Thermodynamic modelling of nuclear waste glasses

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The chemical system of the nuclear glass

- A multicomponent system with more than 40 components

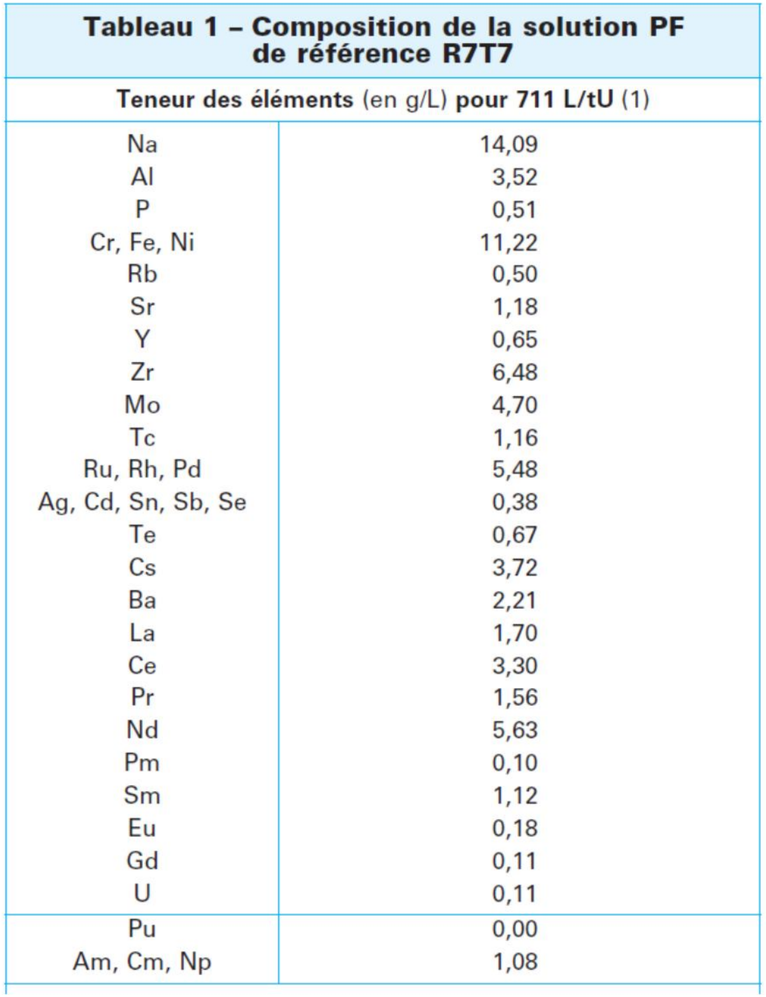


Tableau 1 – Composition de la solution PF de référence R7T7

Teneur des éléments (en g/L) pour 711 L/tU (1)	
Na	14,09
Al	3,52
P	0,51
Cr, Fe, Ni	11,22
Rb	0,50
Sr	1,18
Y	0,65
Zr	6,48
Mo	4,70
Tc	1,16
Ru, Rh, Pd	5,48
Ag, Cd, Sn, Sb, Se	0,38
Te	0,67
Cs	3,72
Ba	2,21
La	1,70
Ce	3,30
Pr	1,56
Nd	5,63
Pm	0,10
Sm	1,12
Eu	0,18
Gd	0,11
U	0,11
Pu	0,00
Am, Cm, Np	1,08

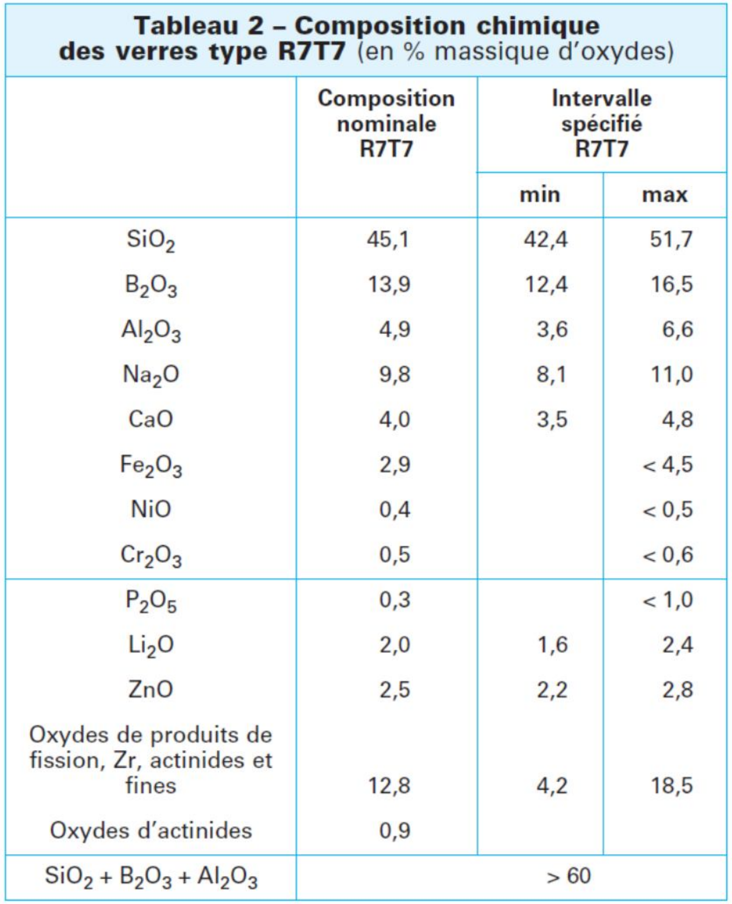


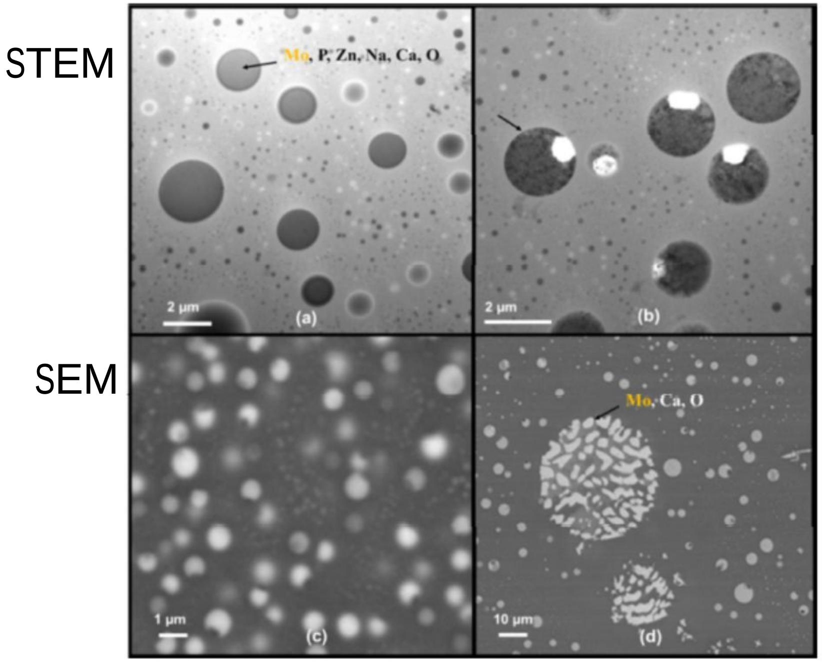
Tableau 2 – Composition chimique des verres type R7T7 (en % massique d'oxydes)

	Composition nominale R7T7	Intervalle spécifié R7T7	
		min	max
SiO_2	45,1	42,4	51,7
B_2O_3	13,9	12,4	16,5
Al_2O_3	4,9	3,6	6,6
Na_2O	9,8	8,1	11,0
CaO	4,0	3,5	4,8
Fe_2O_3	2,9		$< 4,5$
NiO	0,4		$< 0,5$
Cr_2O_3	0,5		$< 0,6$
P_2O_5	0,3		$< 1,0$
Li_2O	2,0	1,6	2,4
ZnO	2,5	2,2	2,8
Oxydes de produits de fission, Zr, actinides et fines	12,8	4,2	18,5
Oxydes d'actinides	0,9		
$SiO_2 + B_2O_3 + Al_2O_3$	> 60		

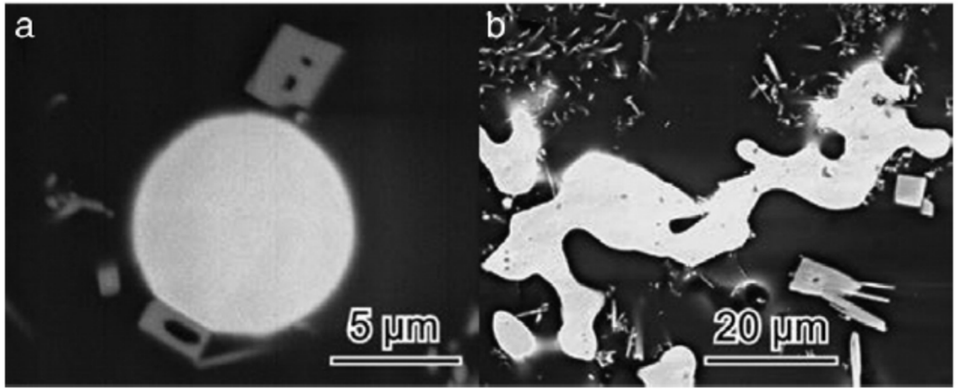
T. Advocat et al., Vitrification des déchets radioactifs, Techniques de l'Ingénieur BN3664 V1 (2008)

The chemical system of the nuclear glass

- **A multiphase system made up of**
- The initial sodium borosilicate liquid that is cooled
  - An immiscible liquid (yellow phase) can also appear
- The glass matrix that is formed
- Various crystalline phases precipitated on cooling because some components have limited solubilities in the melt or in the glass
  - Platinoids Pd, Rh, Ru → RuO_2, Pd-Te…
  - Mo → alkali molybdates
  - Rare Earths (RE) → RE silicates, e.g. oxyapatites



Various microstructures of nuclear glasses enriched in MoO_3 after cooling at 1°C/min (S. Schuller Habilitation Thesis, Montpellier University, France 2014)



SEM images of Pd-Te alloy inclusions
*P. B. Rose, D. I. Woodward, M. I. Ojovan, N. C. Hyatt, and W. E. Lee, J. Non. Cryst. Solids **357**, 2989 (2011)*

The main difficulties

- The multicomponent and multiphase character of the system
- The liquid must be accurately described in a large temperature range below the liquidus, at high undercoolings
- The glass is a phase which is in a non-equilibrium state
  - A specific thermodynamic model is required to describe this phase
- Demixing is a subtle energetic effect that can occur in both the liquid and the glass solution phases
- Experimental thermodynamic data are missing for some of the phases,
  - Including some crystalline ones
  - Particularly for metastable undercooled liquids

Outline

- The simplest thermodynamic model of the unary glass
  - Simon's approximation
- Experimental techniques for the determination of the thermodynamic quantities of the glass
- Multicomponent glass models from the oxide glass community
  - Conradt's model
  - Ideal associated solution model : Vedishcheva et al.
- Glass models from the CALPHAD community
  - 1 state models
  - 2 state models
- Conclusions and perspectives

SIMPLEST THERMODYNAMIC MODEL OF THE UNARY GLASS

Simon’s approximation

- The glass and the crystal have the same composition
- The glass transition range is reduced to a single temperature T_g (corresponding to a typical cooling rate)
- At T_g :
  - The liquid is frozen and becomes a glass
  - The C_P change at the glass transition is approximated by a discontinuity
- Moreover, it is observed that:

$$\text{For } \boldsymbol{T} \leqslant \boldsymbol{T_g} \ : \boldsymbol{C_{pg}} \approx \boldsymbol{C_{pc}} \ \text{ hence } \ \Delta \boldsymbol{C_p} = \boldsymbol{C_{pg}} - \boldsymbol{C_{pc}} \approx 0$$

- As a consequence :

$$\begin{aligned}
&\text{For } \boldsymbol{T} \leqslant \boldsymbol{T_g} \ : \\
&\Delta \boldsymbol{H}(\boldsymbol{T}) = \boldsymbol{H_g}(\boldsymbol{T}) - \boldsymbol{H_c}(\boldsymbol{T}) = \Delta \boldsymbol{H}(\boldsymbol{T_g}) = \Delta \boldsymbol{H_g} = \text{const.} \\
&\Delta \boldsymbol{S}(\boldsymbol{T}) = \boldsymbol{S_g}(\boldsymbol{T}) - \boldsymbol{S_c}(\boldsymbol{T}) = \Delta \boldsymbol{S}(\boldsymbol{T_g}) = \Delta \boldsymbol{S_g} = \text{const.} \\
&\Delta \boldsymbol{G}(\boldsymbol{T}) = \boldsymbol{G_g}(\boldsymbol{T}) - \boldsymbol{G_c}(\boldsymbol{T}) = \Delta \boldsymbol{H_g} - \boldsymbol{T} \, \Delta \boldsymbol{S_g}
\end{aligned}$$

