uniglassAC GmbH

Thermodynamic Functions in Common Glass Systems

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School Thermodynamics of Glass
Erlangen, Sun. 12th May, 11^{10} – 11^{50} h

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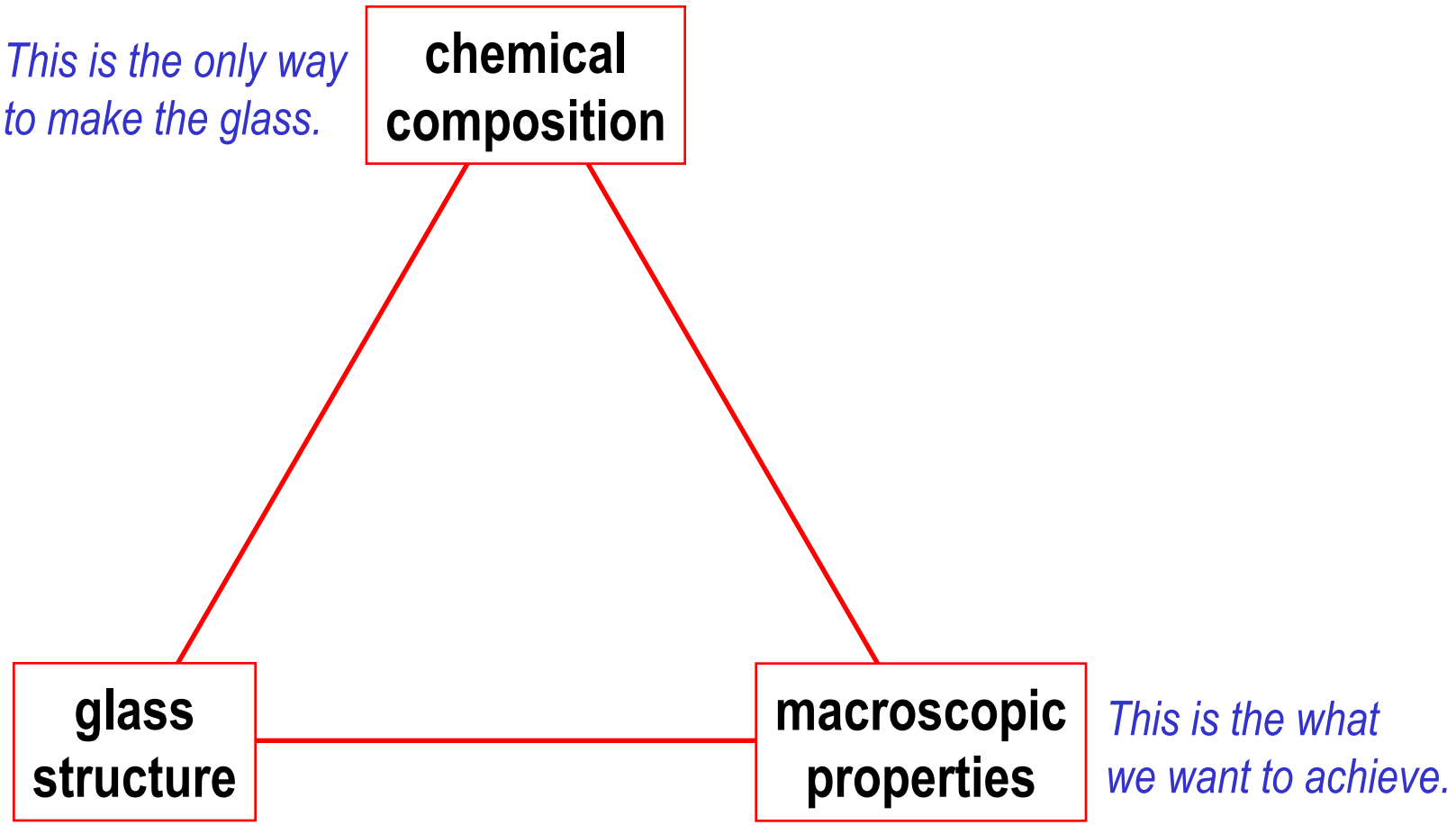
CONTENTS

Thermodynamics vs. Structure

Objective:
enhancing ***scientific understanding*** and
enabling ***technological development***
of industrial glasses



Objective:
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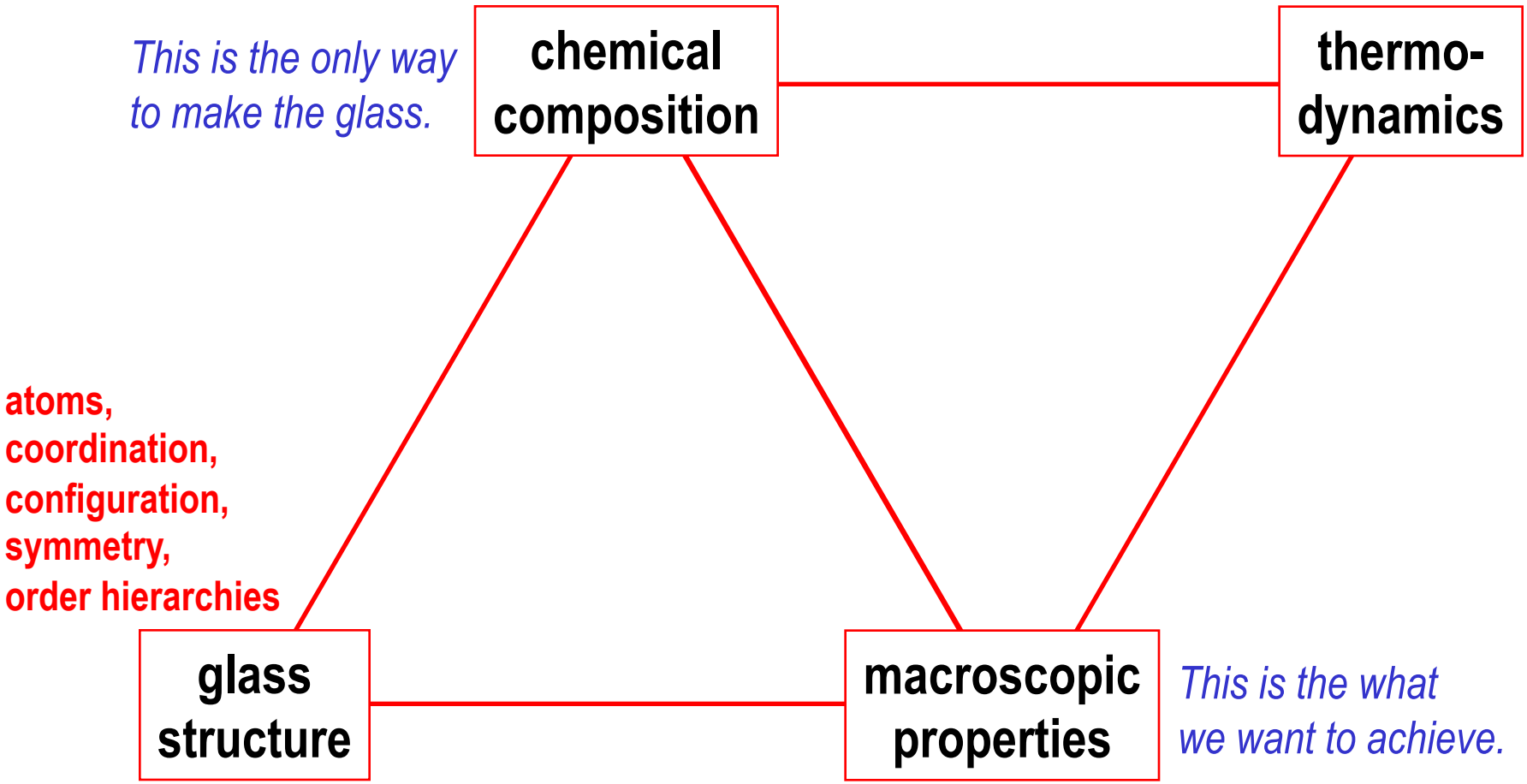
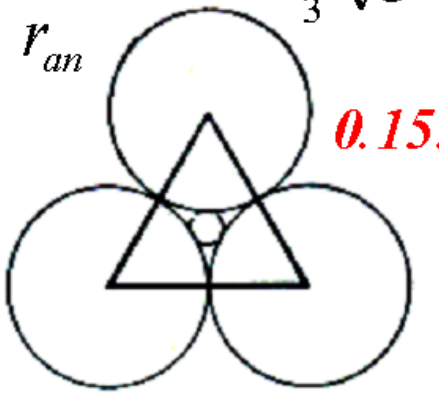


cation-anion packing paradigm

$r(Si^{4+}) = 0.041\,nm, \quad r(O^{2-}) = 0.140\,nm,$

$\frac{r_{cat}}{r_{an}} = 0.293$ "*structures must not rattle*"

$\frac{r_{cat}}{r_{an}} =$ $\frac{2}{3}\sqrt{3}-1,$ $\sqrt{\frac{3}{2}}-1,$ $\sqrt{2}-1,$ $\sqrt{3}-1$

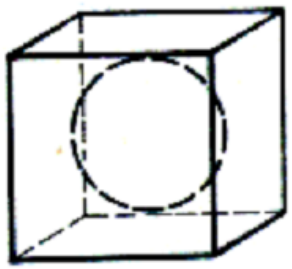


0.155

0.225

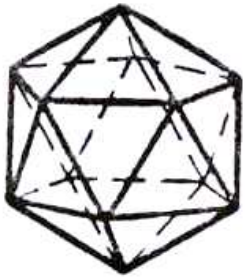
0.414

0.732

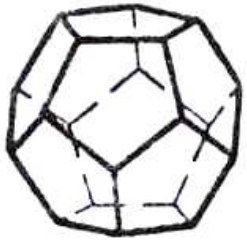


C.N. = 3 4 6 8

12 20



0.902

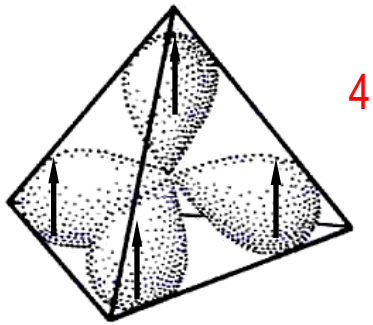


1.803

$\frac{r_{cat}}{r_{an}} = \frac{1}{2}\sqrt{2}\cdot\left(\sqrt{5+\sqrt{5}}\right)-1,$ $\frac{1}{2}\sqrt{3}\cdot\left(1+\sqrt{5}\right)-1$

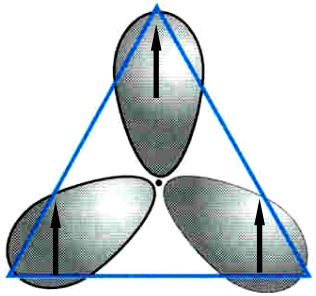
covalent (e^- pair) bond paradigm:

sp^3 structure of Si^{4+}



4 bonds per Si

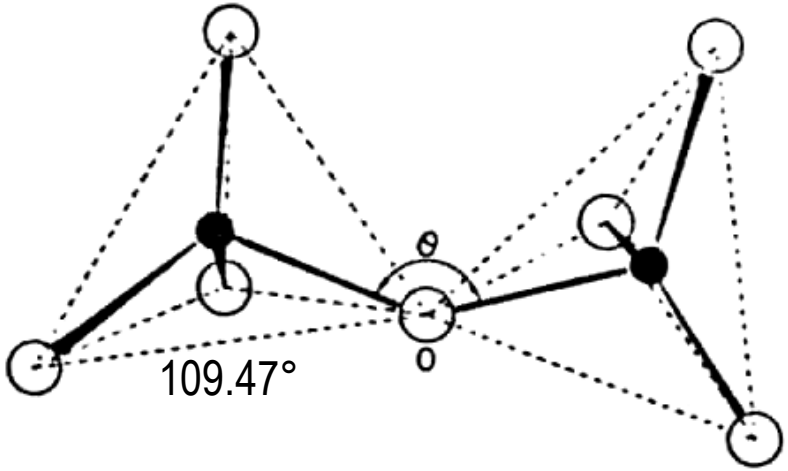
sp^2 structure of B^{3+}



3 bonds per B

$[SiO_4]$ tetrahedron

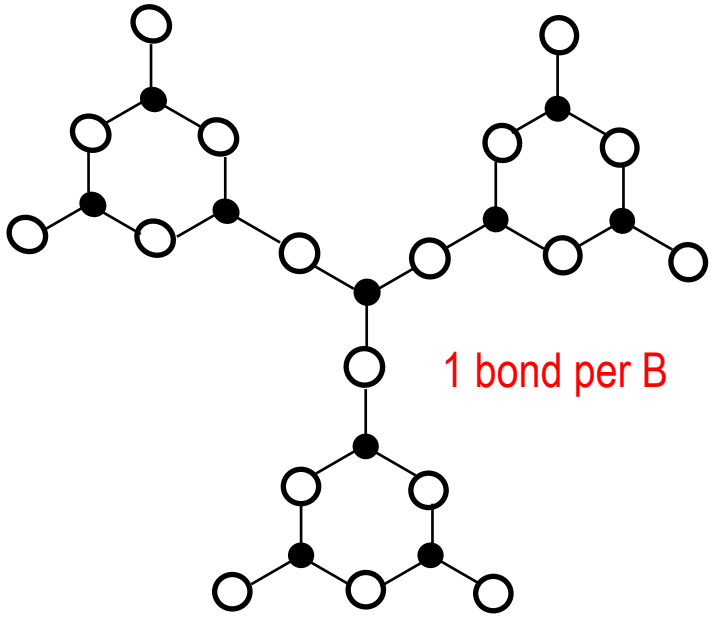
≡Si–O–Si≡ is symmetrical



depending on the type of mineral, the bridge angle θ may vary considerably

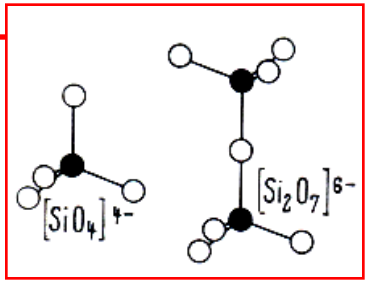
$[BO_3]$ group and $[B_3O_{9/2}]$ boroxol ring

