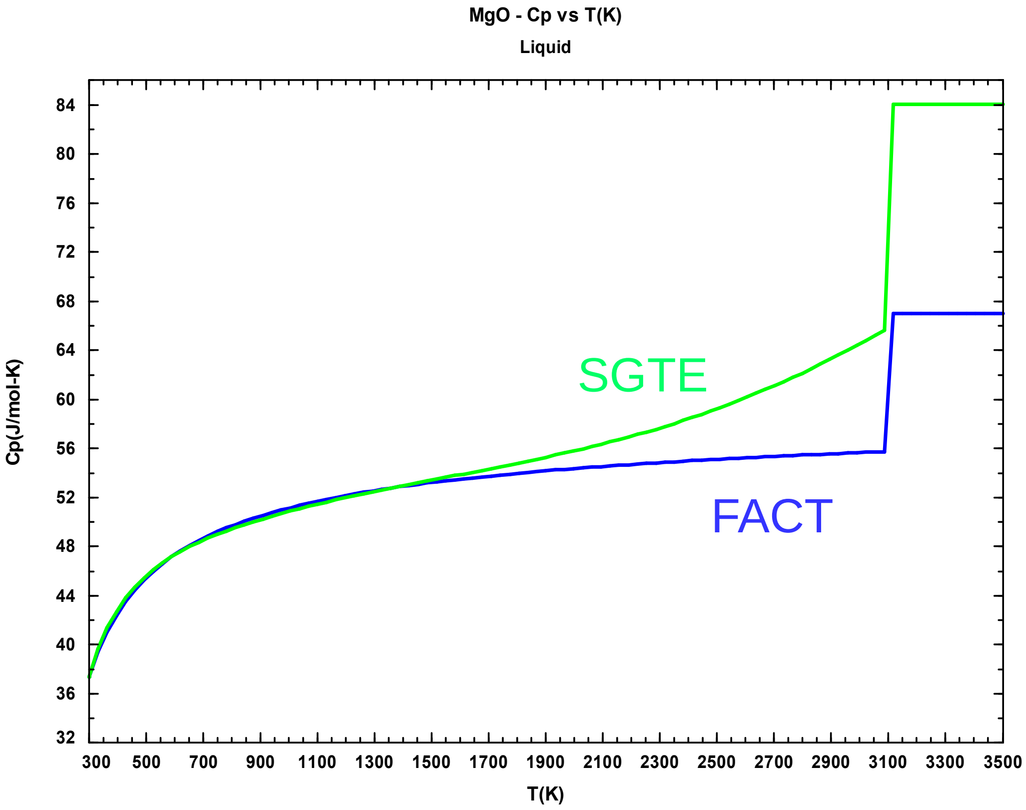
SF = « structural fluctuation »