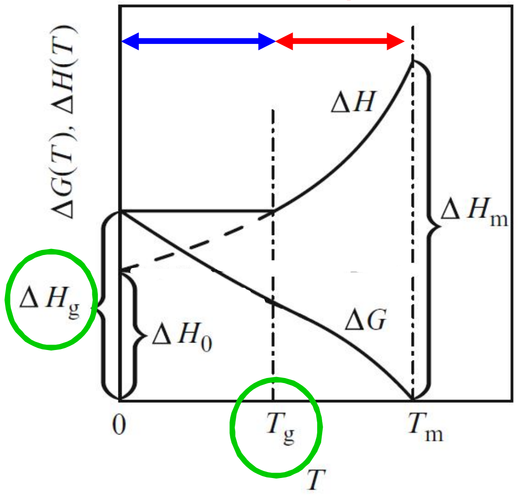
J. Schmelzer and I. Gutzow, Glasses and the Glass Transition (Verlag, Wiley-VCH, Weinheim, Germany, 2011)

Thermodynamic functions of the unary glass according to Simon’s approximation

ΔG, ΔH

Undercooled liquid

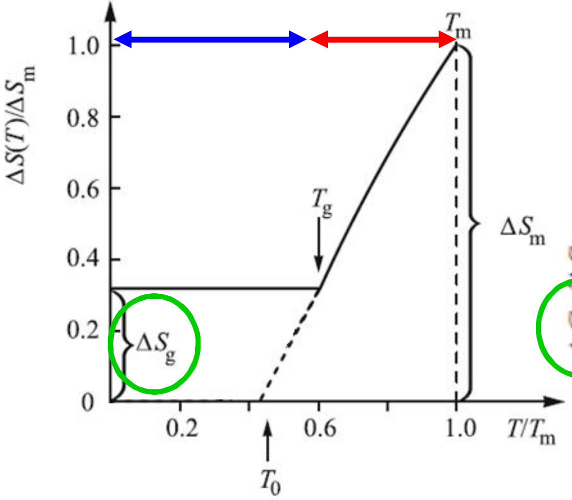
Glass



ΔS

Undercooled liquid

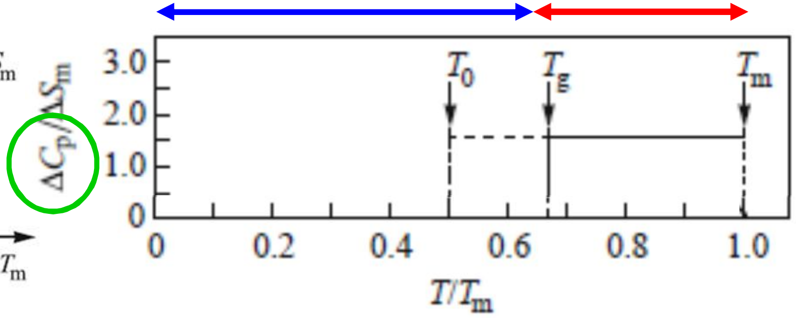
Glass



ΔC_p

Undercooled liquid

Glass



$$\Delta H(T) = H_{g,l}(T) - H_c(T)$$
$$\Delta S(T) = S_{g,l}(T) - S_c(T)$$
$$\Delta G(T) = G_{g,l}(T) - G_c(T)$$

J. Schmelzer and I. Gutzow, Glasses and the Glass Transition (Verlag, Wiley-VCH, Weinheim, Germany, 2011)

Relations between thermodynamic quantities of the glass

- For the undercooled liquid at T

$$\Delta H(T)=\Delta H_g+\int_{T_g}^{T}\Delta C_p\,dT=\Delta H_m-\int_{T}^{T_m}\Delta C_p\,dT$$

$$\Delta H(T)\approx\Delta H_g+\Delta C_p(T-T_g)\approx\Delta H_g-\Delta C_p(T_m-T)$$

$$\boxed{\Delta H_m-\Delta H_g\approx\Delta C_p(T_m-T_g)}$$

$$\Delta S(T)=\Delta S_g+\int_{T_g}^{T}\frac{\Delta C_p}{T}\,dT=\Delta S_m-\int_{T}^{T_m}\frac{\Delta C_p}{T}\,dT$$

$$\boxed{\Delta S_m-\Delta S_g=\Delta C_p\ln\frac{T_m}{T_g}}$$

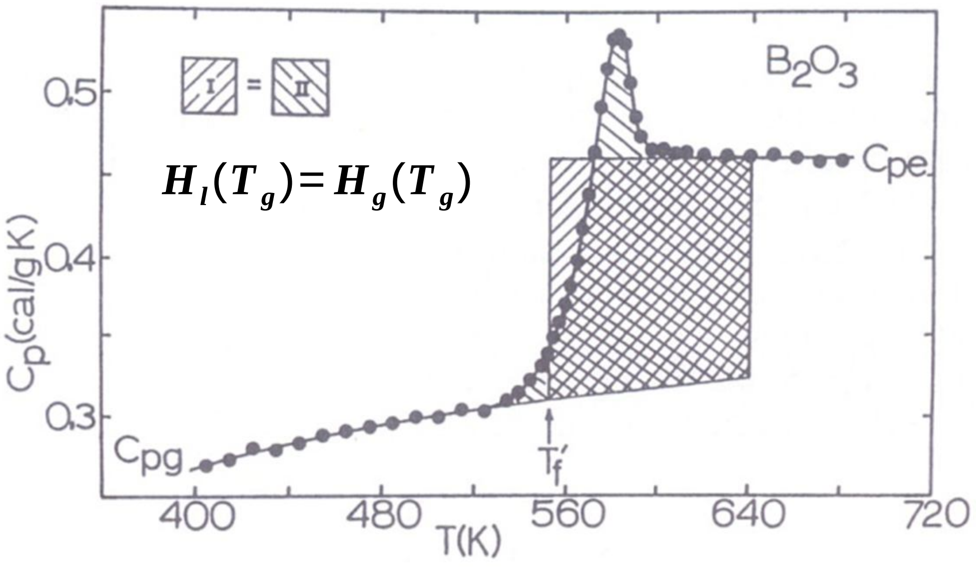
- If ΔH_m and T_m are know: $\Delta S_m=\dfrac{\Delta H_m}{T_m}$
- Only **2 of the 4 thermodynamic quantities describing the glass with respect to the crystal are independent** and need to be determined experimentally

SOME EXPERIMENTAL TECHNIQUES FOR THE DETERMINATION OF THERMODYNAMIC QUANTITIES OF THE GLASS

T_g, ΔC_p determination by DSC

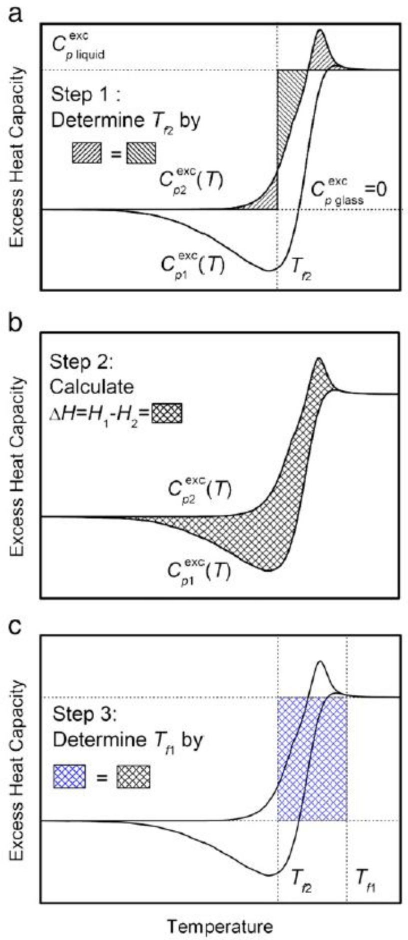
- Signal processing with specific methods

- Method using **1 heating run** when glass cooling rate is comparable to DSC heating rate
  - *M. J. Richardson and N. G. Savill, Polymer 16, 753 (1975)*
  - *C. T. Moynihan, A. J. Easteal, M. A. Debolt, and J. Tucker, J. Am. Ceram. Soc. 8, 12 (1975)*



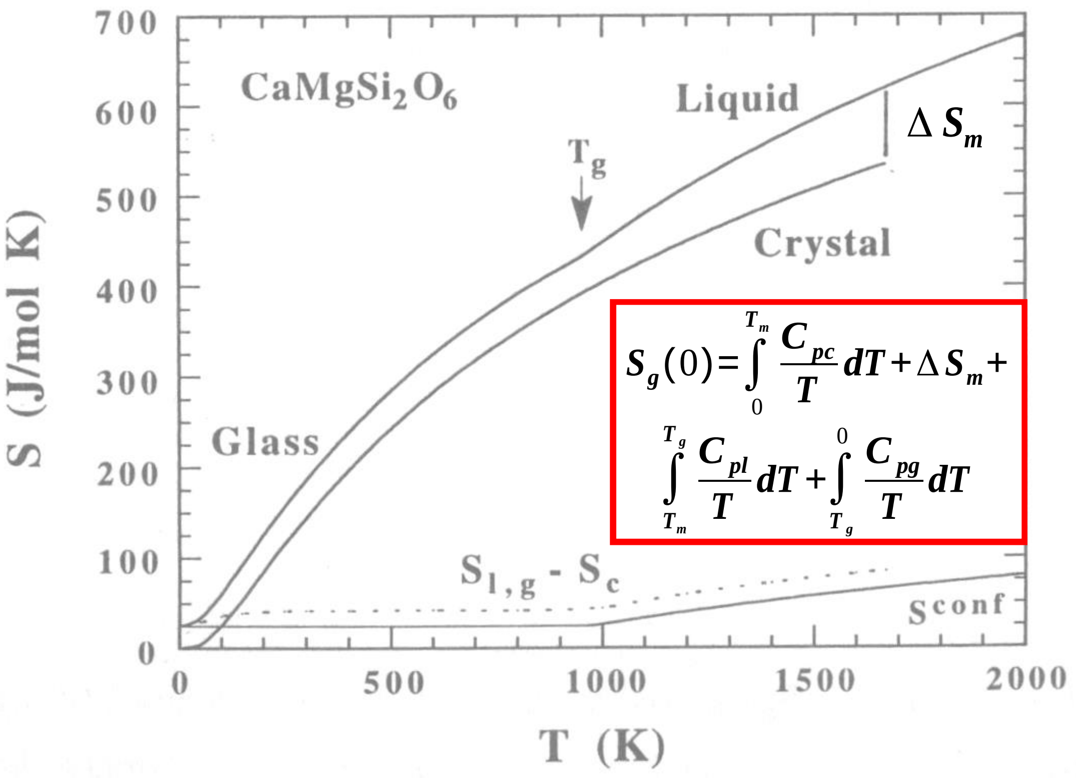
$$H_l(T_g) = H_g(T_g)$$

- Methods using **2 heating runs** for hyper quenched glasses
  - *Y. Z. Yue, J. de C. Christiansen, and S. L. Jensen, Chem. Phys. Lett. 357, 20 (2002)*
  - *X. Guo, M. Potuzak, J. C. Mauro, D. C. Allan, T. J. Kiczenski, and Y. Yue, J. Non. Cryst. Solids 357, 3230 (2011)*



ΔS_g determination by calorimetric cycle or viscosity measurements

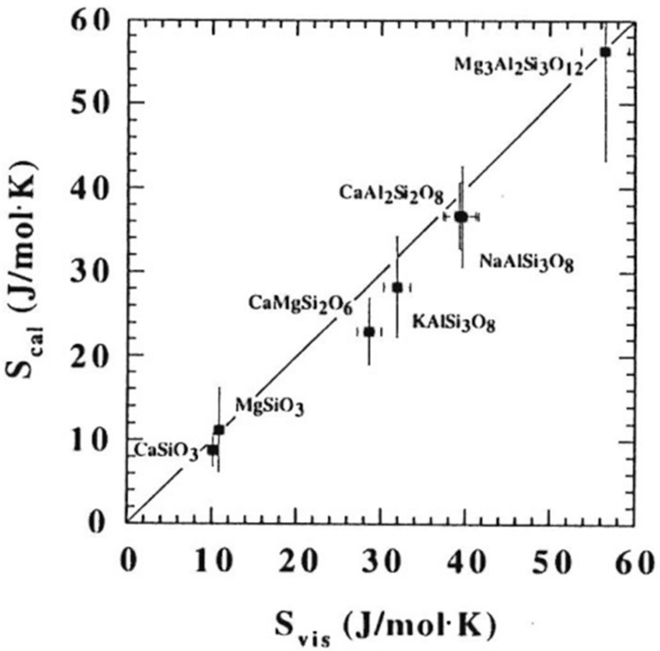
- Combining low temperature adiabatic calorimetry + DSC + drop calorimetry between 0 K and T_m to determine the S(T) curve for the crystal, the liquid and the glass phases
  - Requires that the crystal, the liquid and the glass have the same composition



$$S_g(0)=\int_0^{T_m}\frac{C_{pc}}{T}dT+\Delta S_m+\int_{T_m}^{T_g}\frac{C_{pl}}{T}dT+\int_{T_g}^{0}\frac{C_{pg}}{T}dT$$

P. Richet and Y. Bottinga, in Struct. Dyn. Prop. Silic. Melts - Rev. Mineral. Vol. 32, edited by J. F. Stebbins, P. F. Mc Millan, and D. B. Dingwell (Mineralogical Society of America, Washington D.C., 1995), pp. 67–93.