=B—O–B= is assymmetrical



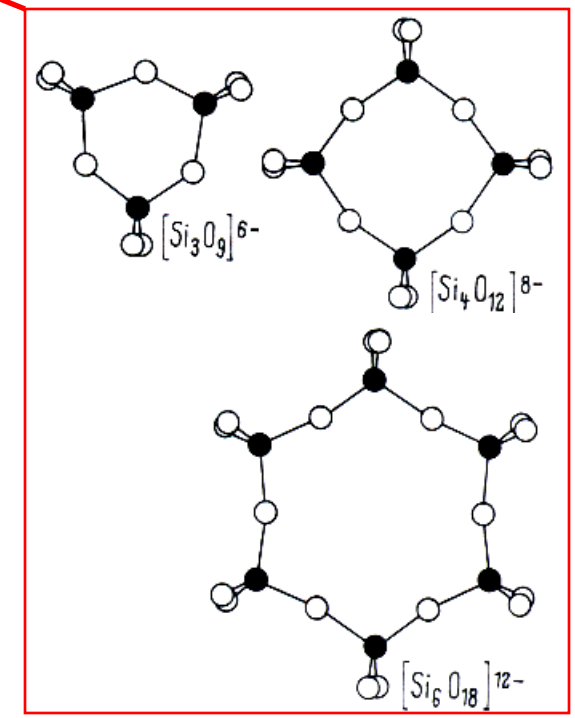
isolated tetrahedra

Mg-Fe silicates
(olivine)



ring structures

Mg-Fe-Al silicates
(codrierite)



single chain structures

Mg-Fe silicates
(pyroxenes)

double chain structures

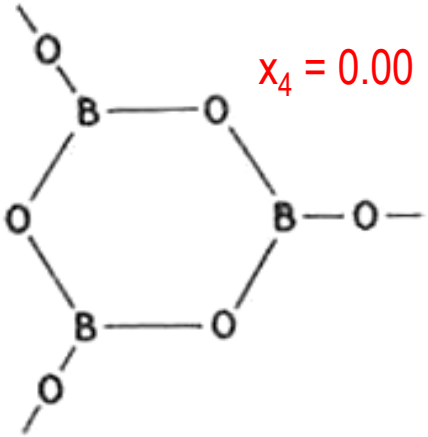
Ca-Mg-Fe silicates
(amphiboles)

sheet structures

Al and K-Al silicates
(kaolinite, mica)

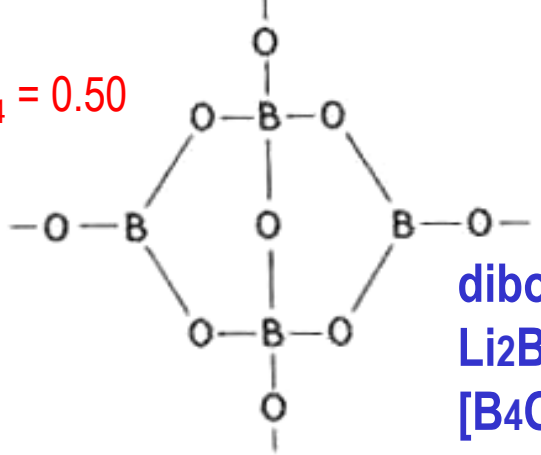
framework structures

R^{+}-R^{2+}-Al silicates
(feldspars, plagioclase; silica)



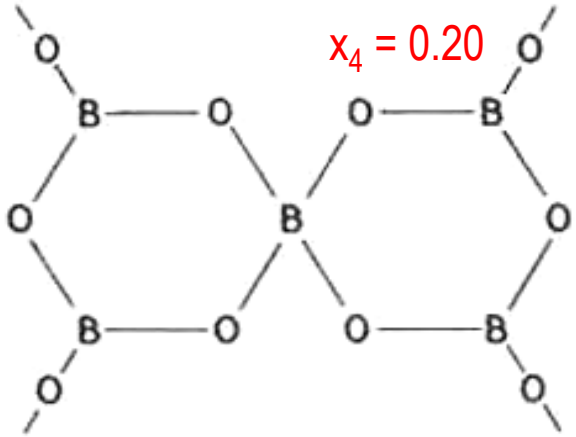
$x_4 = 0.00$

anhydrous boric acid, complex polymer, boroxol ring



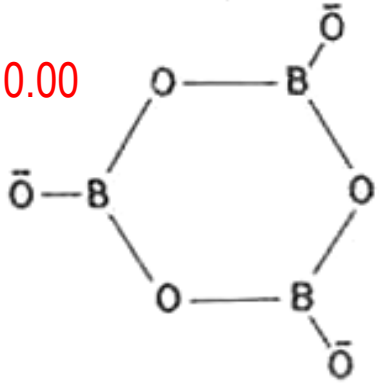
$x_4 = 0.50$

diborate, e.g., $Li_2B_4O_7$, $[B_4O_7]^{2-}$ group



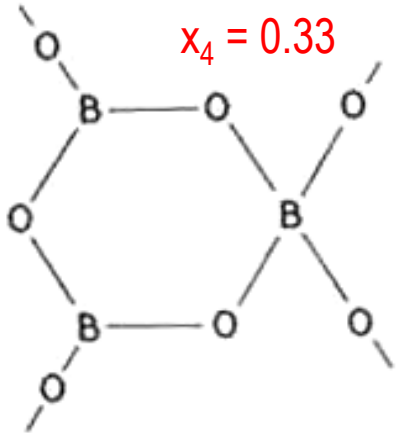
$x_4 = 0.20$

pentaborate, e.g., KB_5O_8, $[B_5O_8]^-$ group



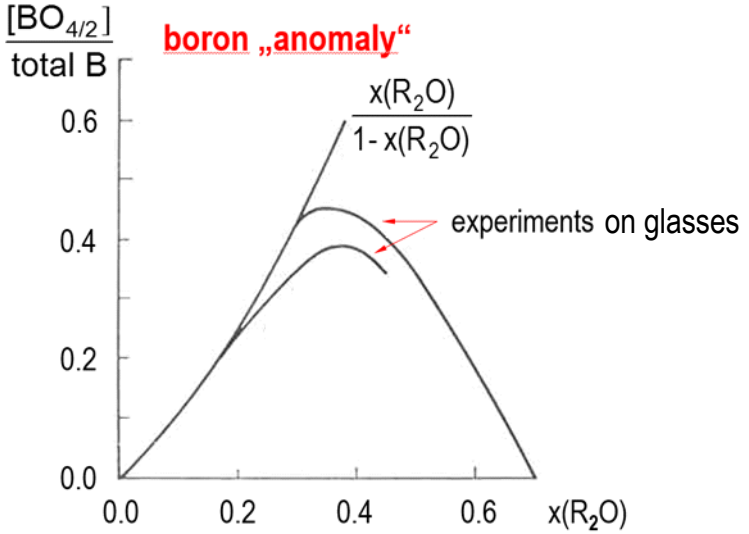
$x_4 = 0.00$

metaborate, e.g., $NaBO_2$, HBO_2, $[B_3O_6]^{3-}$ group

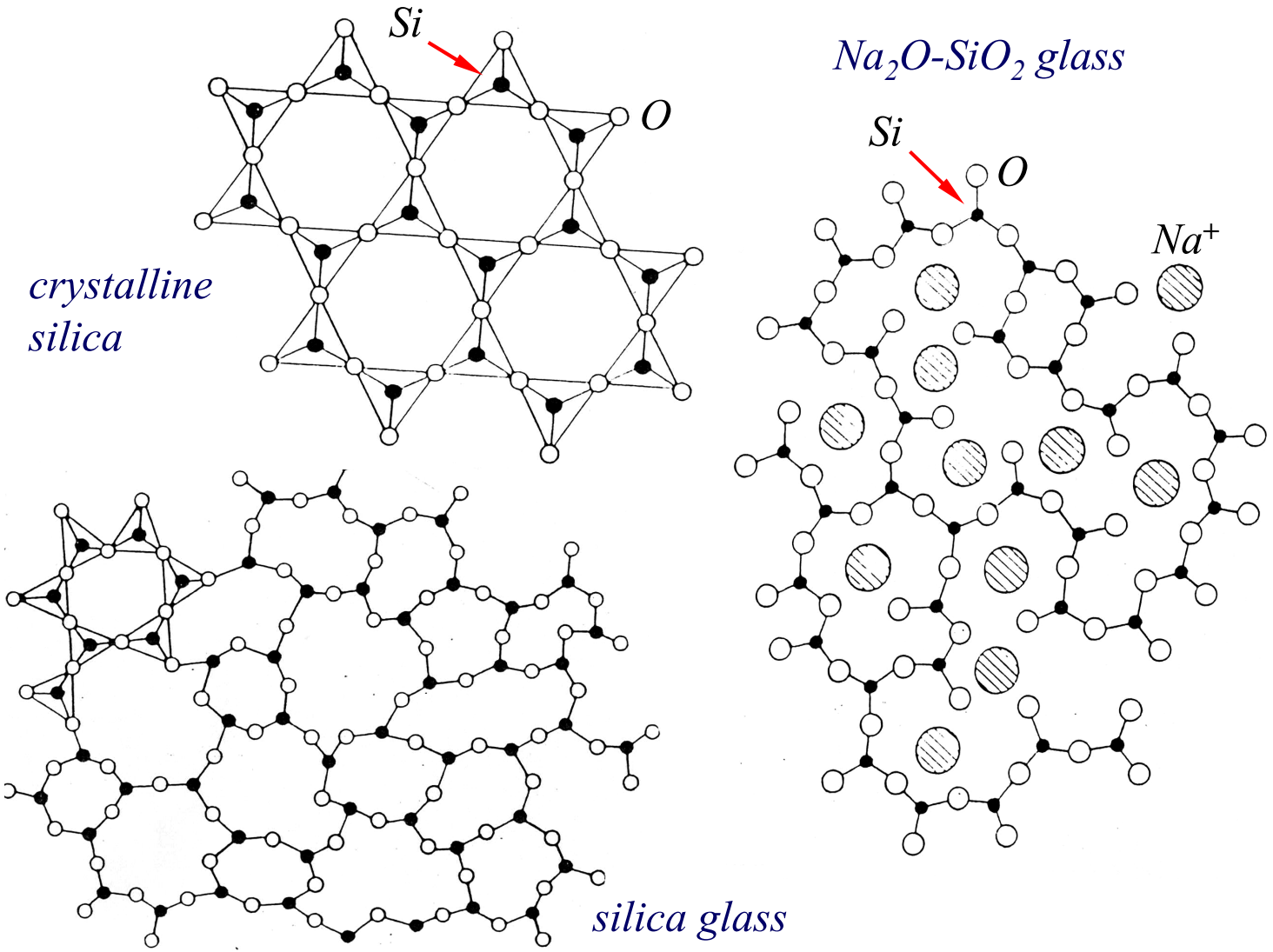


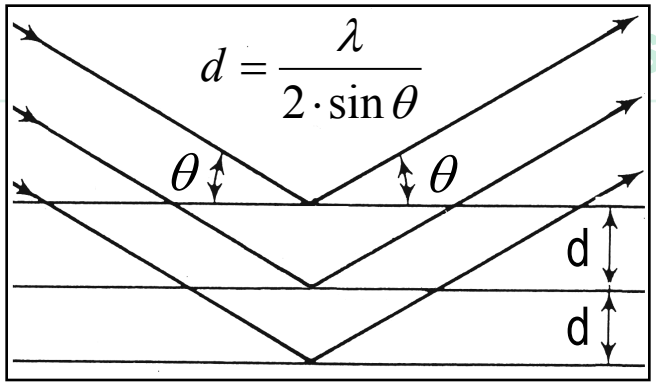
$x_4 = 0.33$

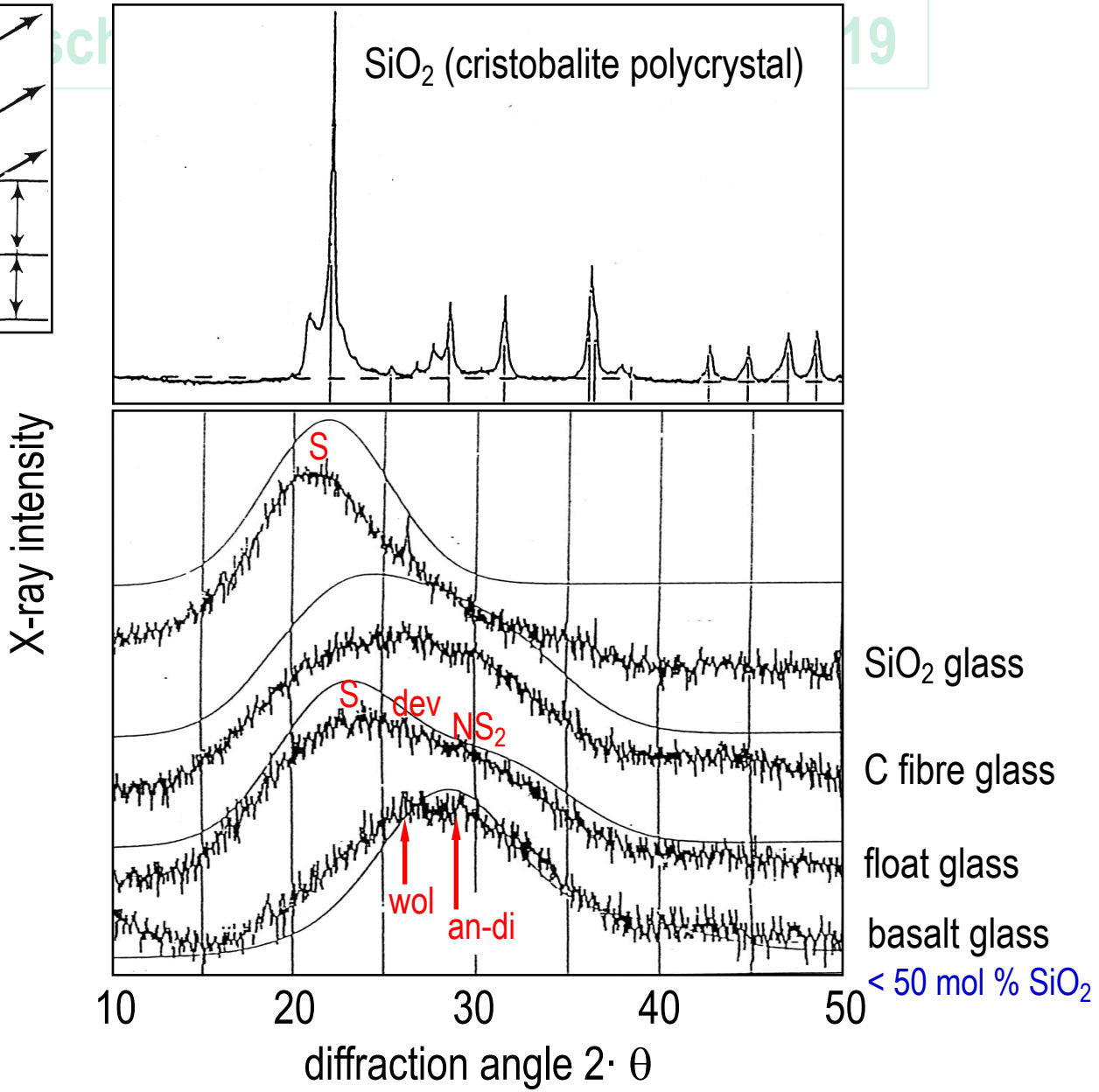
triborate, e.g., CsB_3O_5, $[B_3O_5]^-$ group