SF can be interpreted as vacancy without any mass

G(CaO) = Gcryst + A+BT
G(SF) = 60000 – RT

Interaction : L0, L1

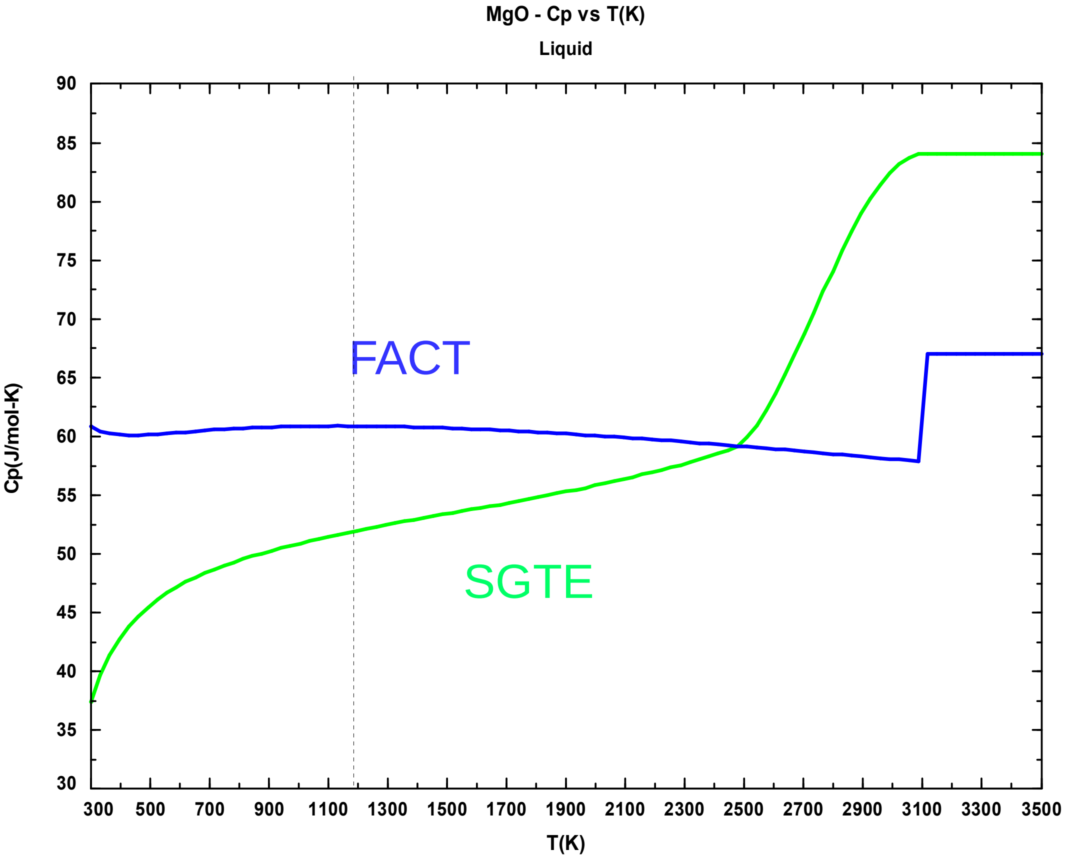
MgO - solid



Identical melting point in both databases

Differences in Cp function and cp for T>Tf

MgO - liquid



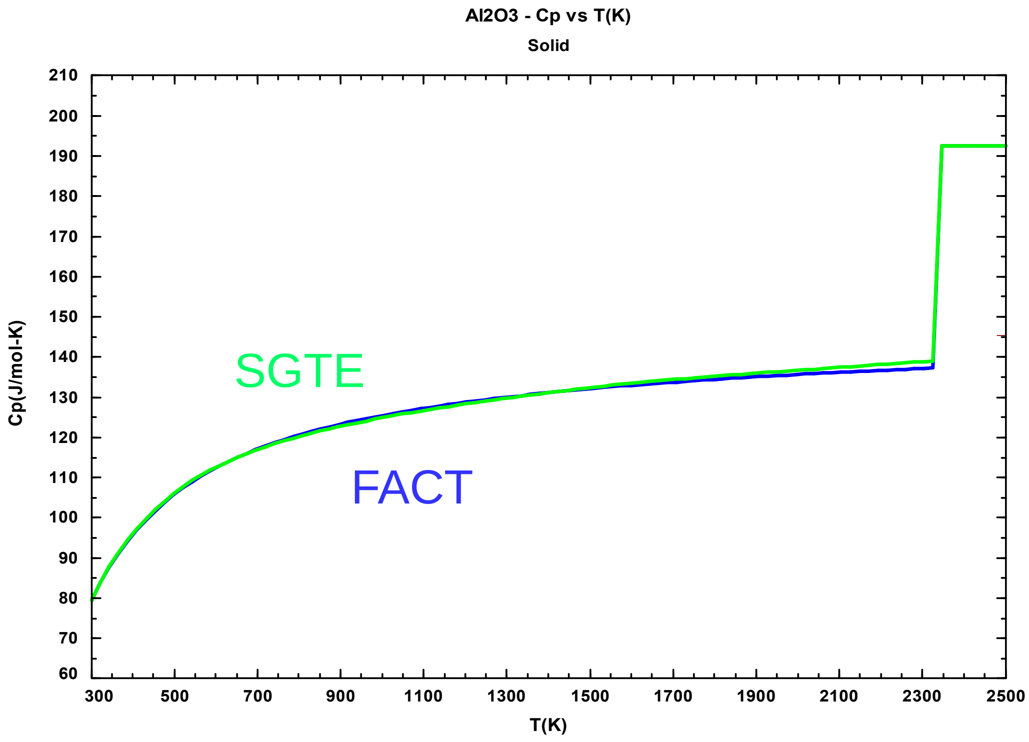
Different Cp extrapolation to RT in both databases.