- Entropy can also be derived from viscosity curves on the basis of the Adam-Gibbs theory



ΔH_g determination by solution calorimetry

(1) Glass + Solvent → Solution (Δl_g)
(2) Crystal + Solvent → Solution (Δl_c)

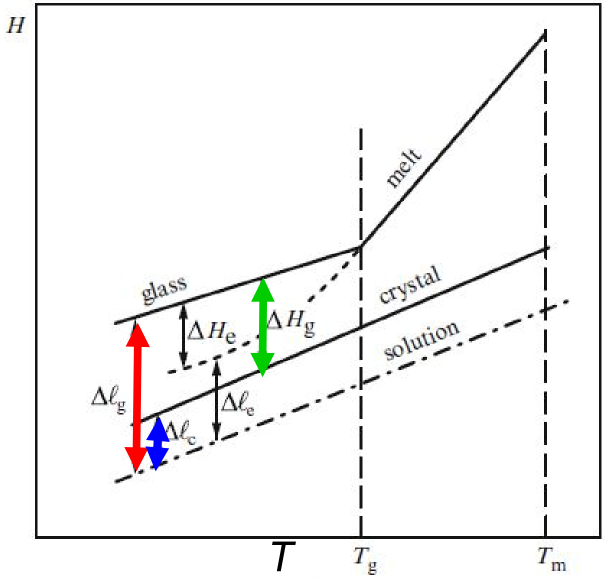
(1)–(2) Glass → Crystal (ΔH_g)

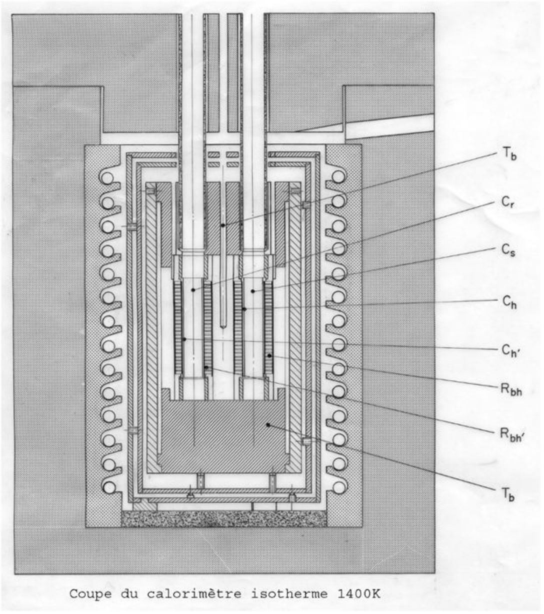
$$\Delta H_g = \Delta l_g - \Delta l_c$$

- Calorimetric experiments can be performed
  - At room T, in aqueous acid solutions
  - At high T (700-800°C), in oxide melt ($2PbO\text{-}B_2O_3$)

- For a ternary glass = $x\ SiO_2$, $y\ B_2O_3$, $z\ Na_2O$
- Separate dissolution of the glass and of its crystalline oxide constituents in a solvent S at T
- Glass + 3 S → $((x\ SiO_2, y\ B_2O_3, z\ Na_2O))_{3S}$ (a)
  - $x <SiO_2> + S \rightarrow ((x\ SiO_2))_S$ (b)
  - $y <B_2O_3> + S \rightarrow ((y\ B_2O_3))_S$ (c)
  - $z <Na_2O> + S \rightarrow ((z\ Na_2O))_S$ (d)

- The glass formation reaction is written as:
  - $x <SiO_2> + y <B_2O_3> + z <Na_2O> \rightarrow$ Glass
  - $\Delta_f H(\text{Glass}) = \Delta_{sol}H^\infty(b) + \Delta_{sol}H^\infty(c) + \Delta_{sol}H^\infty(d) - \Delta_{sol}H^\infty(a)$





Tian-Calvet calorimeter for high T < 1400K solution or drop-solution experiments

MULTICOMPONENT GLASS MODELS FROM THE OXIDE GLASS COMMUNITY

Selected bibliography

- Conradt's model
  - *Conradt, R. (2001). Modeling of the thermochemical properties of* ***multicomponent oxide melts****. Zeitschrift Für Metallkunde, 92(10), 1158–1162*
  - *Conradt, R. (2004). Chemical structure, medium range order, and crystalline reference state of* ***multicomponent oxide liquids and glasses****. Journal of Non-Crystalline Solids, 345–346, 16–23*
  - *Conradt, R. (2008).* ***The industrial glass melting process****. In K. Hack (Ed.), The SGTE Casebook Thermodynamics at work (2nd ed., pp. 282-303). Cambridge, England: Woodhead Publishing Ltd, CRC Press*
- Ideal associated solution model of Vedishcheva et al.
  - *Shakhmatkin, B. A., Vedishcheva, N. M., Shultz, M. M., & Wright, A. C. (1994). The thermodynamic properties of oxide glasses and glass-forming liquids and their chemical structure. Journal of Non-Crystalline Solids, 177(C), 249–256.*
  - *Schneider, J., Mastelaro, V. R., Zanotto, E. D., Shakhmatkin, B. A., Vedishcheva, N. M., Wright, A. C., & Panepucci, H. (2003). Qn distribution in stoichiometric* ***silicate glasses****: Thermodynamic calculations and 29Si high resolution NMR measurements. Journal of Non-Crystalline Solids, 325(1–3), 164–178.*
  - *Vedishcheva, N. M., Shakhmatkin, B. A., & Wright, A. C. (2004). The structure of* ***sodium borosilicate glasses****: Thermodynamic modelling vs. experiment. Journal of Non-Crystalline Solids, 345–346, 39–44.*
  - *Vedishcheva, N. M., Shakhmatkin, B. A., & Wright, A. C. (2005). Thermodynamic modelling of the structure and properties of glasses in the systems* $\mathbf{Na_2O–B_2O_3–SiO_2}$ *and* $\mathbf{Na_2O–CaO–SiO_2}$*. Phys. Chem. Glasses, 46(2), 99–105.*
  - *Vedishcheva, N. M., Shakhmatkin, B. a., & Wright, A. C. (2008). The Structure-Property Relationship in Oxide Glasses: A Thermodynamic Approach. Advanced Materials Research, 39–40, 103–110.*
  - *Vedishcheva, Natalia M. Polyakova, I. G., & Wright, A. C. (2014). Short and intermediate range order in* ***sodium borosilicate glasses****: a quantitative thermodynamic approach. Physics and Chemistry of Glasses - European Journal of Glass Science and Technology Part B, 55(6), 225–236.*

Conradt's model

- Description of the unary glass similar to Simon's approximation
- Multicomponent glass model
  - Determination of the **Crystalline Reference State (CRS) of the glass** = the assembly, nature and quantity, of the crystalline mineral phases that would exist at T_g under equilibrium conditions
    - not derived through the Gibbs energy minimization of the system but combining
      - the knowledge of the predominant quaternary phase diagram (= 85 – 95% of the oxides) → major mineral phases of the CRS
      - the CIPW (Cross, Iddings, Pirsson, and Washington) norm → minor phases of the CRS
  - The **CRS is assumed to reflect the Short Range Order (SRO) in both the liquid and glass**
  - The thermodynamic functions of the glass are calculated by a weighed average of the functions of the CRS components
    - assuming that the liquid and the glass are described using entities having the same stoichiometry as the crystalline phases of the CRS
    - **This is an associated model in which both the ideal entropy of mixing and the excess term are neglected**
- The model accuracy is
  - Limited by its simplicity (and the quality of the database)
  - < 5 % for integral quantities (H, G)
  - < a factor of 2 for the activity coefficients of individual oxides

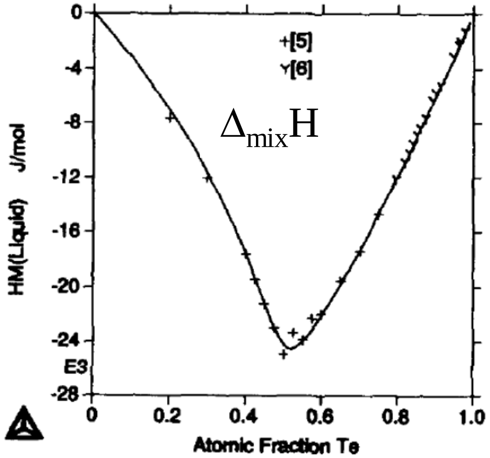
Ideal associated solution model of Vedishcheva et al.

- The glass is described as **an associated solution of the binary oxides and the products of their reactions ;** this solution is considered **ideal**
- These products, called **chemical groupings**, have
  - the same stoichiometry as the crystalline compounds of the phase diagram,
  - A structural similarity with the crystalline compounds in term of the ratio between the basic structural unit which characterize the SRO
- The nature and the proportions of the oxides and groupings are calculated using the Gibbs energy of formation of all the compounds by **solving a non linear system of equations**
  - mass balance + law of mass action equations
- As in Conradt's model, the glass/liquid solution is described by an associated model in which the **associates have the same compositions as the compounds of the phase diagram**
  - No clear distinction between the liquid and the glass in the model
- The model is validated towards experimental results on glasses
  - structure : XRD, NMR, IR, Raman, neutron scattering
  - macroscopic properties : e.g. density
- This validation requires to establish a link between the concentrations
  - of the chemical groupings which are predicted by the model
  - of the basic structural units Q^n, B^n which reflect the **SRO (Short-Range Order**),
  - of the Super-Structural Units (**SSU**) at the 1-2 nm scale which reflect the **MRO (Medium-Range Order**)
- Example of results : SSU concentrations are predicted with an uncertainty < 2%

Interactions in liquids

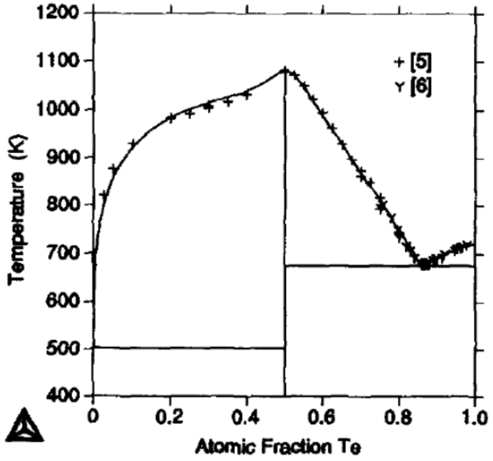
- A liquid cannot systematically be described using an associate corresponding to a compound of the phase diagram

Sn-Te system

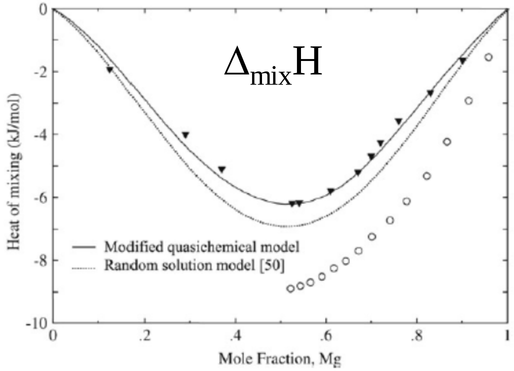


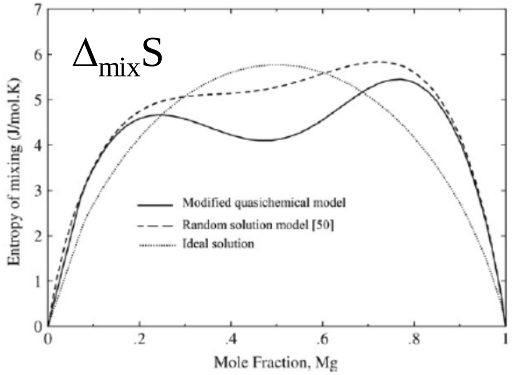
Strong interaction in the liquid $\Delta_{mix}H$ has a V-shape

Clavaguera-Mora, M. T., Comas, C., & Clavaguera, N. (1994). Calculations of the tin-tellurium system. Calphad, 18(2), 141–155