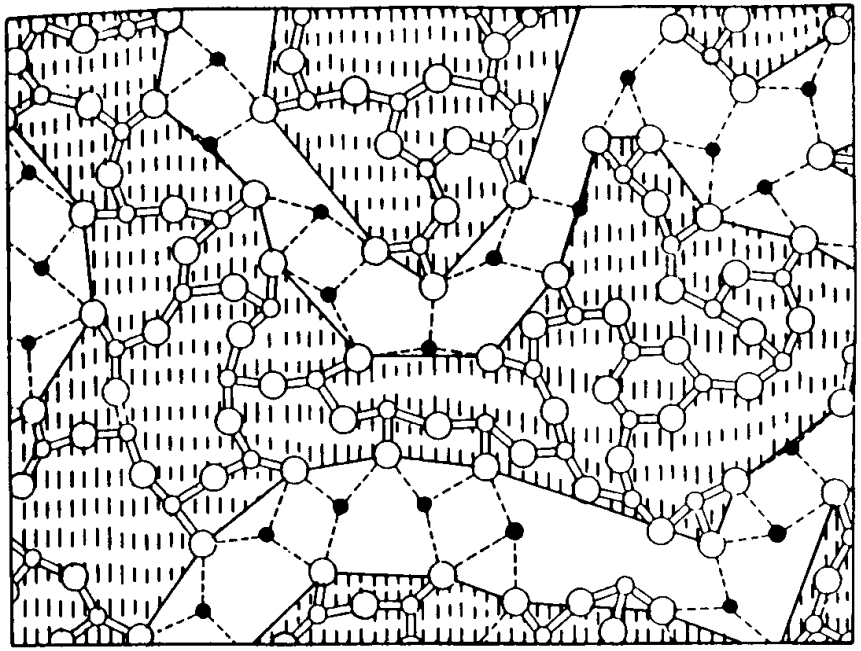
concept of random network (*Zachariasen, J. Chem. Soc. 1932*)



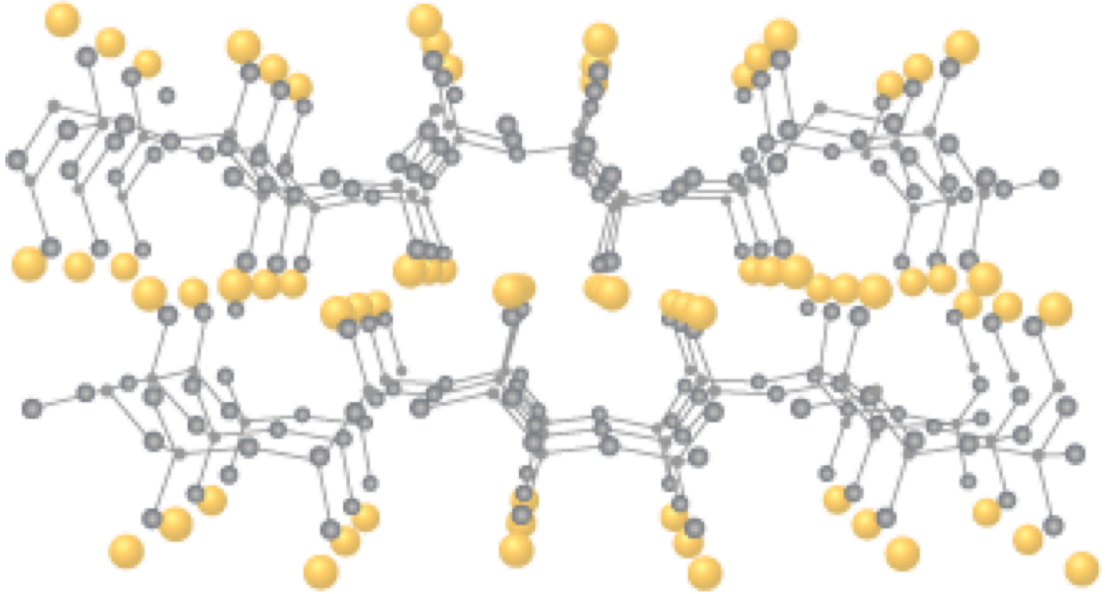




Lebedev 1921:
The “glass humps” bear the signature of the crystalline reference system.



concept of modified random network
(*Greaves, JNCS 1985*),
sodium silicate glass



structure of crystalline
sodium disilicate

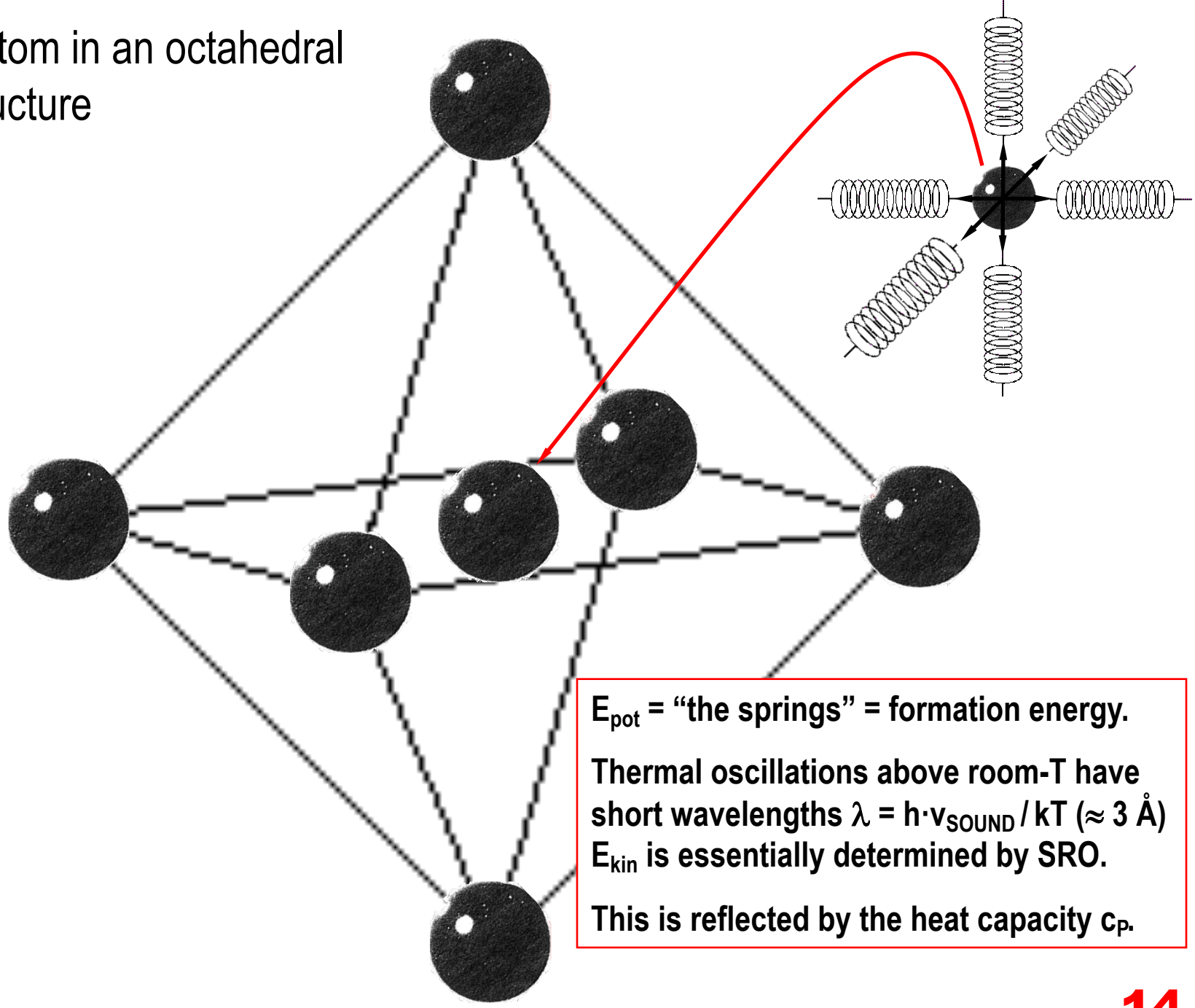
structural hierarchies of a silicate glass:

SRO nature of cation polyhedra

MRO nature of the linkage of these polyhedral (via corners, edges, faces)

What is the relation to thermodynamics?

central atom in an octahedral SRO structure

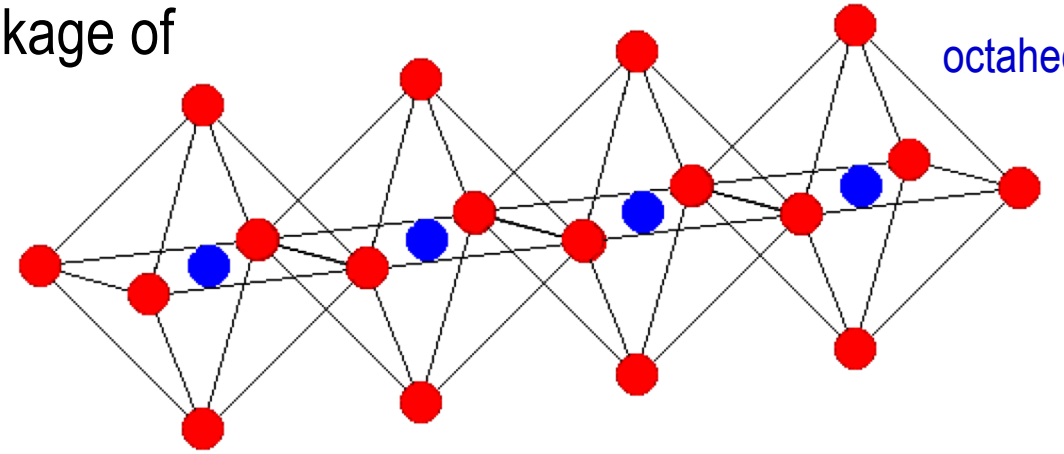


E_{pot} = “the springs” = formation energy.

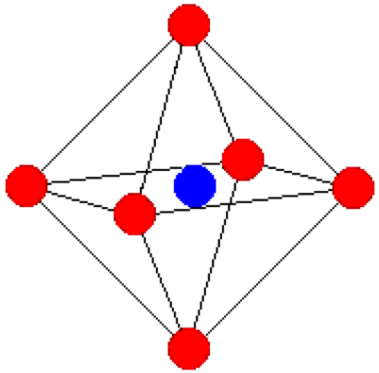
Thermal oscillations above room-T have short wavelengths $\lambda = h \cdot v_{SOUND} / kT$ (≈ 3 Å)
E_{kin} is essentially determined by SRO.

This is reflected by the heat capacity c_P.