Cp vs T in FACT almost constant

CP vs T in SGTE with broad transition below Tf

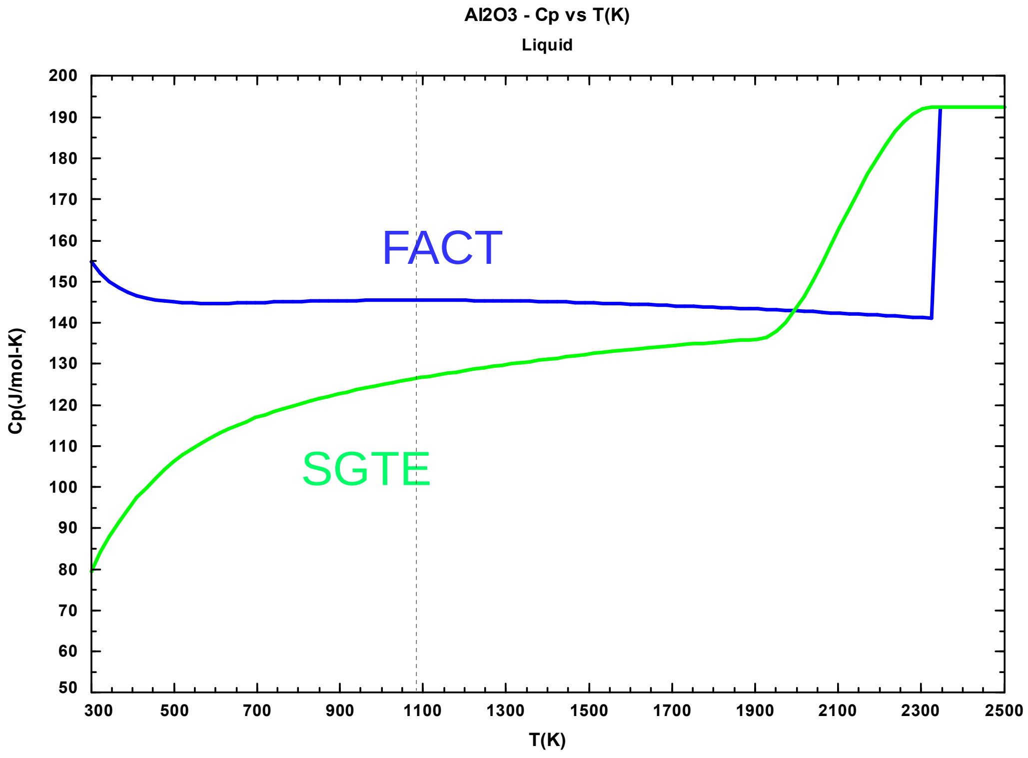
	S298K	Cp(298K)
Exp	30.6 30.7	38.24
SGTE	49.5	37.22
FACT	27.0	60.81