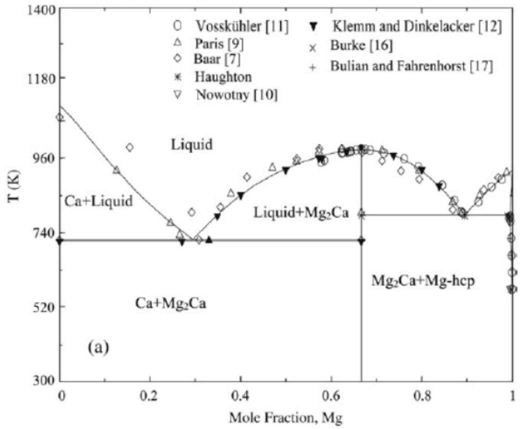


Ca-Mg system



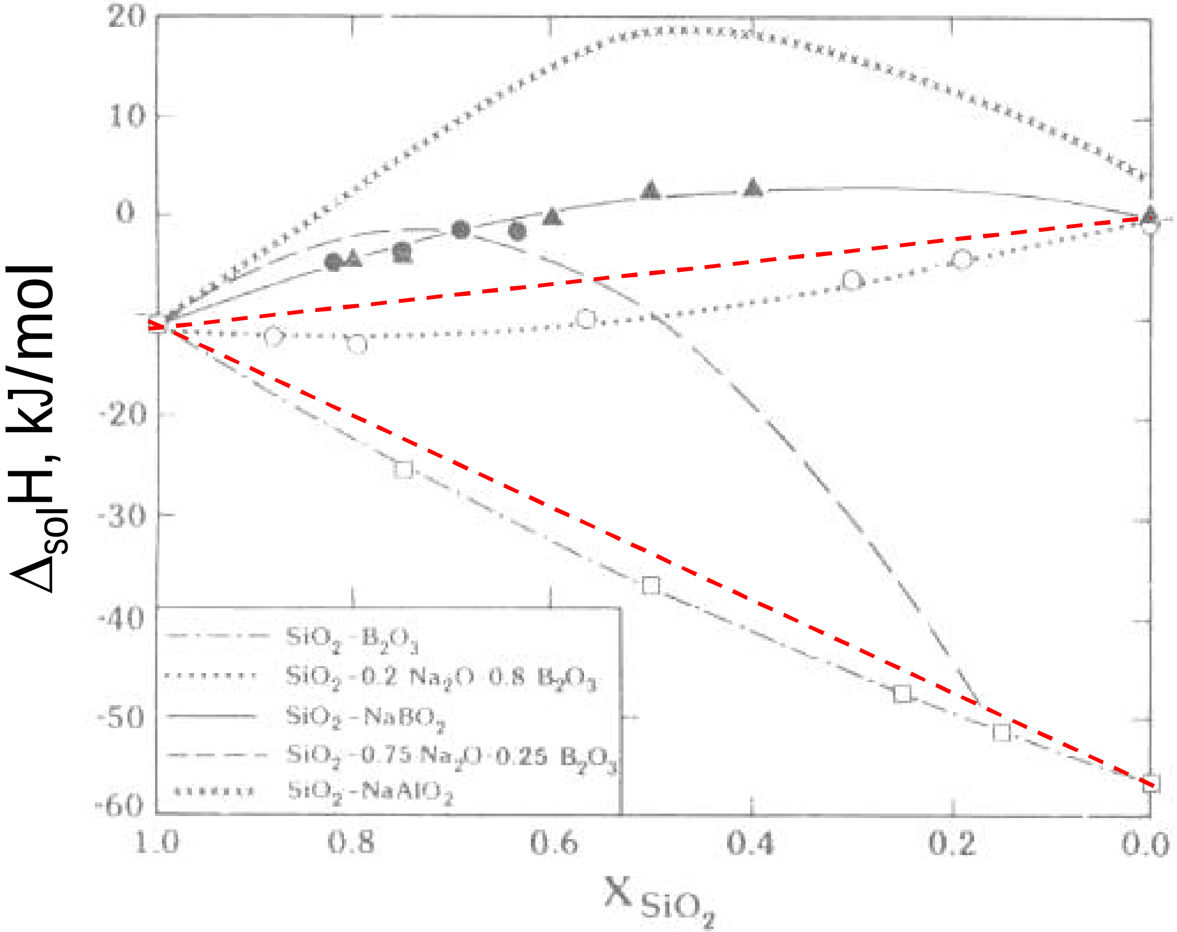


Aljarrah, M., & Medraj, M. (2008). Thermodynamic modelling of the Mg-Ca, Mg-Sr, Ca-Sr and Mg-Ca-Sr systems using the modified quasichemical model. Calphad, 32(2), 240–251.



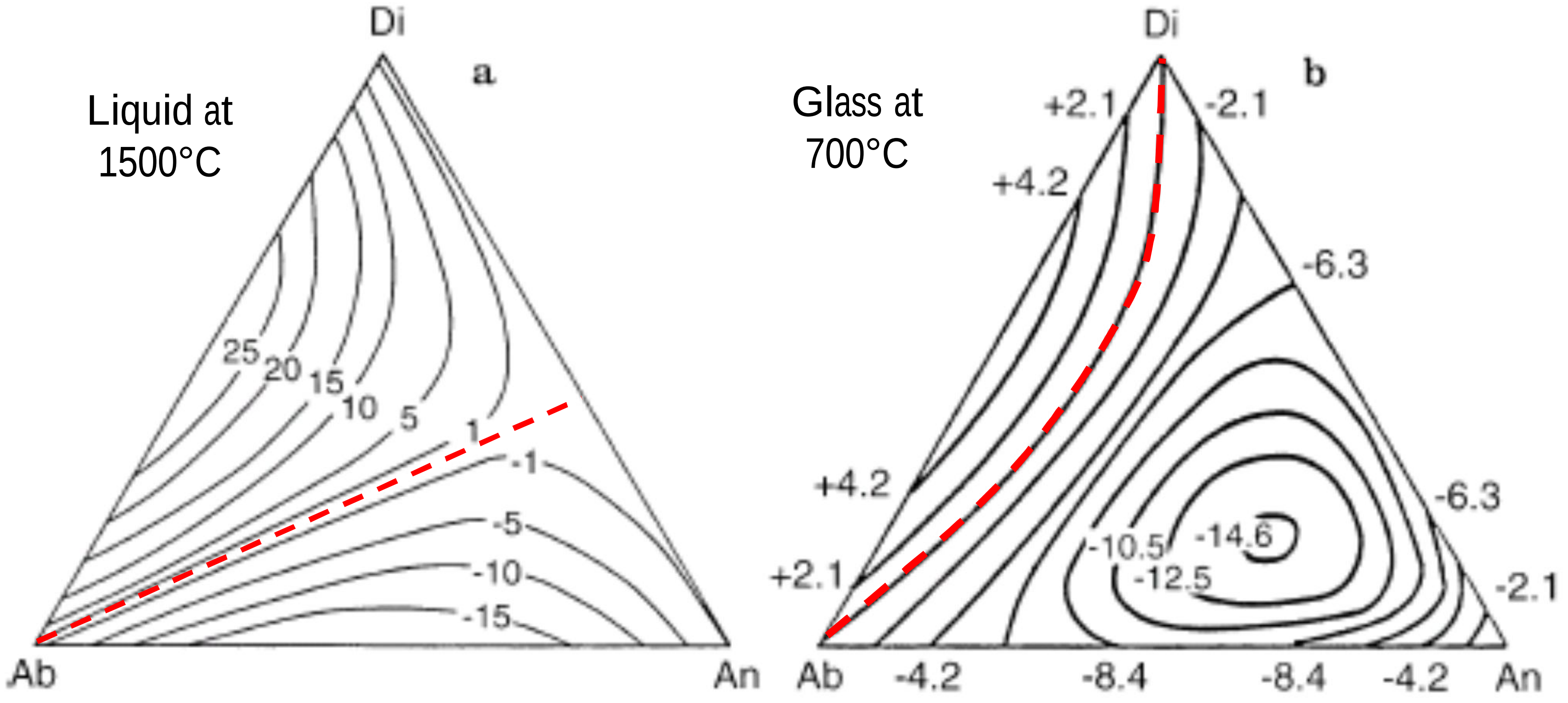
Mixing enthalpies in SiO_2 – B_2O_3 – Na_2O glasses

- Measured by solution calorimetry in $2PbO\text{-}B_2O_3$ molten at 974K
  - *R. L. Hervig and A. Navrotsky, J. Am. Ceram. Soc.* ***68****, 314 (1985)*



Mixing enthalpies surfaces in the Ab-An-Di liquid and glass

Albite = $NaAlSi_3O_8$ – Anorthite = $CaAl_2Si_2O_8$ – Diopside = $CaMgSi_2O_6$



A. Navrotsky, Phys. Chem. Miner. ***24****, 222 (1997).*

Requirements on the models

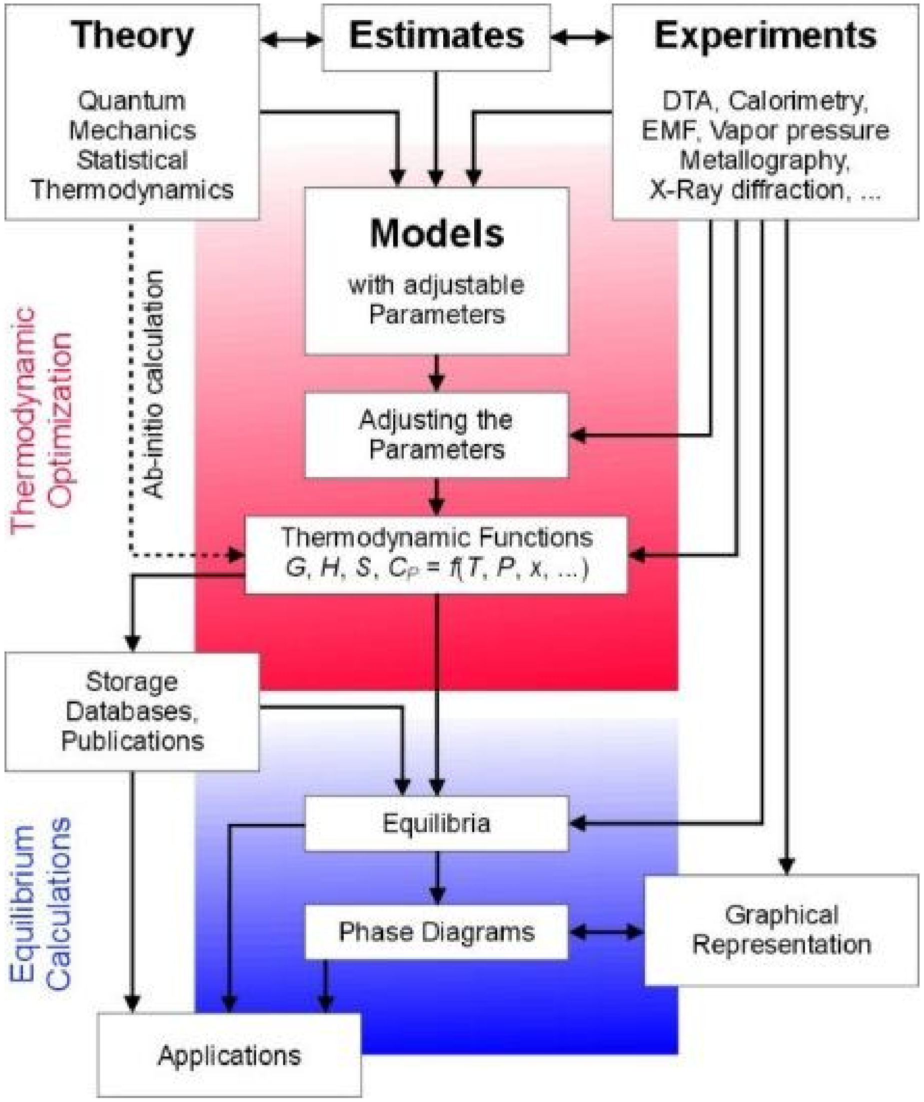
- The mixing enthalpies in liquid and glasses
  - Are weak (≈ few kJ/mol)
  - And sometimes endothermic (> 0), the glass or liquid solutions are then only stabilized by the mixing entropic term
- These solutions can be destabilized by a decrease in temperature leading to a demixing phenomenon
- An oversimplified model will not be able to predict such subtle energetic effects
- The liquid and the glass are two different solutions both qualitatively and quantitatively

MODELS FROM THE CALPHAD COMMUNITY

The CALPHAD method

- The **Calphad method** is the most firmly established method for thermodynamic modeling of multicomponent multiphase systems
- It means the use of all available experimental and theoretical data to assess the parameters of the Gibbs energy models selected for each phase

H. L. Lukas, S. G. Fries, and B. Sundman, Computational Thermodynamics: The Calphad Method (Cambridge University Press, 2007)



Coupling with kinetic models: diffusion, precipitation…

Description of solution phases in the CALPHAD approach

$$G^{\phi} = \boxed{{}^{ref}G^{\phi}} + \boxed{{}^{id}G^{\phi}} + \boxed{{}^{xs}G^{\phi}}$$