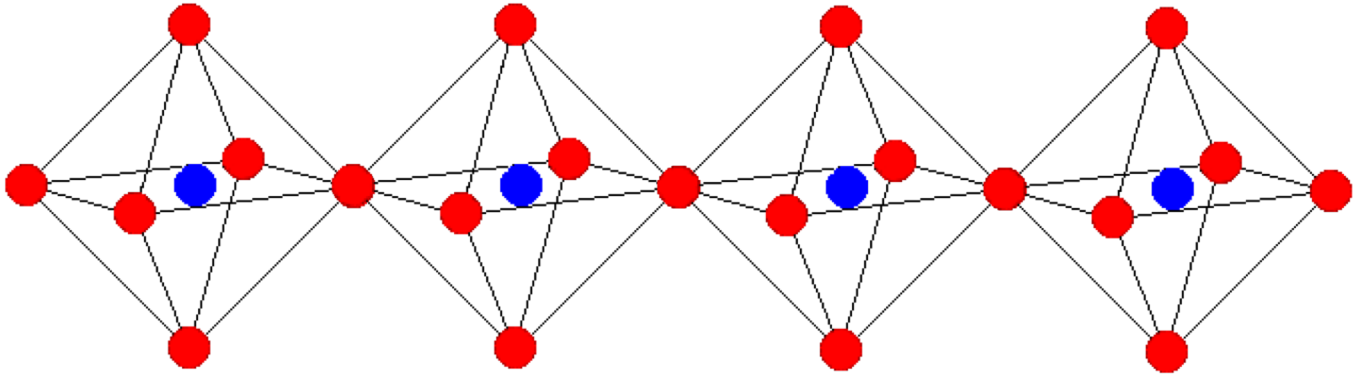
MRO structure: linkage of SRO polyhedra



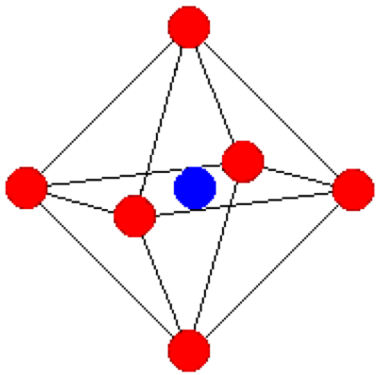
octahedra share edges

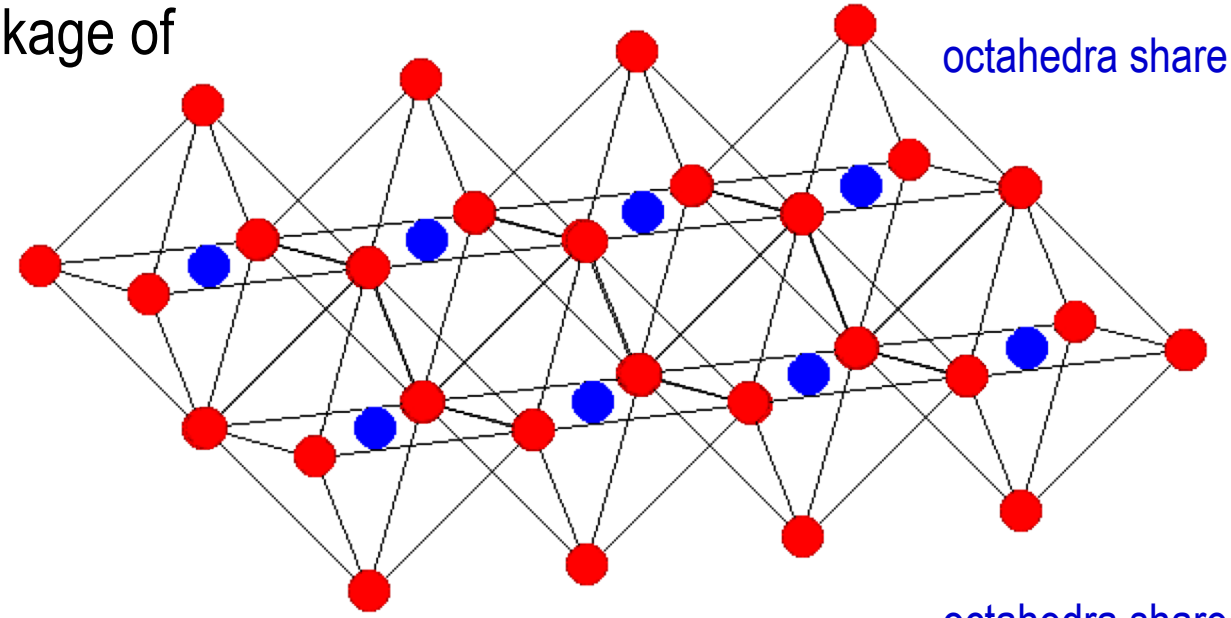


octahedra share corners



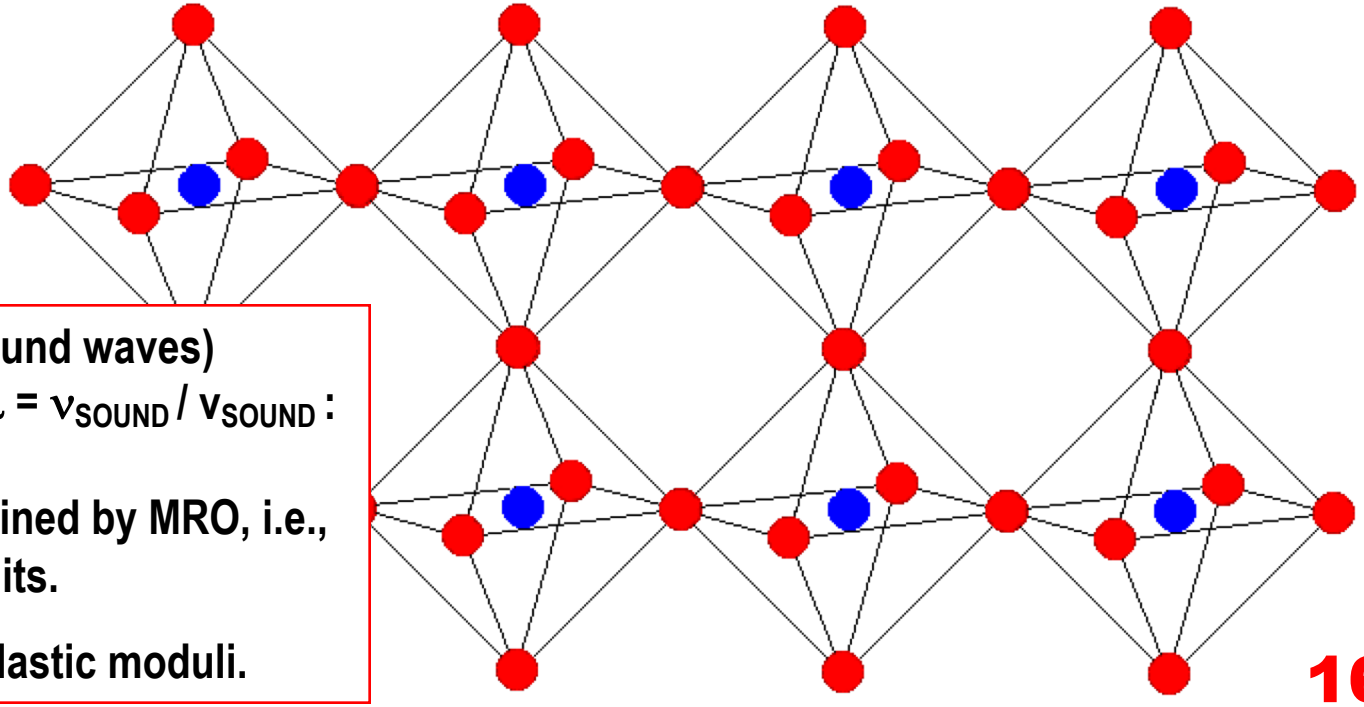
MRO structure: linkage of SRO polyhedra





octahedra share edges

octahedra share corners

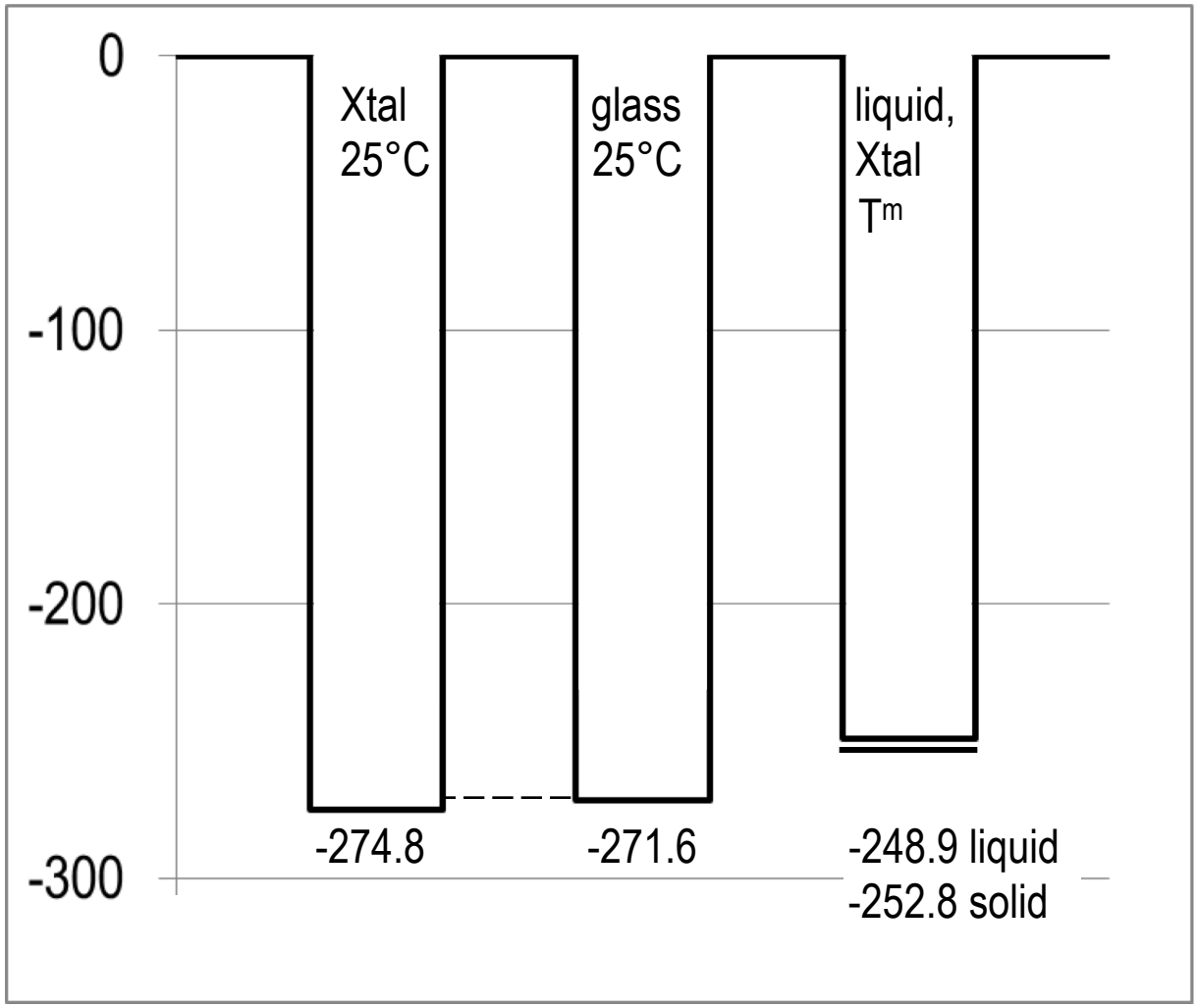


Acoustic oscillations (sound waves) have long wavelengths $\lambda = \nu_{SOUND} / v_{SOUND}$: 1 MHz $\rightarrow$ 3 mm.
E_{kin} is essentially determined by MRO, i.e., by the linkage of SRO units.

This is reflected by the elastic moduli.

$Na_2Si_2O_5$

H^f in kJ/g-atom



J. Frenkel: Kinetic Theory of Liquids. 1946

In view of the small energetic and entropic differences,
the structures of liquids and glasses cannot differ dramatically from the structures of their isochemical crystals.