Al2O3 - solid



Cp functions inFACT and SGTE databases are identical

Al2O3- liquid



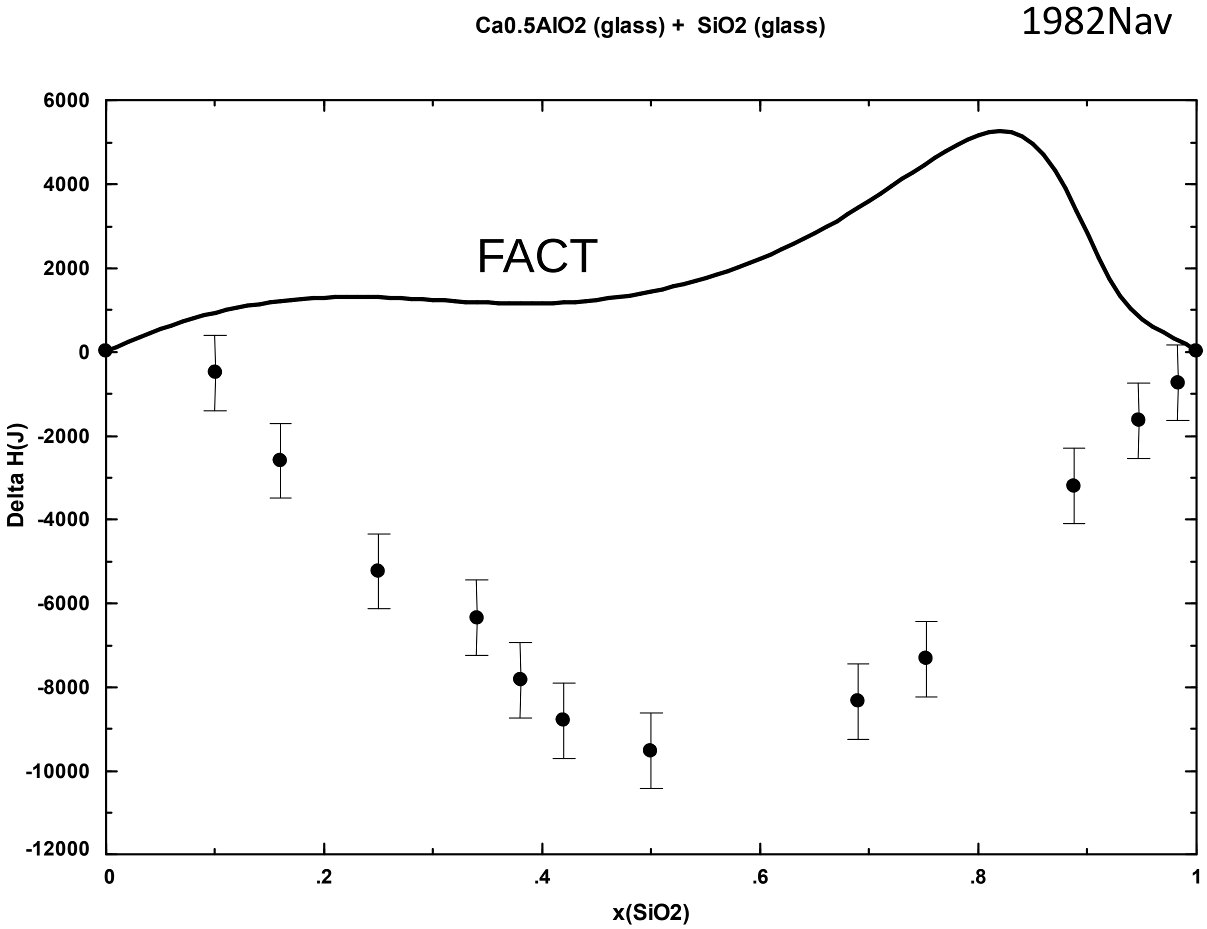
Different Cp extrapolation to RT in both databases.

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 Ca0.5AlO2 – SiO2



Vitrification CaAl2O4

Exp :
25682 J/mol

Calc (FACT) :
19598 J/mol

Heat of vitrification for selected compounds

	Vitrification (985K)		Fusion	
	exp	calc (FACT)	exp	
NaAlSi3O8 (Albite)	51890	59440	65350	67659
CaAl2Si2O8 (Anorthite)	77755	156063	133648	160555
CaMgSi2O6 (Diopside)	85600	128158	129704	129568

Comparison of standard entropies of selected compounds

	S298K – glass		S298K – crystal	
	exp	calc	exp	calc
SiO2	43.3	50.3	41.4	41.5
CaSiO3 - PW	86.2	117.0 112.0	87.2	86.9
CaSiO3 - W			81.7	79.8 82.0
CaMgSi2O6 (Diopside)	159.9	202.7	142.0	142.5
MgSiO3	74.1	74.1 79.5	66.3	66.6
CaAl2Si2O8 (anorthite)	198.7	233.3	199.3	200.2
Mg2Al4Si5O13 (Cordierite)	414.5	427.2	407.1	418.0

Conclusions

- The heat capacities of pure 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 modeled, even for SiO2(glass) for which experimental data exists
- The experimental heat 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)