- Mechanical mixture of the unaries
  - A unary is an element of the periodic table but can also be a compound under conditions that it does not decompose into other components

$$\boxed{{}^{ref}G^{\phi} = \sum_i x_i \, {}^{\circ}G_i^{\phi}}$$

Taken from a unary database e.g. SGTE elements or substance databases

- Ideal entropy term

$$\boxed{{}^{id}G^{\phi} = \sum_i x_i \ln x_i}$$

- Excess term for a binary solution

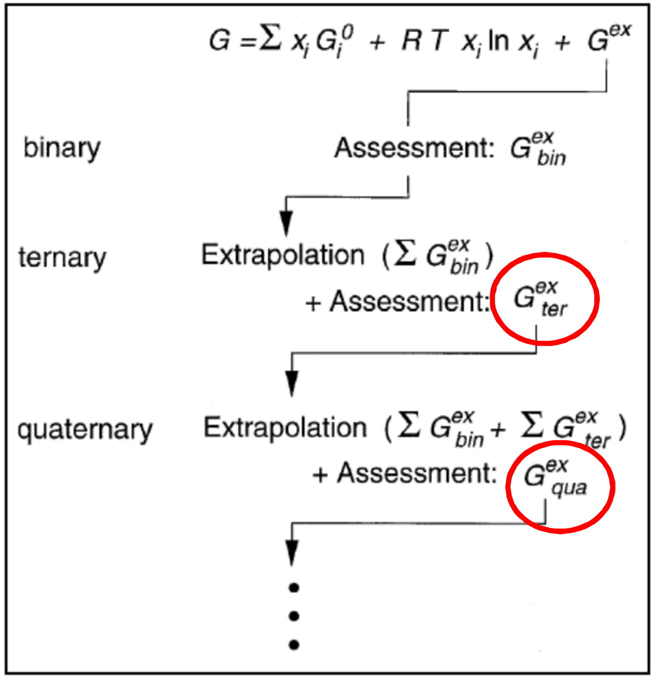
$$\boxed{{}^{xs}G^{\phi} = x_i x_j \sum_{\nu=0} {}^{\nu}L^{\phi} (x_i - x_j)^{\nu}}$$

$${}^{\nu}L^{\phi} = {}^{\nu}a^{\phi} + {}^{\nu}b^{\phi} T$$

$\nu = 0, 1, 2$

Parameters adjusted during the assessment

- Extrapolation to higher order systems



U. R. Kattner, Jom 49, 14 (1997)

Selected bibliography

- 2 comprehensive reviews on the application of the CALPHAD method to glasses
    - *Palumbo, M., & Battezzati, L. (2008). Thermodynamics and kinetics of metallic amorphous phases in the framework of the CALPHAD approach. Calphad: Computer Coupling of Phase Diagrams and Thermochemistry, 32(2), 295–314.*
    - *Becker, C. a., Ågren, J., Baricco, M., Chen, Q., Decterov, S. a., Kattner, U. R., … Selleby, M. (2014). Thermodynamic modelling of liquids: CALPHAD approaches and contributions from statistical physics. Physica Status Solidi (B), 52(1), 33–52.*
- 2 types of models
    - 1-state models
        - **Bormann et al.**
        - Shao et al.
        - **Schnurre et al.**
    - 2-state models
        - **Agren et al.**
        - **Golczewski et al.**

Selected bibliography of 1-state models

- Bormann et al.
  - **Ni-Ti, Ni-Zr, Nb-Al** : Bormann, R., Gärtner, F., & Zöltzer, K. (1988). *Application of the CALPHAD method for the prediction of amorphous phase formation. Journal of The Less-Common Metals, 145(C), 19–29.*
  - **Ni-Ti** : Bormann, R., & Zöltzer, K. (1992). *Determination of the Thermodynamic Functions and Calculation of Phase Diagrams for Metastable Phases. Phys. Status Solidi A, 131, 691–705.*
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  - **Fe-B :** Palumbo, M., Cacciamani, G., Bosco, E., & Baricco, M. (2001). *Thermodynamic analysis of glass formation in Fe-B system. Calphad, 25(4), 625–637.*
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Model of Bormann et al.

- CALPHAD expression for G of a solution: $G^{\varphi} = {}^{\mathrm{ref}}G^{\varphi} + {}^{id}G^{\varphi} + {}^{ex}G^{\varphi}$
- with : $${}^{id}G^{\varphi} = RT \sum_{i} x_i \ln x_i \, .$$
- and : $${}^{ex}G^{\varphi} = \sum_{i} \sum_{j>i} x_i x_j \sum_{\nu} {}^{\nu}L^{\varphi}_{ij} \left(x_i - x_j\right)^{\nu} .$$
- For a binary solution : $${}^{ex}G^{\varphi} = x_A x_B \sum_{\nu} {}^{\nu}L^{\varphi}_{A,B} (x_A - x_B)^{\nu}$$
- For the binary liquid, Bormann et al. have written the dependency of the order 0 parameter of the excess term as :

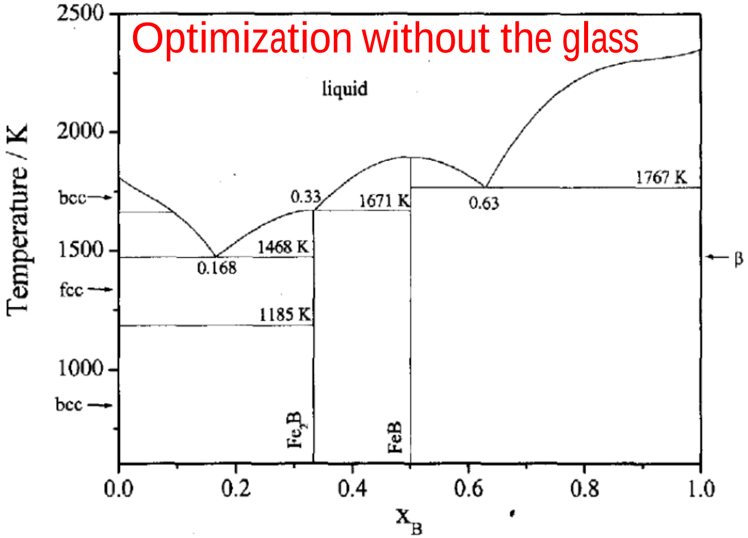
$${}^{0}L^{\mathrm{liq}}_{A,B} = A^{\mathrm{liq}}_{0} + B^{\mathrm{liq}}_{0} \cdot T \boxed{+ C^{\mathrm{liq}}_{0} \cdot T^{-1}}$$

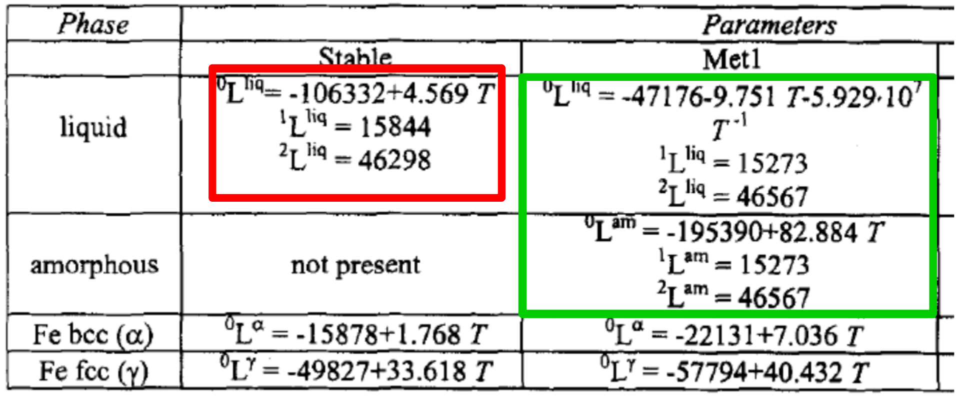
- And for the glass : $${}^{0}L^{am}_{A,B} = A^{am}_{0} + B^{am}_{0} \cdot T \, .$$

Model of Bormann et al.

- $$C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{P,n_i}$$ hence: $${}^{ex}C_p^{liq} = \frac{-2x_A x_B C_0^{liq}}{T^2}$$
- At the temperature T_g of the glass transition, the first derivatives (H and S) of G are continuous :
  - $\Delta S^{am-liq} = 0$ implies that $A_0^{am} = A_0^{\mathrm{liq}} + 2 \cdot C_0^{\mathrm{liq}} \cdot T_g^{-1}$
  - $\Delta H^{am-liq} = 0$ implies that $B_0^{am} = B_0^{\mathrm{liq}} - C_0^{\mathrm{liq}} \cdot T_g^{-2}.$
- The liquid and the glass are treated as a single phase, the heat capacity of which has **two distinct analytical expressions** depending whether $T > T_g$ or $T < T_g$
  - Discontinuity of C_p at T_g
  - Composition dependency of T_g is not taken into account

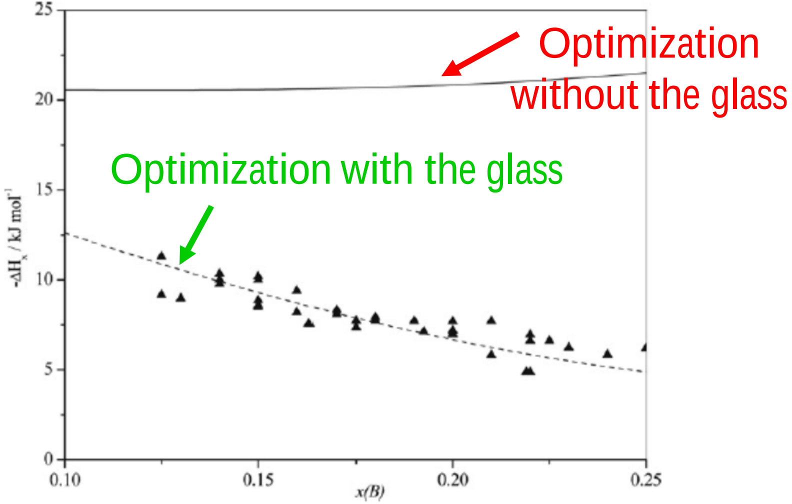
Model of Bormann et al. applied to the Fe-B system


Optimization without the glass



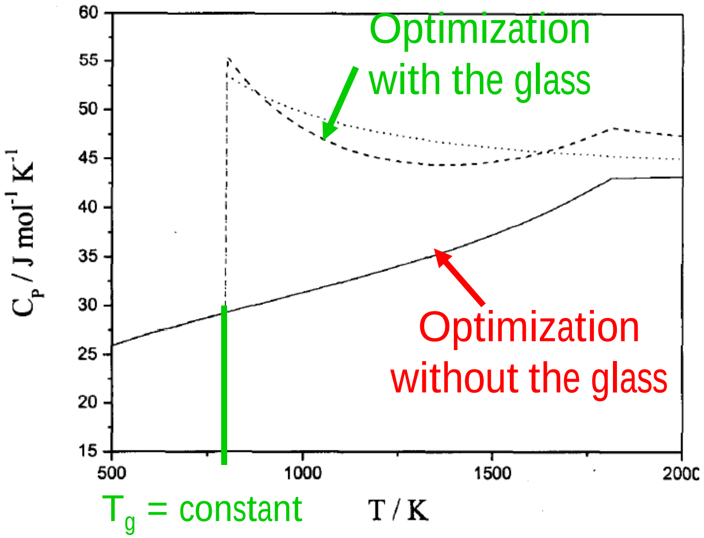
Phase	Parameters	
	Stable	Met1
liquid	$^0L^{liq} = -106332+4.569\,T$ $^1L^{liq} = 15844$ $^2L^{liq} = 46298$	$^0L^{liq} = -47176-9.751\,T-5.929{\cdot}10^7\,T^{-1}$ $^1L^{liq} = 15273$ $^2L^{liq} = 46567$
amorphous	not present	$^0L^{am} = -195390+82.884\,T$ $^1L^{am} = 15273$ $^2L^{am} = 46567$
Fe bcc (α)	$^0L^{\alpha} = -15878+1.768\,T$	$^0L^{\alpha} = -22131+7.036\,T$
Fe fcc (γ)	$^0L^{\gamma} = -49827+33.618\,T$	$^0L^{\gamma} = -57794+40.432\,T$

Crystallization enthalpy


Optimization without the glass

Optimization with the glass

C_p vs. T for $Fe_{83}B_{17}$ alloy


Optimization with the glass

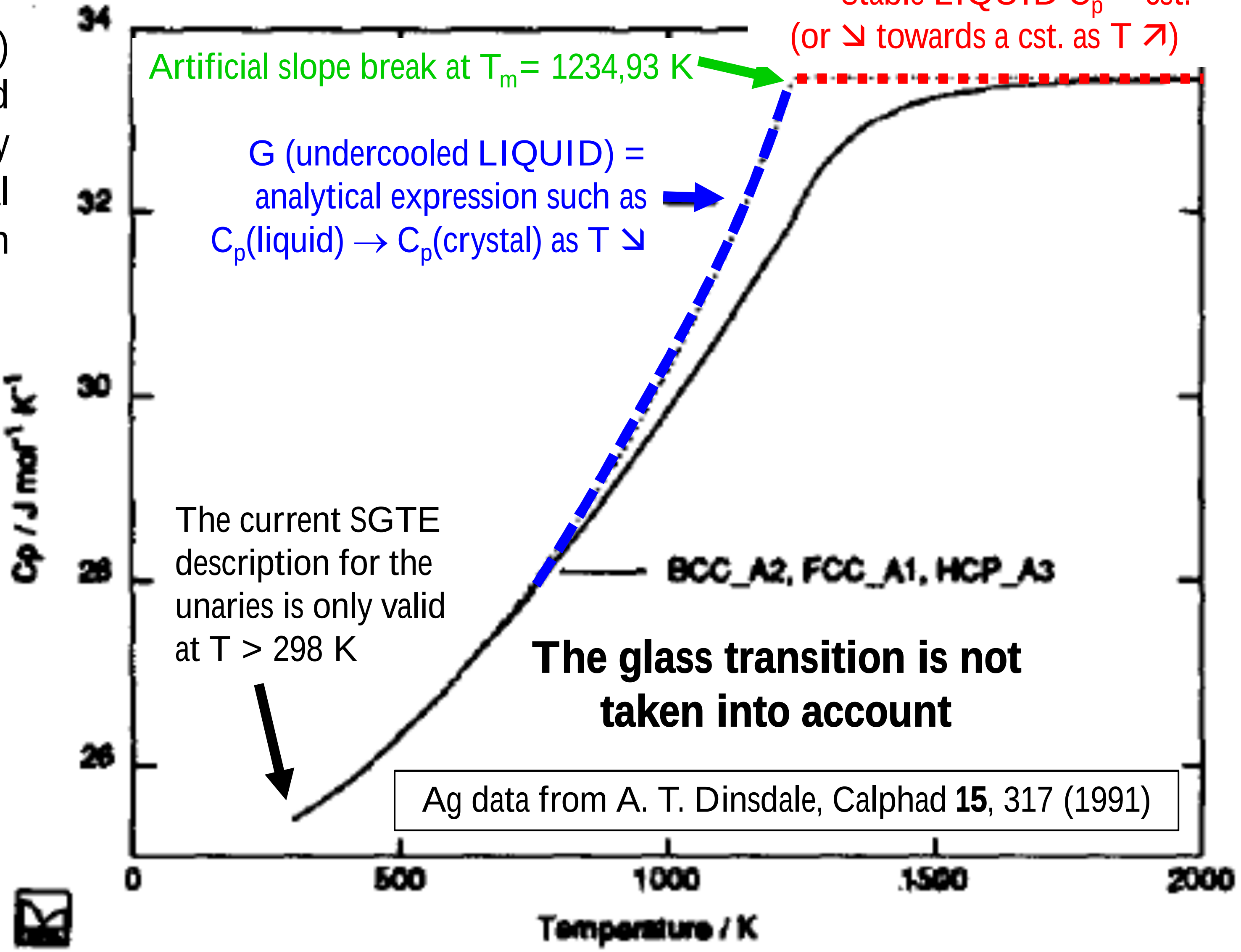
Optimization without the glass

T_g = constant = 800 K

Palumbo, M., Cacciamani, G., Bosco, E., & Baricco, M. (2001). Thermodynamic analysis of glass formation in Fe-B system. Calphad, 25(4), 625–637