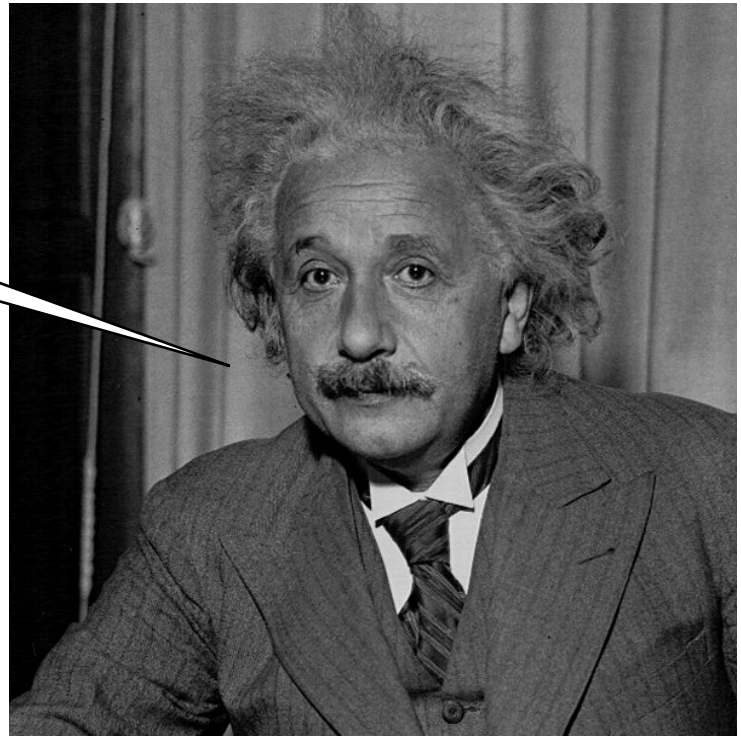
One-Component Glasses

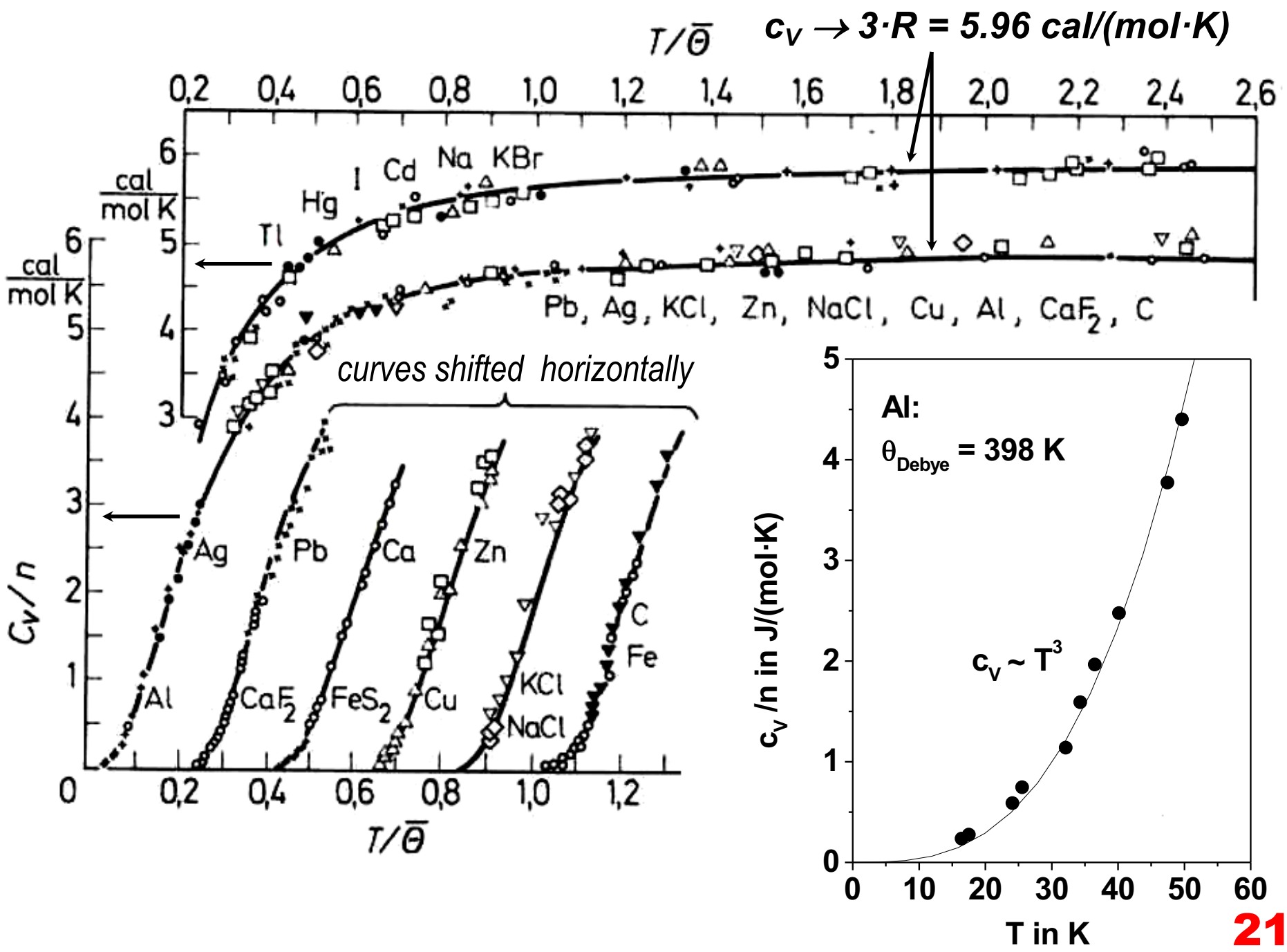
-

SRO based behavior

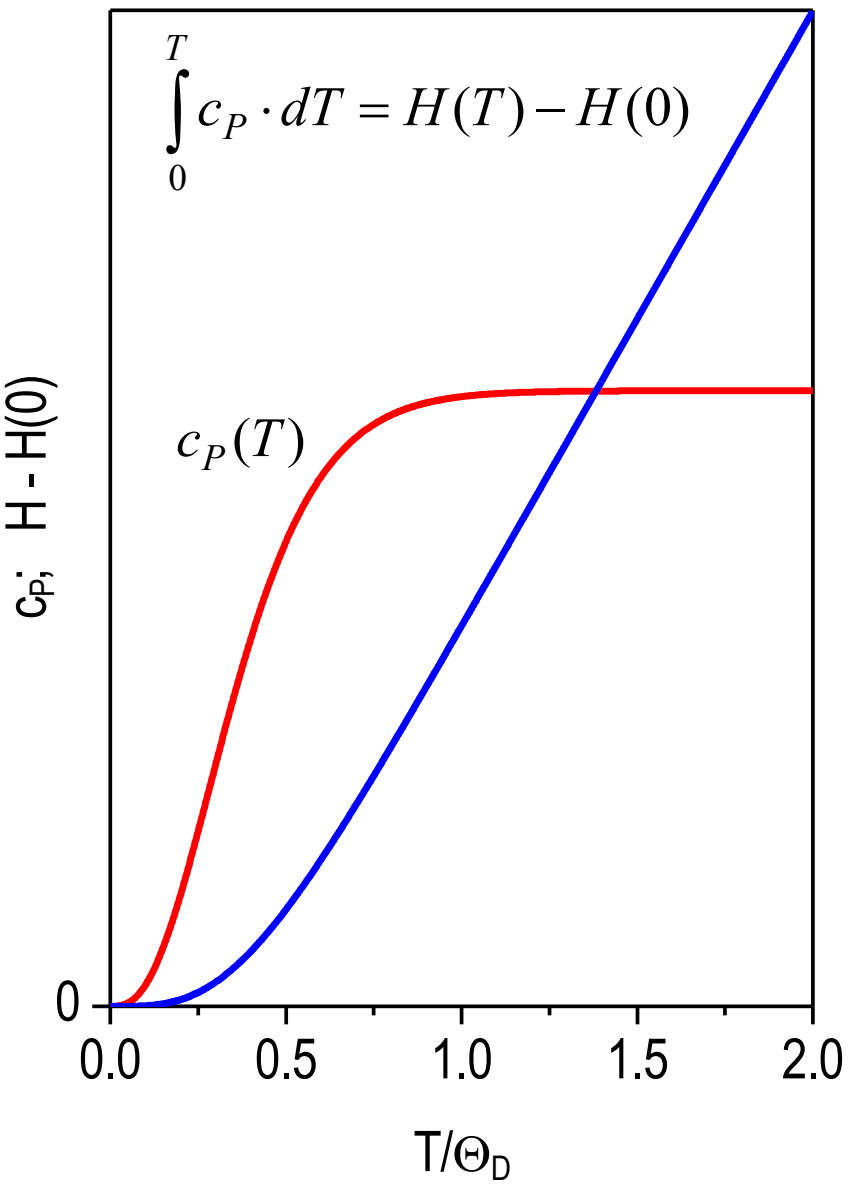
Evaluating Heat Capacities

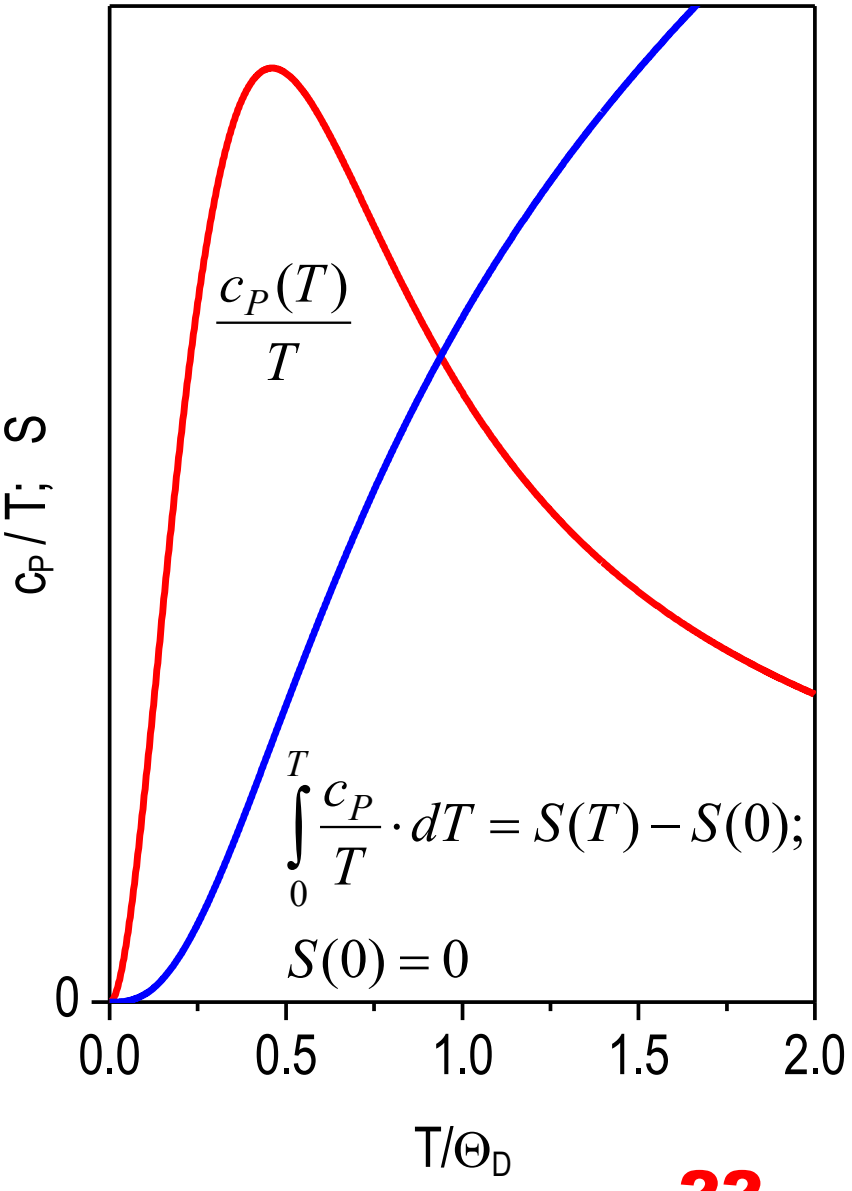
If you have only one chance to perform a measurement on a material, then measure c_P!



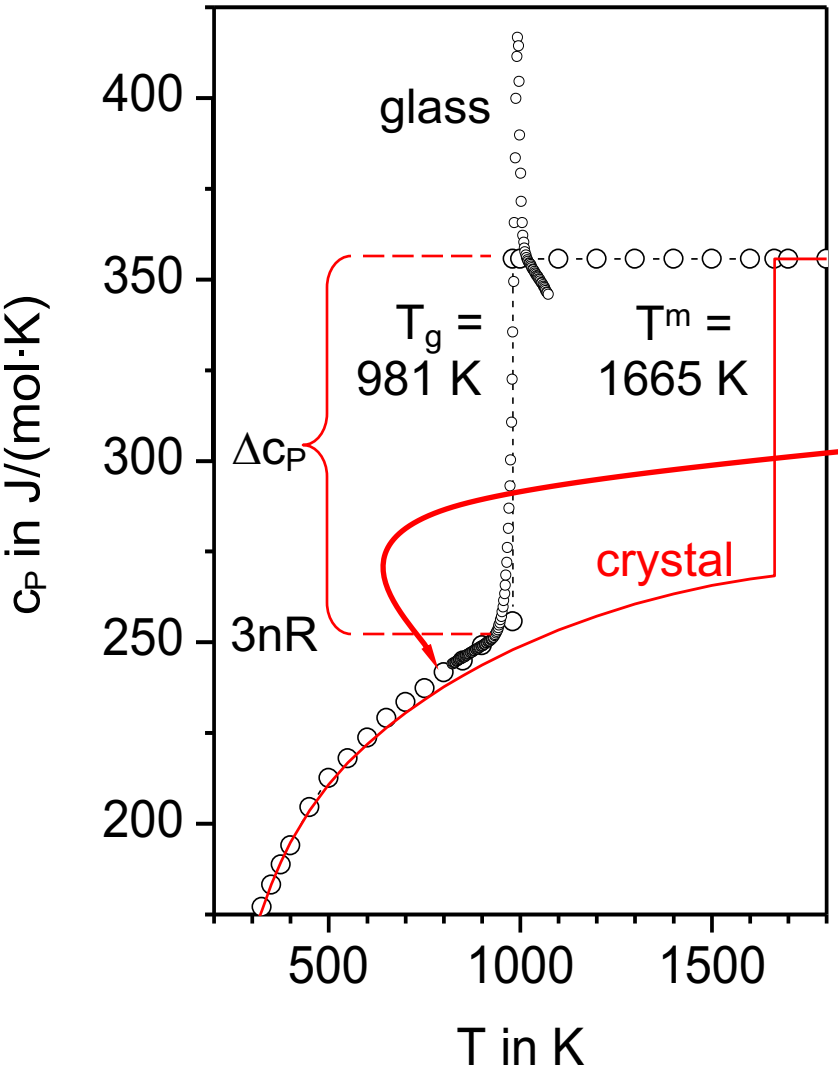

$c_V \rightarrow 3 \cdot R = 5.96$ cal/(mol·K)
T/Θ
0,2 0,4 0,6 0,8 1,0 1,2 1,4 1,6 1,8 2,0 2,2 2,4 2,6
cal / mol K
Tl
Hg
I
Cd
Na
KBr
Pb, Ag, KCl, Zn, NaCl, Cu, Al, CaF_2, C
curves shifted horizontally
C_V/n
Ag
Pb
Ca
Zn
C
Fe
Al
CaF_2
FeS_2
Cu
KCl
NaCl
0 0,2 0,4 0,6 0,8 1,0 1,2
T/Θ
Al:
θ_{Debye} = 398 K
$c_V \sim T^3$
c_V /n in J/(mol·K)
0 10 20 30 40 50 60
T in K

heat capacity as the basis of thermochemical standard data

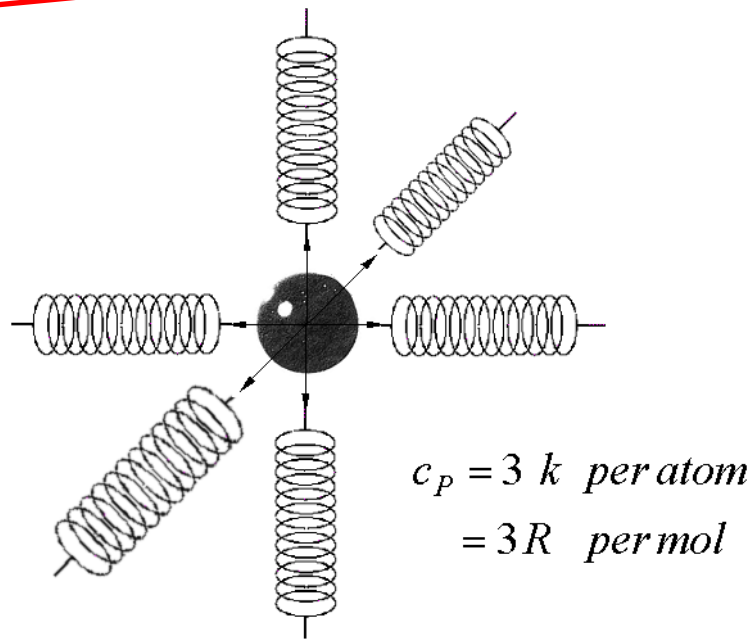




example: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)