Drawbacks of 1-state models for unaries

The whole $C_p(T)$ curve of the liquid cannot be fitted by a single analytical expression



Stable LIQUID C_p = cst.
(or ↘ towards a cst. as T ↗)

Artificial slope break at T_m= 1234,93 K

G (undercooled LIQUID) =
analytical expression such as
C_p(liquid) → C_p(crystal) as T ↘

The current SGTE description for the unaries is only valid at T > 298 K

The glass transition is not taken into account

Ag data from A. T. Dinsdale, Calphad **15**, 317 (1991)

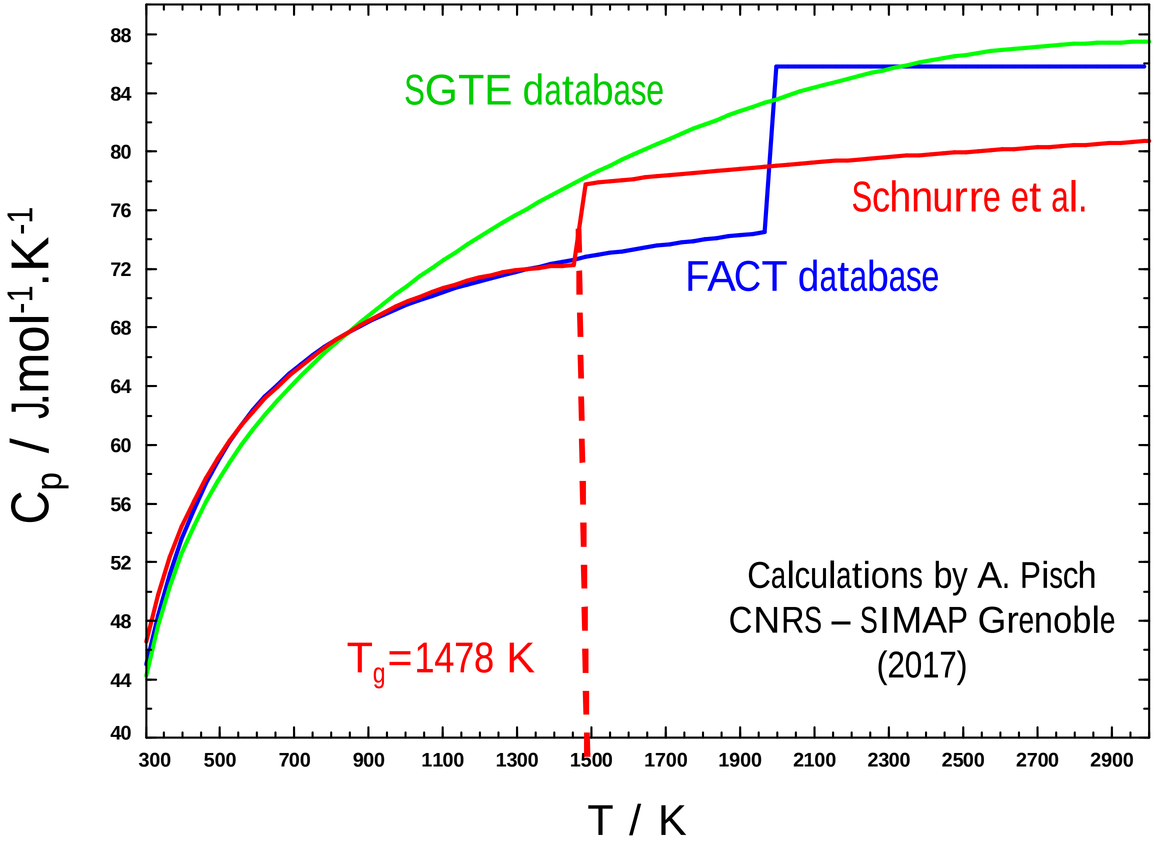
Attempt to improve the unary description – case of SiO_2

$$G^{\mathrm{L}}_{\mathrm{SiO_2}} = -9.1911513996 \times 10^5 + 318.651821118 \cdot T - 52.80500652 \cdot T \cdot \ln T - 0.013894085 \cdot T^2 + 1.609929477 \times 10^{-6} \cdot T^3 + 6.17817813 \times 10^5 \cdot T^{-1}$$

$273 < T < 1478$ Glass

$$G^{\mathrm{L}}_{\mathrm{SiO_2}} = -9.35481224 \times 10^5 + 479.632422808 \cdot T - 75.461508414 \cdot T \cdot \ln T - 1.206802642 \times 10^{-3} \cdot T^2 + 3.37604755 \times 10^{-8} \cdot T^3 + 9.26045761 \times 10^5 \cdot T^{-1}$$

$1478 < T < 6000$ Liquid and supercooled liquid

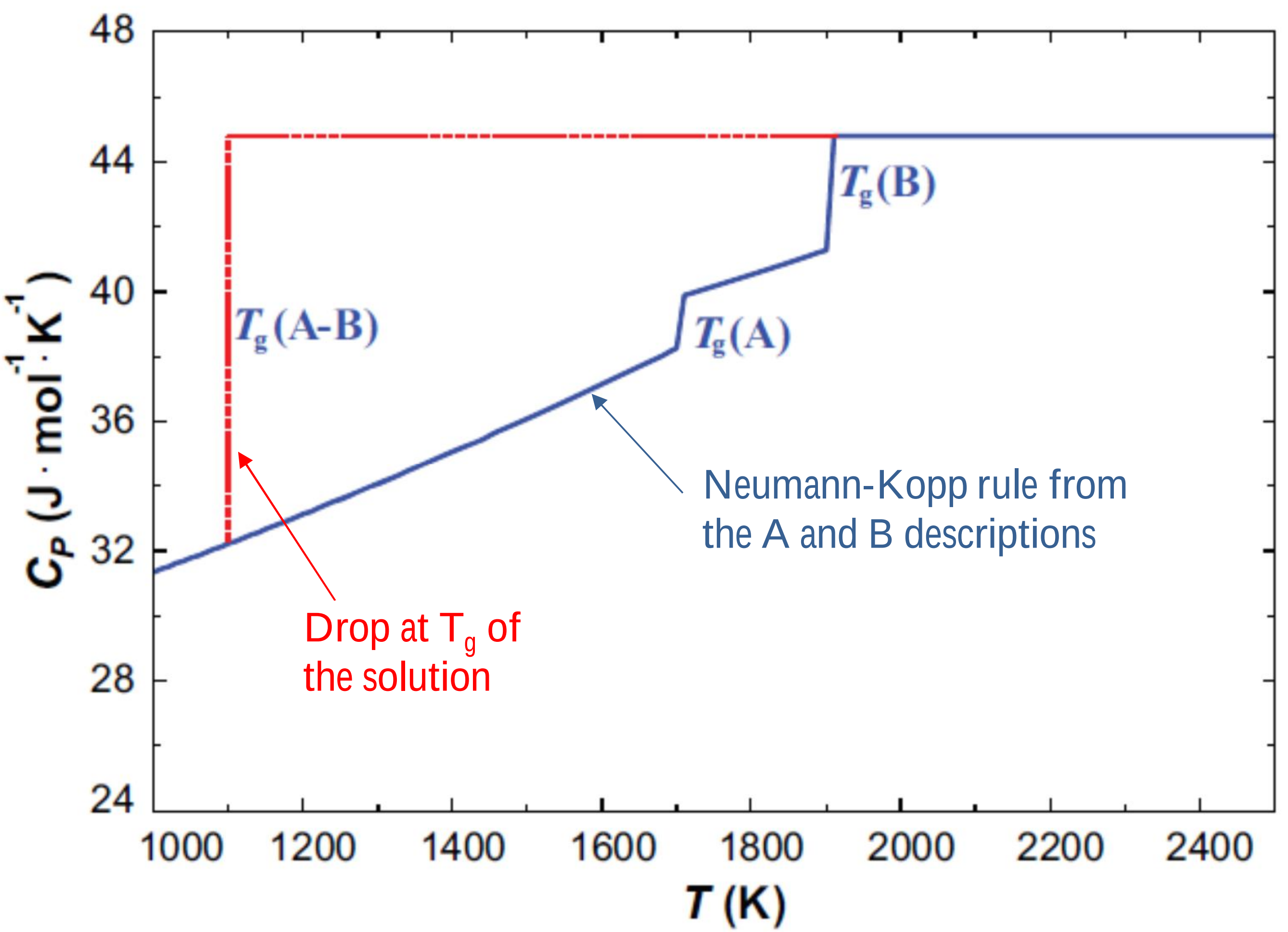


Calculations by A. Pisch
CNRS – SIMAP Grenoble
(2017)

S.M. Schnurre, J. Gröbner, R. Schmid-Fetzer, Thermodynamics and phase stability in the Si-O system, J. Non. Cryst. Solids. 336 (2004) 1–25

Drawbacks of 1-state models for binaries

Hypothetical $A_{0.5}B_{0.5}$ binary alloy



Neumann-Kopp rule from
the A and B descriptions

Drop at T_g of
the solution

C. a. Becker, J. Ågren, M. Baricco, Q. Chen, S. a. Decterov, U.R. Kattner, et al., Phys. Status Solidi. 52 (2014) 33–52

2-STATE MODELS

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- Model of Agren et al.
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- Model of Golczewski et al.
  - **SiO$_2$-Al$_2$O$_3$-CaO-MgO:** *Golczewski, J. A., Seifert, H. J., & Aldinger, F. (1998). A Thermodynamic Model of Amorphous Silicates. Calphad, 22(3), 381–396.*

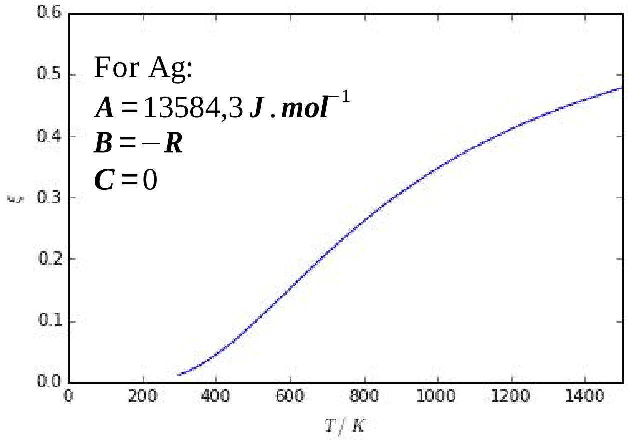
Comparison of 2-state models

- **Agren et al.:** model developed for **metals**,
  - As T ↘, a fraction of the atoms in the liquid lose their translational degrees of freedom and becomes solid-like
  - If ξ **= fraction of liquid-like atoms**, the molar Gibbs energy of the liquid phase can be written as $G_m^L = (1-\xi)\, G_m^{sol} + \xi\, G_m^{liq} + R\,T\,(\xi \ln \xi + (1-\xi) \ln (1-\xi))$
  - With $G_m^{liq} - G_m^{sol} = \Delta G_d = \enclose{circle}{A} + \enclose{circle}{B}\,T + \enclose{circle}{C}\,T \ln T + \ldots$

$$\boxed{G_m^L = \enclose{circle}{G_m^{sol}} + \xi\, \Delta G_d + R\,T\,(\xi \ln \xi + (1-\xi) \ln (1-\xi))}$$

  - The fraction of liquid-like atoms is obtained through Gibbs energy minimization

$$\frac{\partial G_m^L}{\partial \xi} = 0 \quad \Rightarrow \quad \xi = \frac{\exp\left(-\Delta G_d / R\,T\right)}{1 + \exp\left(-\Delta G_d / R\,T\right)}$$



For Ag:

$A = 13584{,}3\ J\,.\,mol^{-1}$

$B = -R$

$C = 0$

- **Golczewski et al.:** model developed for **oxides**,
  - the basic structural units of the liquid and the glass are not simple atoms,
  - a virtual Structural Fluctuations (SF) component with no mass is introduced in the G function of the amorphous oxide, y_{SF} = fraction of SF

$$\boxed{G_{OX}^{am} = \enclose{circle}{G_{OX}^{id}} + y_{SF}\, G_{SF} + R\,T\left(y_{SF} \ln y_{SF} + (1-y_{SF}) \ln (1-y_{SF})\right) + G^{ex}}$$

    - with $G_{SF} = \enclose{circle}{\Delta E} - R\,T$
  - An excess term is also added: $G^{ex} = y_{SF}\,(1-y_{SF})\,(\enclose{circle}{L_0} + \enclose{circle}{L_1}\,(1-2\,y_{SF}))$

2-state model of Agren et al.

- All other functions (S, H, C_p) are derived from the G expression using classical thermodynamic relations e.g.

$$H_m^L = H_m^{sol} + \xi \Delta H_d$$

$$C_p^L = C_p^{sol} + \xi \frac{d \Delta H_d}{dT} + \Delta H_d \frac{d \xi}{dT}$$

- The hypothetical solid-like amorphous phase, in which all constituents have only vibrational degrees of freedom, is described with respect to the crystal phase by: $G_m^{sol} = G_m^{crys} + \boxed{a} + \boxed{d} T^2$
- From the descriptions of pure amorphous A and B, the model can be extended to an amorphous binary A-B alloy on the basis of the regular solution model :

$$G_m^{sol} = x_A^L G_A^{sol} + x_B^L G_B^{sol} + x_A^L x_B^L \boxed{L_{AB}^L}$$

$$\Delta G_d = x_A^L \Delta G_d^A + x_B^L \Delta G_d^B + x_A^L x_B^L \boxed{\Delta G_d^{AB}}$$

*J. Agren, B. Cheynet, M. T. Clavaguera-mora, K. Hack, J. Hertz, F. Sommer, and U. Kattner, Calphad **19**, 449 (1995).*

Principle of Golczewski et al. approach

- **Quaternary oxide system SiO_2-Al_2O_3-CaO-MgO**
- Estimation of $(H_T\text{-}H_{298})$ T_g, and ΔH_g of the hypothetical amorphous ideal unary oxides Al_2O_3, CaO, MgO
  - Using thermodynamic data on SiO_2 and 3 silicates that exist at the glassy state
- The Gibbs Energy of unary oxides is described with a 2-state model
- The quaternary glass solution is described as an ideal solution of the amorphous unary oxides
  - The model is validated on 2 ternary glasses: cordierite and pyrope

Estimation of H(T) – H(298) and T_g of the hypothetical amorphous unary oxides

- Binary and ternary silicates at the glassy state:

WOLLASTONITE = $CaO + SiO_2$
ANORTHITE = $CaO + Al_2O_3 + 2(SiO_2)$
DIOPSIDE = $CaO + MgO + 2(SiO_2)$

$$H^{am}(T) - H^{am}(298\ K) = a_i + b_i T + c_i T^2 + d_i/T$$

- Enthalpy of complex oxide = weighed sum of unary oxides enthalpies (ideality)

$$[H_{ox}{}^{am}(T) - H_{ox}{}^{am}(298K)]_i =$$

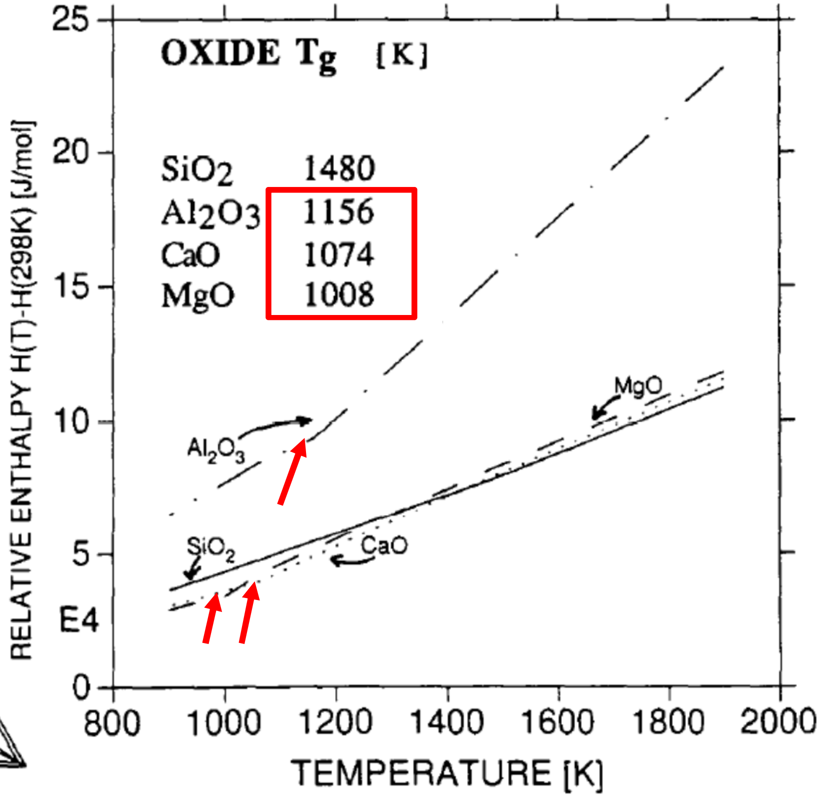
$$\Sigma_j\, n_{ij}[H^{am}(T) - H^{am}(298K)]_j$$

- System of 3 equations with 3 unknowns then:

$$\Delta H^{am}(CaO) = \Delta H^{am}(WOLL) - \Delta H^{am}(SiO_2)$$

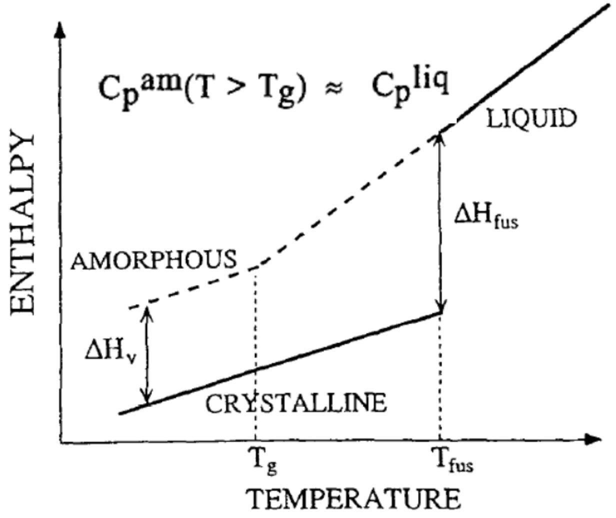
$$\Delta H^{am}(MgO) = \Delta H^{am}(DIOP) - \Delta H^{am}(WOLL) - \Delta H^{am}(SiO_2)$$

$$\Delta H^{am}(Al_2O_3) = \Delta H^{am}(ANOR) - \Delta H^{am}(WOLL) - \Delta H^{am}(SiO_2)$$



J. A. Golczewski, H. J. Seifert, and F. Aldinger, Calphad ***22****, 381 (1998).*

Estimation of the vitrification enthalpy ΔH_v of the hypothetical amorphous unary oxides



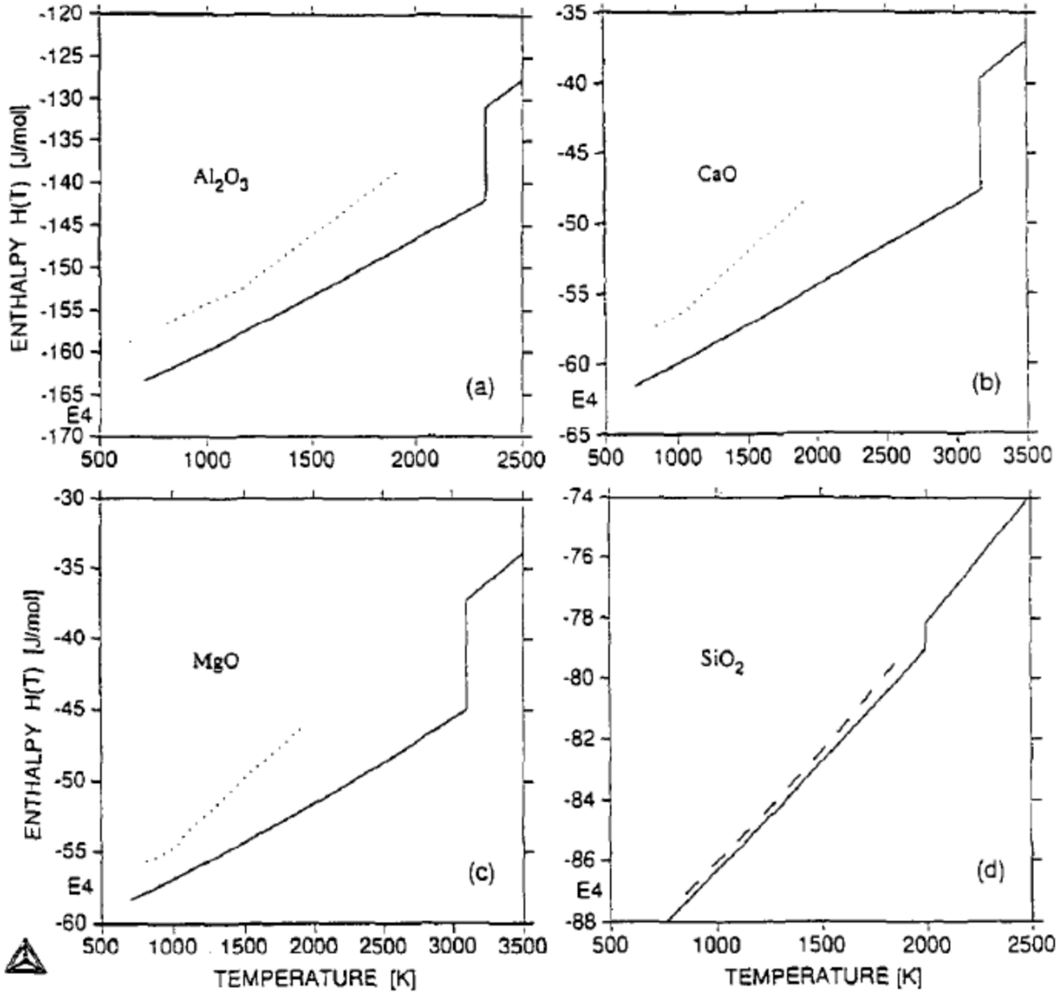
$$H^{am}(298K) = H^{cr}(298\ K) + \Delta H_v$$

$$\boxed{\Delta H_v = \Delta H_f - (C^{liq}_p - C^{cr}_p)(T_{fus} - T_g)}$$

- Hence:

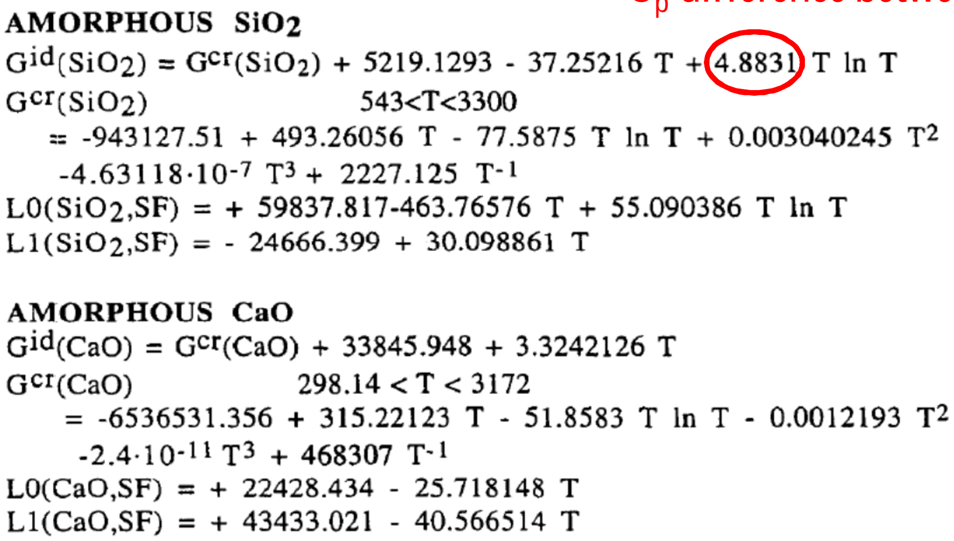
OXIDE	T_{fus} [K]	ΔH_{fus} [kJ/mol]	T_g [K]	ΔH_v [kJ/mol]
SiO_2	1996	8.9	1480	4.3
Al_2O_3	2327	111.1	1156	57.1
CaO	3172	80.0	1074	19.2
MgO	3100	77.0	1008	20.5