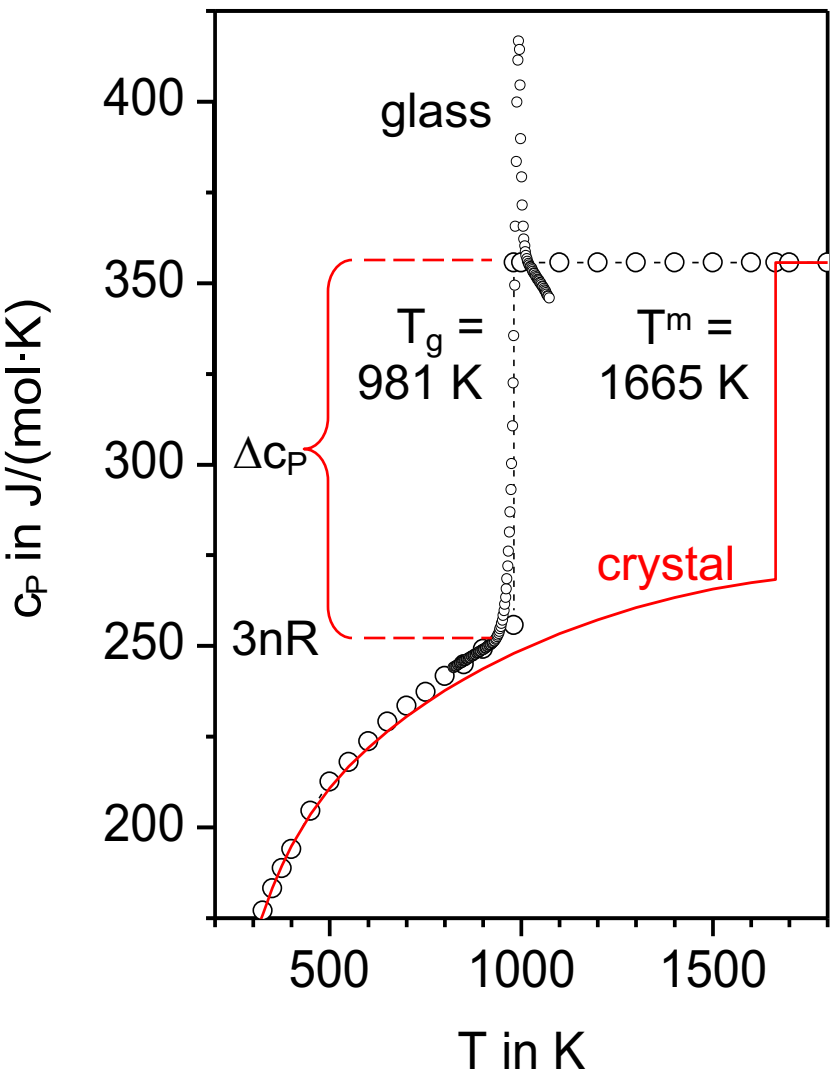


essentially the same as in the isochemical low-P crystal, hence $c_P(\text{crystal}) \approx c_P(\text{glass})$



Robie et al. (1978); Martens et. al. (1987)
Richet & Bottinga (1995); Courtial et. al. (2000)

allows integration from 0 to T, yielding H(T) and S(T)



Robie et al. (1978); Martens et. al. (1987)
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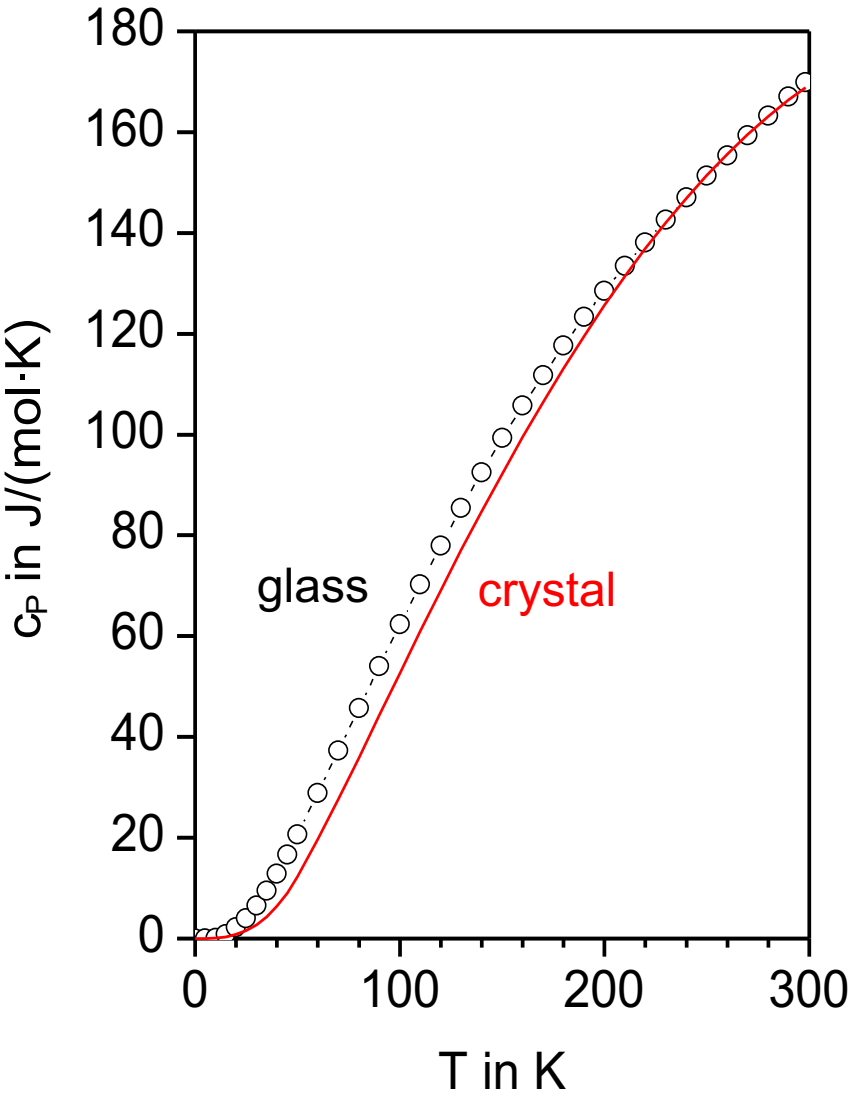
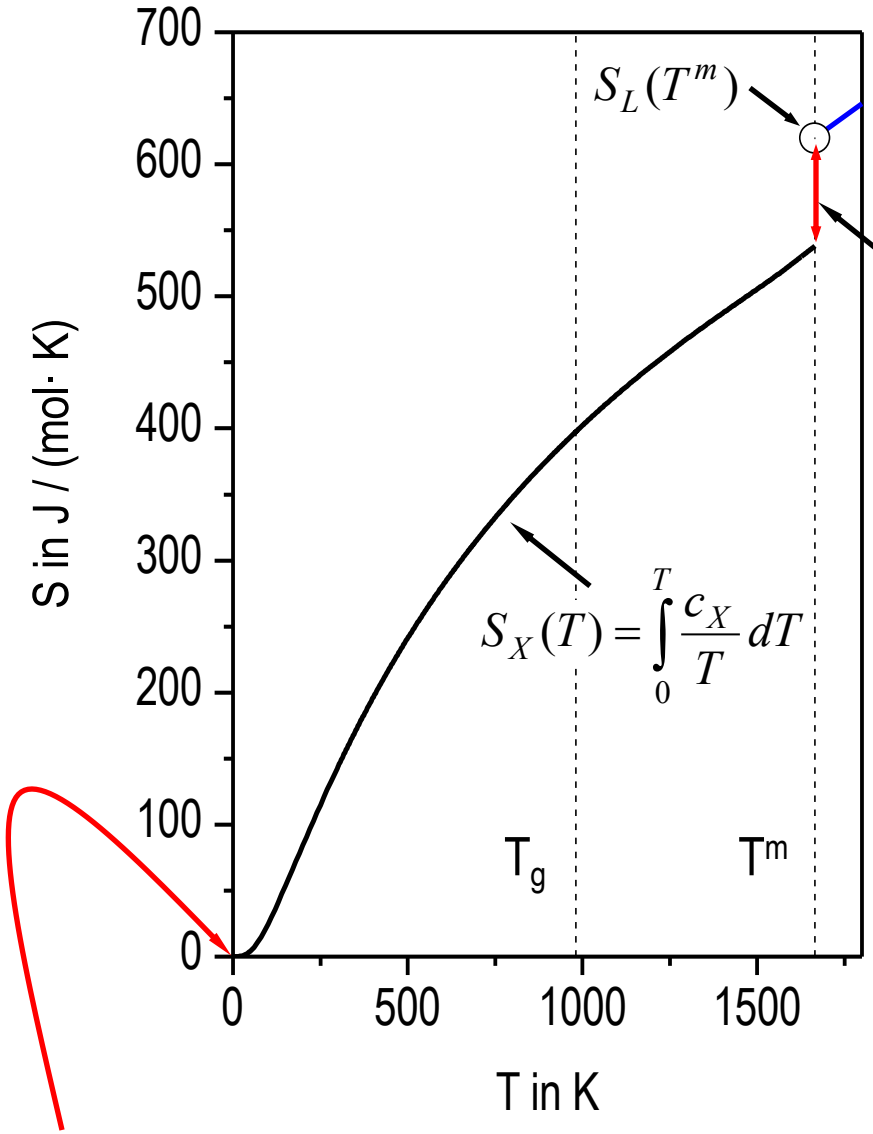


Krupka, Robie, Hemingway (1985)
Richet, Robie, Heminway (1986)

results: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)



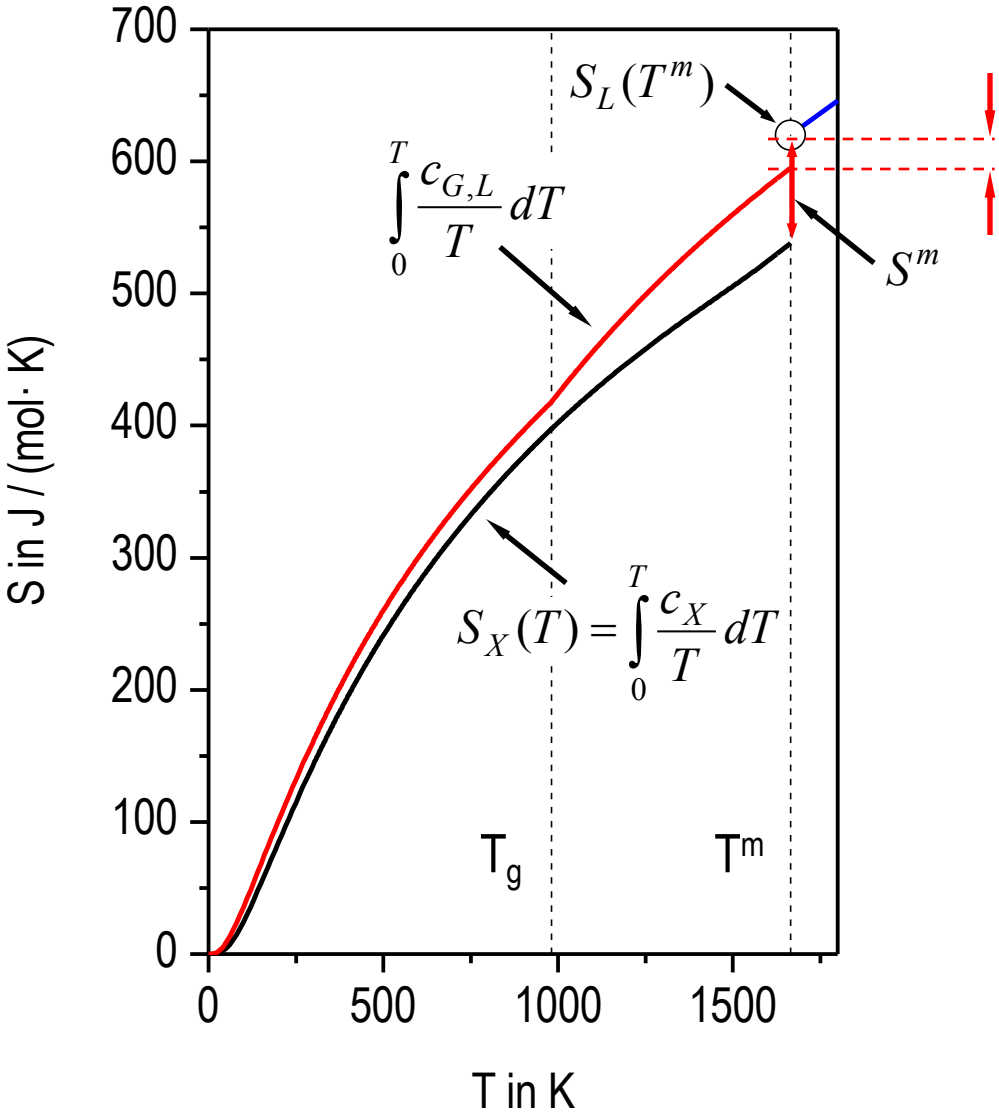
$S_L(T^m)$ = 619.8±1.0 J / (mol·K) *)

S^m = 85.7 J / (mol·K) *)