Enthalpy curves of amorphous unary oxides



Gibbs energy functions of unary oxides

C_p difference between crystalline and ideal glassy SiO_2



AMORPHOUS SiO_2

$G^{id}(SiO_2) = G^{cr}(SiO_2) + 5219.1293 - 37.25216\ T + \boxed{4.8831}\ T \ln T$

$G^{cr}(SiO_2)$ $543<T<3300$

$= -943127.51 + 493.26056\ T - 77.5875\ T \ln T + 0.003040245\ T^2$

$-4.63118 \cdot 10^{-7}\ T^3 + 2227.125\ T^{-1}$

$L0(SiO_2,SF) = + 59837.817 - 463.76576\ T + 55.090386\ T \ln T$

$L1(SiO_2,SF) = - 24666.399 + 30.098861\ T$

AMORPHOUS CaO

$G^{id}(CaO) = G^{cr}(CaO) + 33845.948 + 3.3242126\ T$

$G^{cr}(CaO)$ $298.14 < T < 3172$

$= -6536531.356 + 315.22123\ T - 51.8583\ T \ln T - 0.0012193\ T^2$

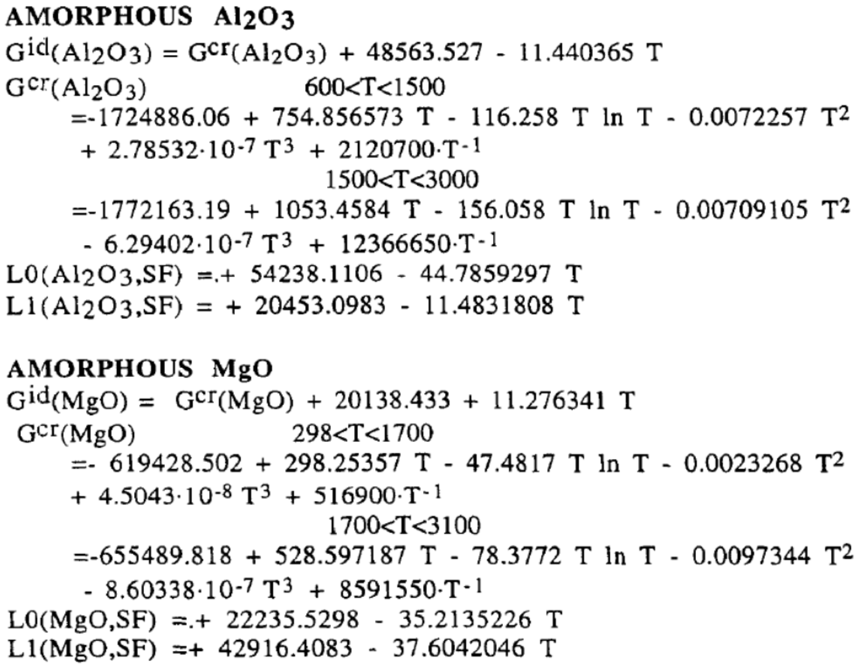
$-2.4 \cdot 10^{-11}\ T^3 + 468307\ T^{-1}$

$L0(CaO,SF) = + 22428.434 - 25.718148\ T$

$L1(CaO,SF) = + 43433.021 - 40.566514\ T$

Same C_p for crystalline and ideal glassy CaO, Al_2O_3 and MgO

J. A. Golczewski, H. J. Seifert, and F. Aldinger, Calphad ***22****, 381 (1998).*



AMORPHOUS Al_2O_3

$G^{id}(Al_2O_3) = G^{cr}(Al_2O_3) + 48563.527 - 11.440365\ T$

$G^{cr}(Al_2O_3)$ $600<T<1500$

$= -1724886.06 + 754.856573\ T - 116.258\ T \ln T - 0.0072257\ T^2$

$+ 2.78532 \cdot 10^{-7}\ T^3 + 2120700 \cdot T^{-1}$

$1500<T<3000$

$= -1772163.19 + 1053.4584\ T - 156.058\ T \ln T - 0.00709105\ T^2$

$- 6.29402 \cdot 10^{-7}\ T^3 + 12366650 \cdot T^{-1}$

$L0(Al_2O_3,SF) =.+ 54238.1106 - 44.7859297\ T$

$L1(Al_2O_3,SF) = + 20453.0983 - 11.4831808\ T$

AMORPHOUS MgO

$G^{id}(MgO) = G^{cr}(MgO) + 20138.433 + 11.276341\ T$

$G^{cr}(MgO)$ $298<T<1700$

$=- 619428.502 + 298.25357\ T - 47.4817\ T \ln T - 0.0023268\ T^2$

$+ 4.5043 \cdot 10^{-8}\ T^3 + 516900 \cdot T^{-1}$

$1700<T<3100$

$= -655489.818 + 528.597187\ T - 78.3772\ T \ln T - 0.0097344\ T^2$

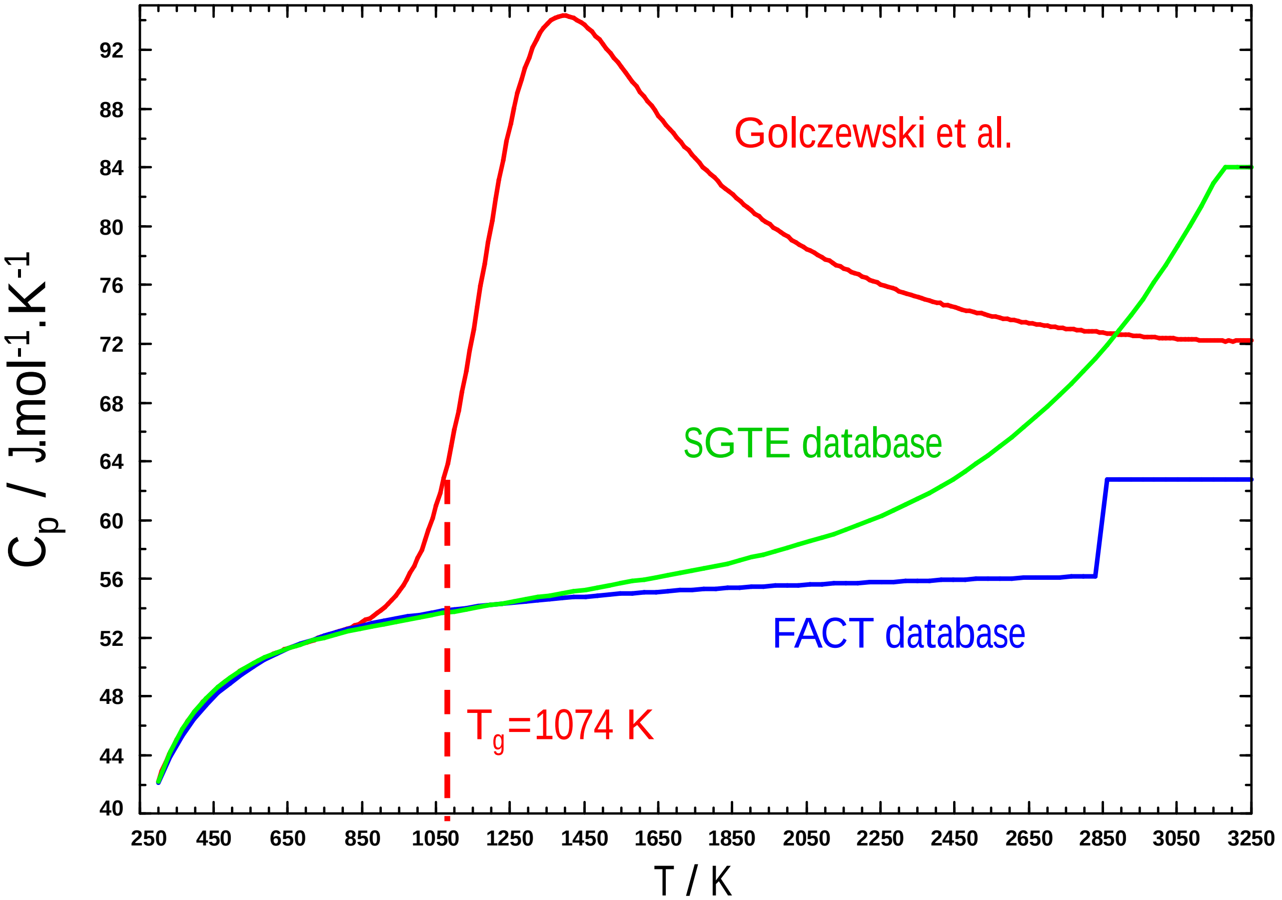
$- 8.60338 \cdot 10^{-7}\ T^3 + 8591550 \cdot T^{-1}$

$L0(MgO,SF) =.+ 22235.5298 - 35.2135226\ T$

$L1(MgO,SF) =+ 42916.4083 - 37.6042046\ T$

Comparison of various unary descriptions for CaO

- Heat capacity of liquid CaO vs. T



Calculations by A. Pisch CNRS – SIMAP Grenoble (2017)

G model of the multicomponent glass

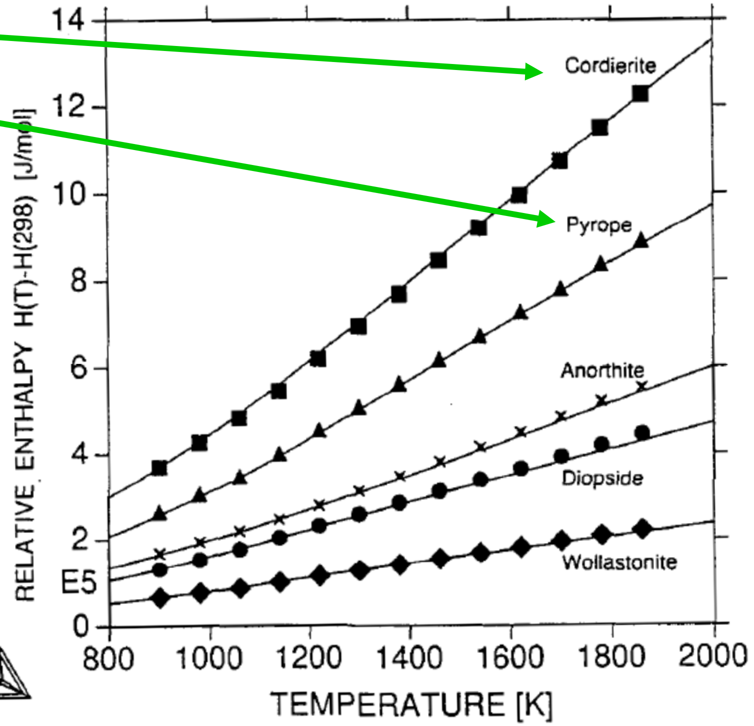
- Ideal solution of unary amorphous oxides:

$$G_{glass} = \Sigma_j \left[n_j \left(G_{ox}{}^{am}\right)_j + RT\, n_j \ln(n_j) \right]$$

- Model predictions for 2 ternary silicates:

CORDIERITE = $2(MgO) + 2(Al_2O_3) + 5(SiO_2)$

PYROPE = $3(MgO) + Al_2O_3 + 3(SiO_2)$



J. A. Golczewski, H. J. Seifert, and F. Aldinger, Calphad ***22****, 381 (1998).*

Conclusions and perspectives

- Choice of the model depends on the specific target
  - None of these purely thermodynamic models take into account the kinetic/relaxation aspect of the glass transition
- Simple models, based on associates in the liquid, and developed for multicomponent oxide systems have already been applied with success to real glasses having a large number of constituents e.g. for process engineering calculations or for comparison with structural data, however
  - they are not sufficient for accurate description of the liquid and glass phases, the prediction of demixing in these solutions or the future coupling with kinetic models like nucleation and growth and/or diffusion models
  - Introducing such a large number of associates is not considered a good practice in CALPHAD type modeling
- Descriptions of the undercooled liquid in available CALPHAD databases (SGTE, FACT) are not satisfying
  - The glass transition is not taken into account
- Development of new CALPHAD models is needed but it is a long term project which requires new assessments

Conclusions and perspectives

- 1-state type models suffers from several drawbacks
  - Several analytical expressions are necessary to cover the whole temperature range of interest
  - Artificial slope breaks at T_m and discontinuities at T_g are introduced in the C_p curves of the unaries, which can lead to problems for the modelling of higher order systems
- The 2-state models
  - Greatly improves the description of the undercooled liquid and glass phases but requires to reassess all the relevant unaries, before being able to model the multicomponent glass
  - So far mainly metallic elements and binary systems of such elements have been modelled, application to oxides has only been attempted once by Golczewski et al. but seems promising
    - the validity of using a single type of defects for modelling a structurally complex liquid and the necessity of adding an excess term will have to be tested
  - An informal group formed by few researchers from various French laboratories (CEA-Marcoule, CEA-Saclay, CNRS-SIMAP Grenoble, CNRS-IM2NP Marseille) has started to work on this project
    - The first step will be to test the model on SiO_2 which has been extensively studied in literature both at the undercooled liquid and glassy states

Acknowledgements

- The organizers for inviting me at this workshop
- The CNRS research groups (GDR)
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  - "Verres"
  - for fruitful discussions and collaborative work on this project
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