*) *Knacke, Kubachewski, Hesselmann (1991)*

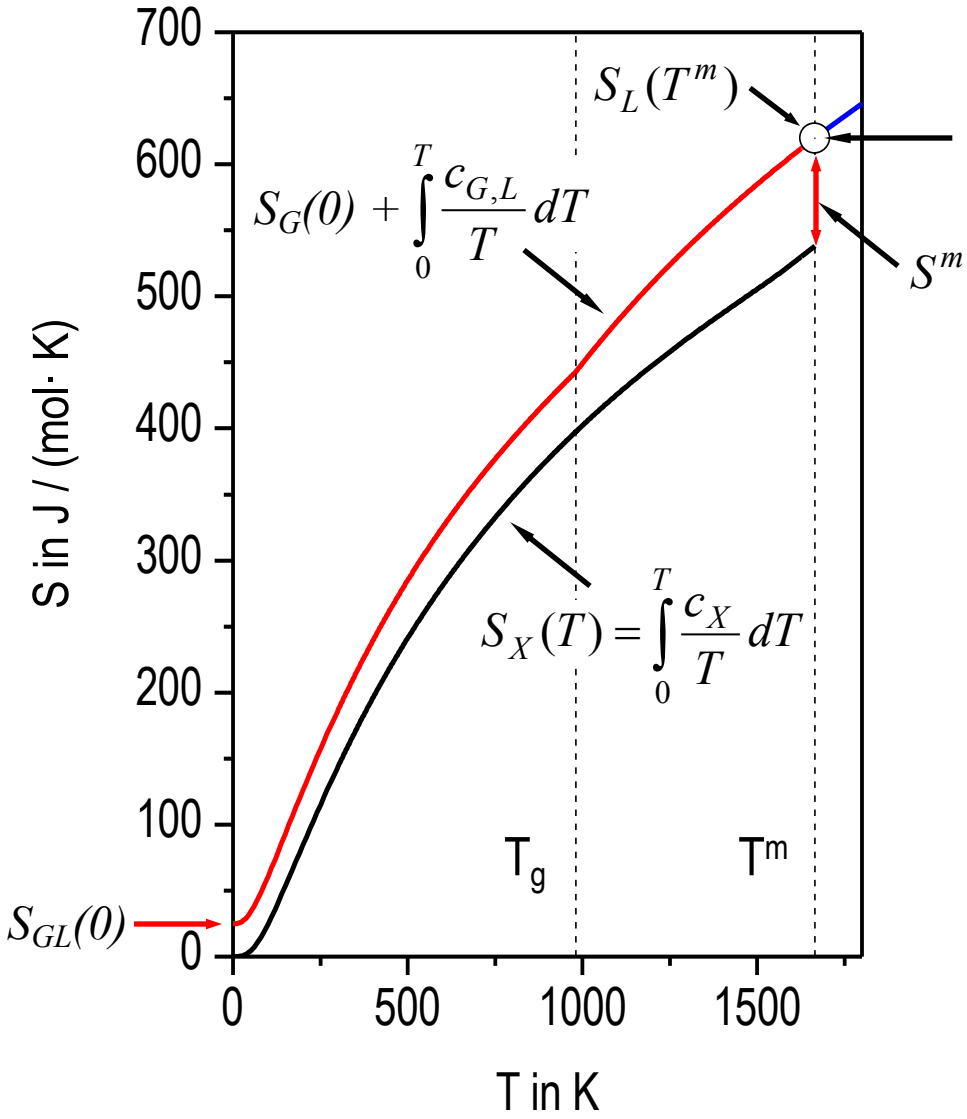
3rd law: the black curve must be fixed at S = 0 for T = 0.

results: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)



At T^m, X an G,L must merge to an identical state, the eq. liquid.

results: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)



The read curve must terminate **here**.

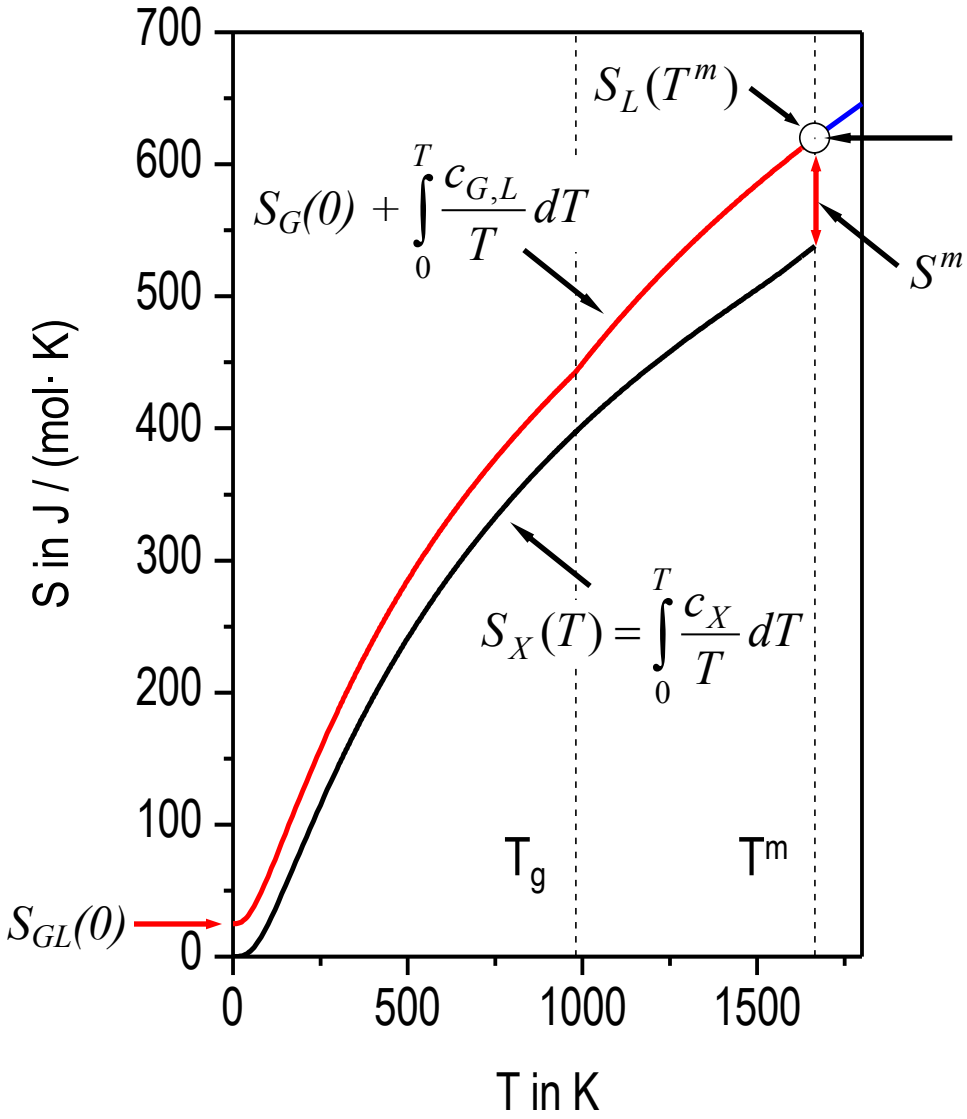
⇒

The integration constant $S_{GL}(0)$ of the red curve is non-zero:

$S_{GL}(0) = 24.8 \pm 3.0$ J/(mol·K)

Richet & Bottinga 1995

results: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)



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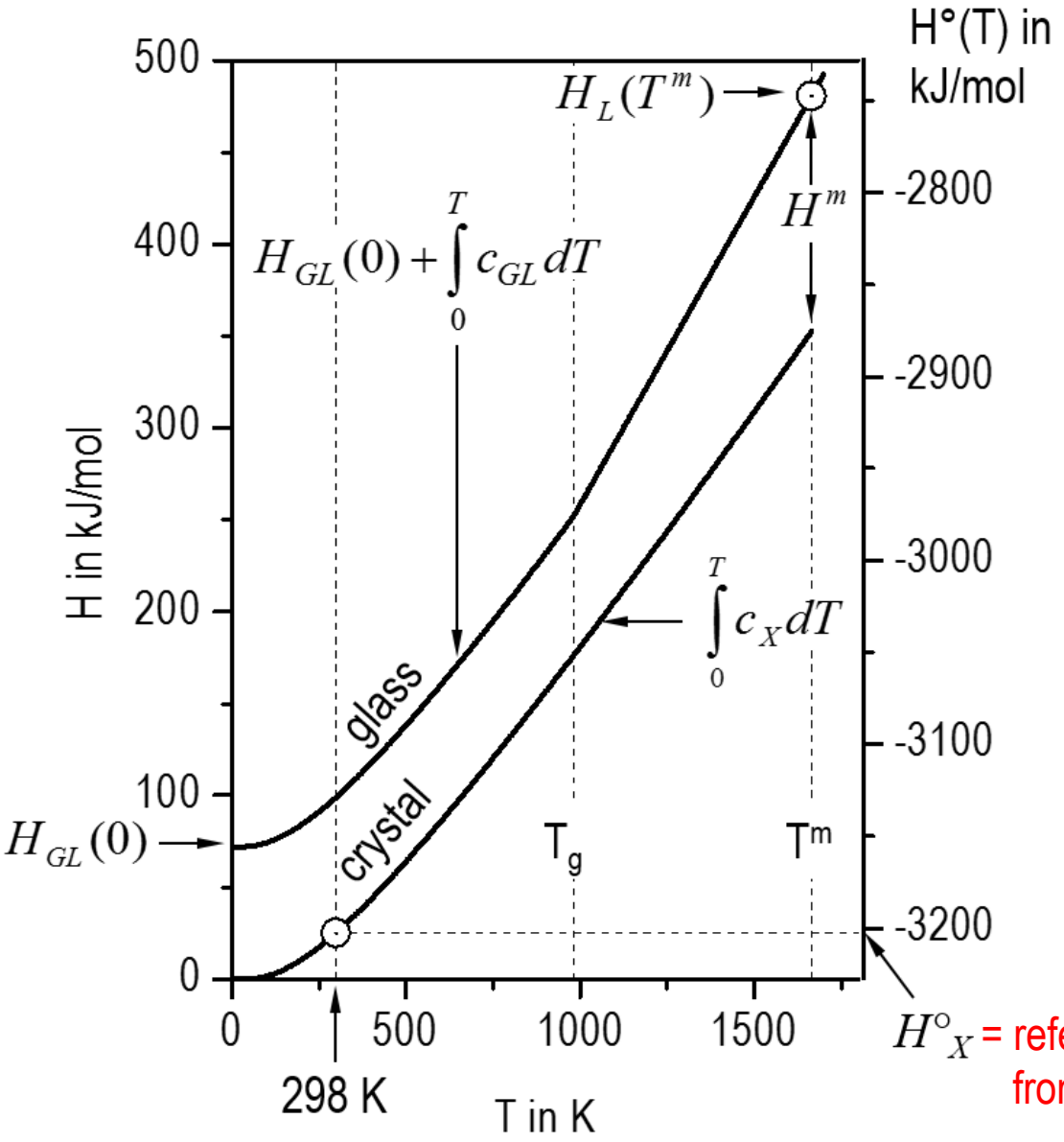
Richet & Bottinga 1995

Calorimetry measures the reversible part S of entropy only, not the entropy generation σ during measurement, **BUT**
$\sigma << S_{GL}(0)$, hence,
$S_{GL}(0)$ is a lower bound of the true residual entropy of a glass.

Guijrati, Entropy 2018

results: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)



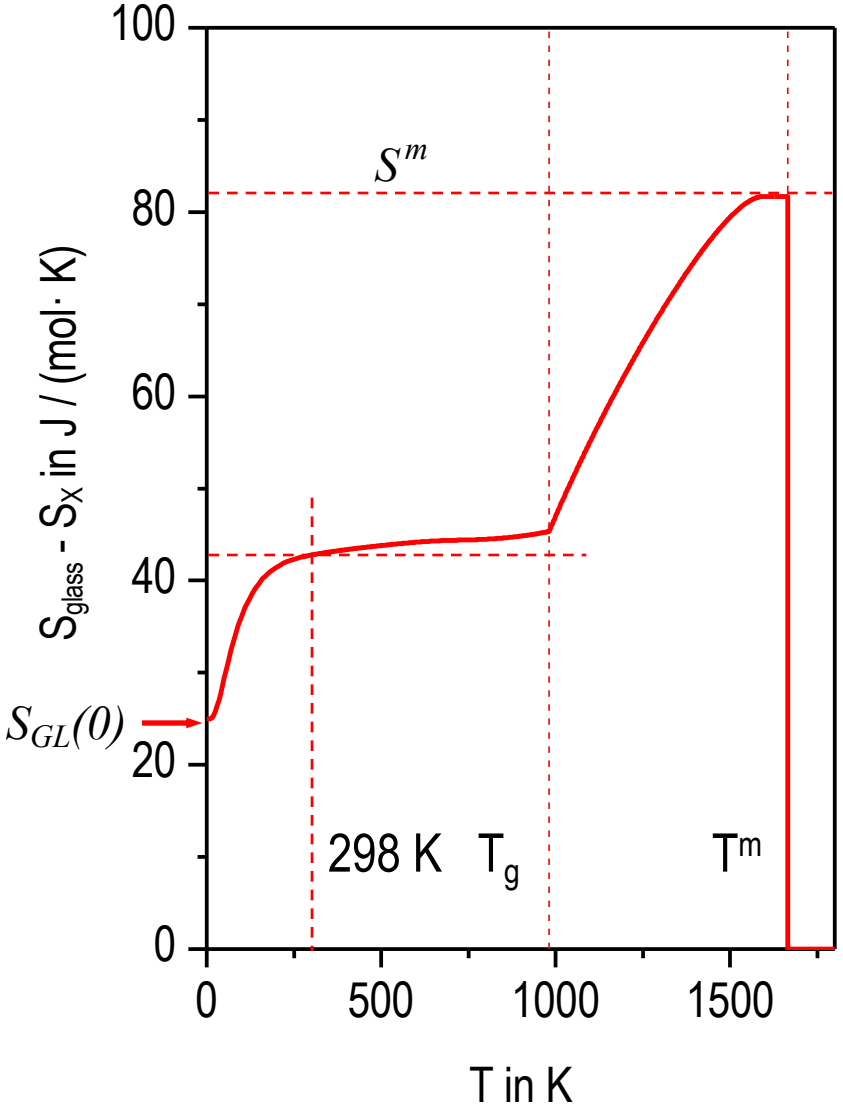
Curve must match with $H_L(T^m)$.

For H, both X and GL have non-zero integration constants.

H°_X = reference state: heat of formation of the crystal from the elements at 298 K, 1 bar

results: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)

Deriving an engineer's concept S^{vit} from the scientific concept $S_{GL}(0)$



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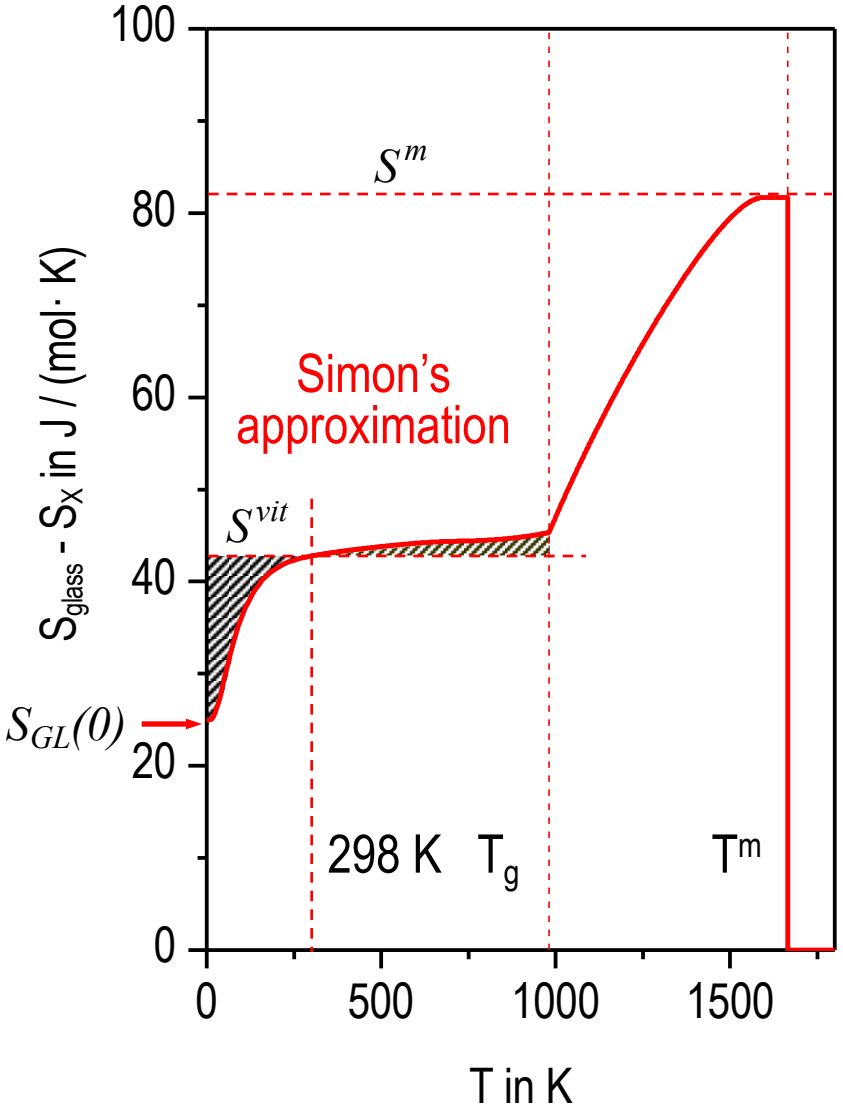
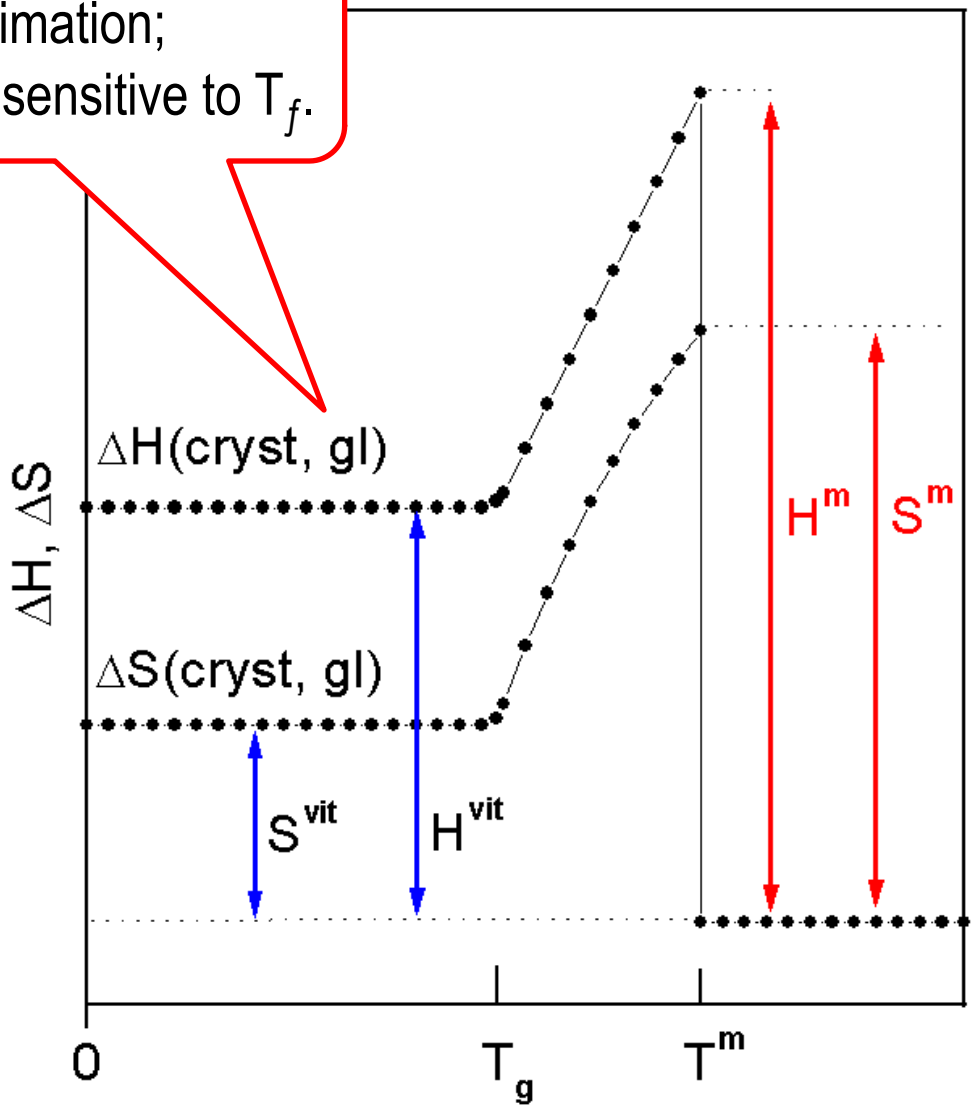


Energetics of one-component glasses

Simon's approximation;
H^{vit} and S^{vit} are sensitive to T_f.



One-Component Glasses

-

low-T behavior

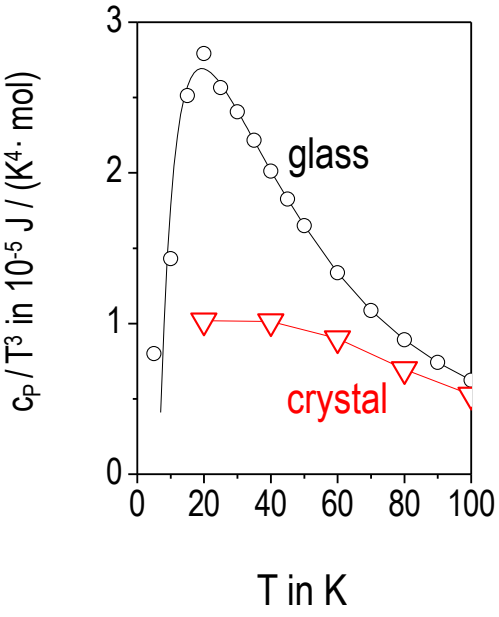
example: $CaO \cdot MgO \cdot 2SiO_2$ (diopside)

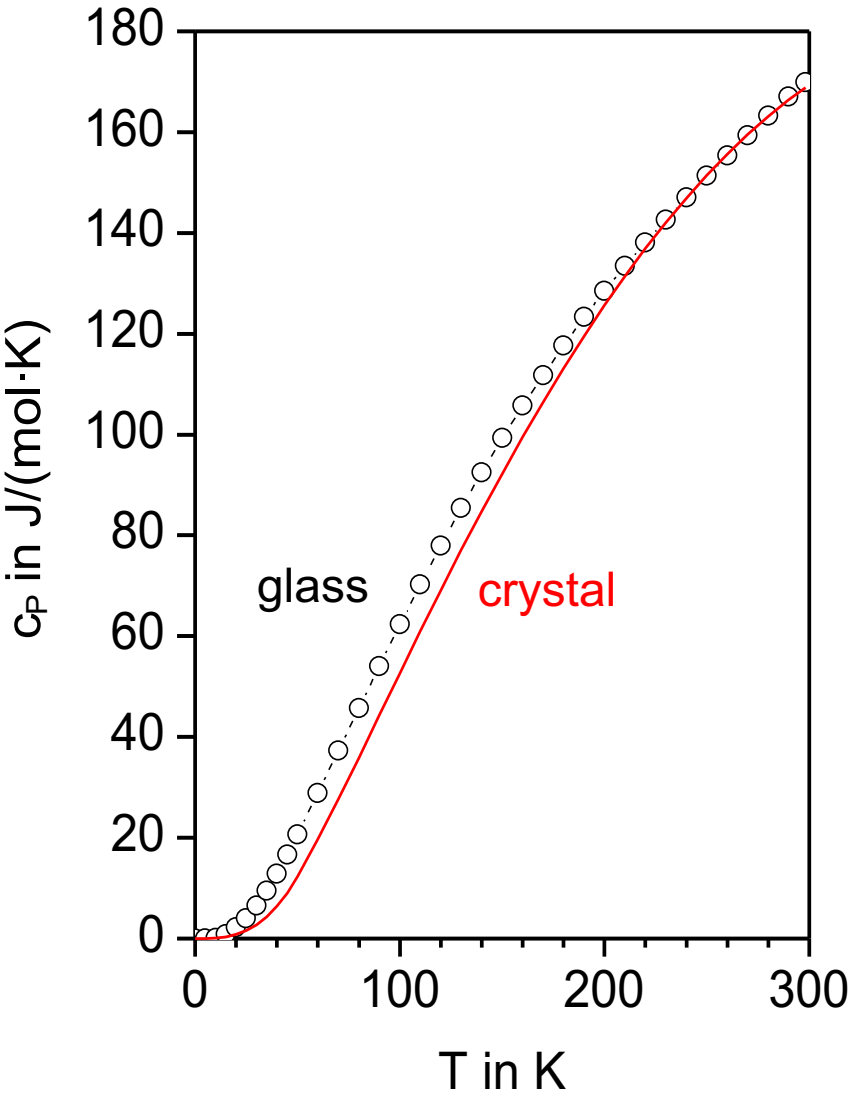
the calorimetric Boson peak:

maximum deviation from T^3 law at 20 K

$$L = \frac{\lambda_{excess}}{2} = \frac{h \cdot u}{2 \cdot k \cdot T_{\max}} \approx 2\,nm$$

Duval (1990), Chamgagnon (1998)

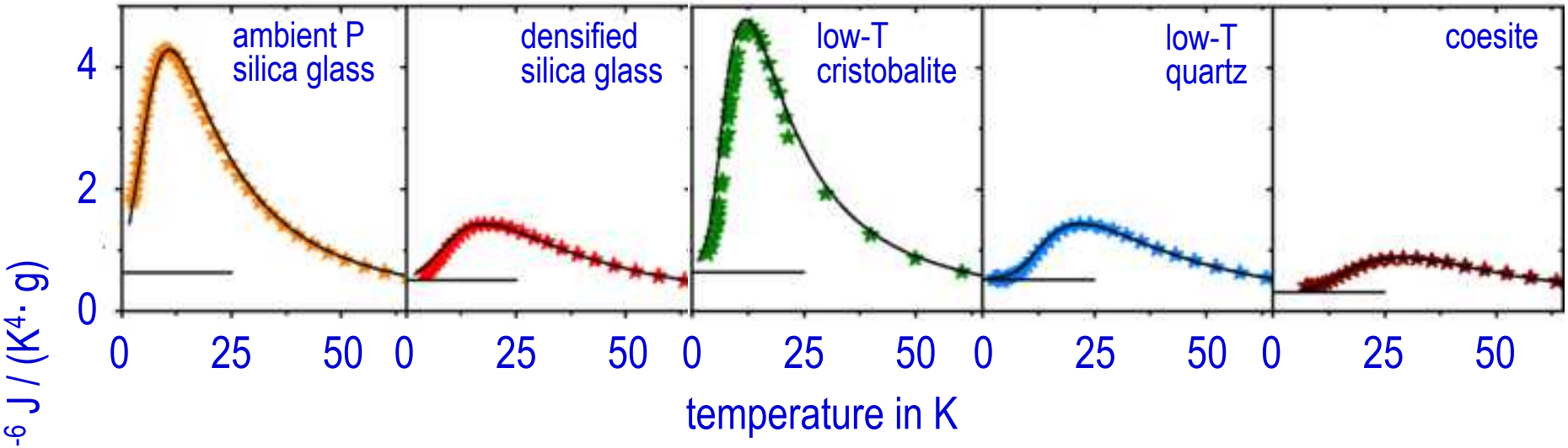


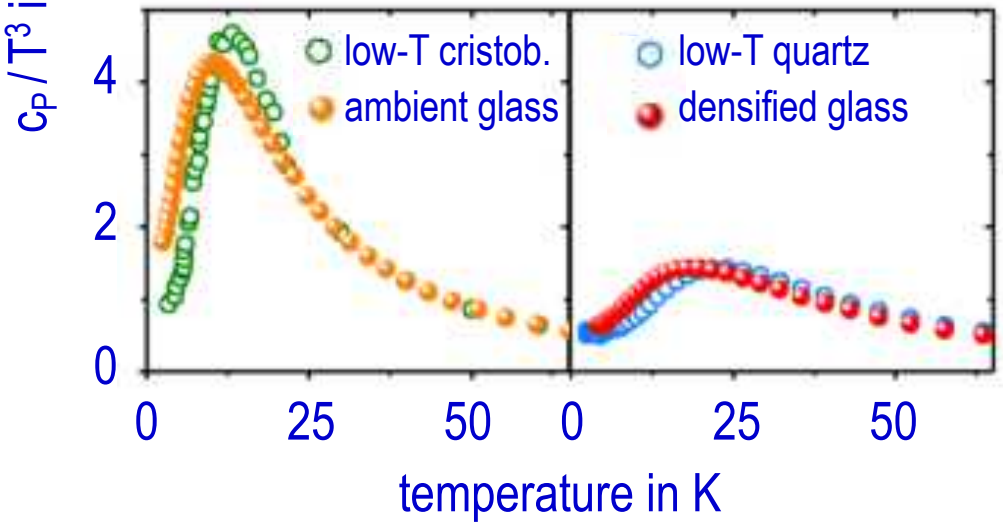


Krupka, Robie, Hemingway (1985)
Richet, Robie, Heminway (1986)

the calorimetric Boson peak:

- predominant role of the molar volume V^M
- presence or absence of translational symmetry is almost irrelevant





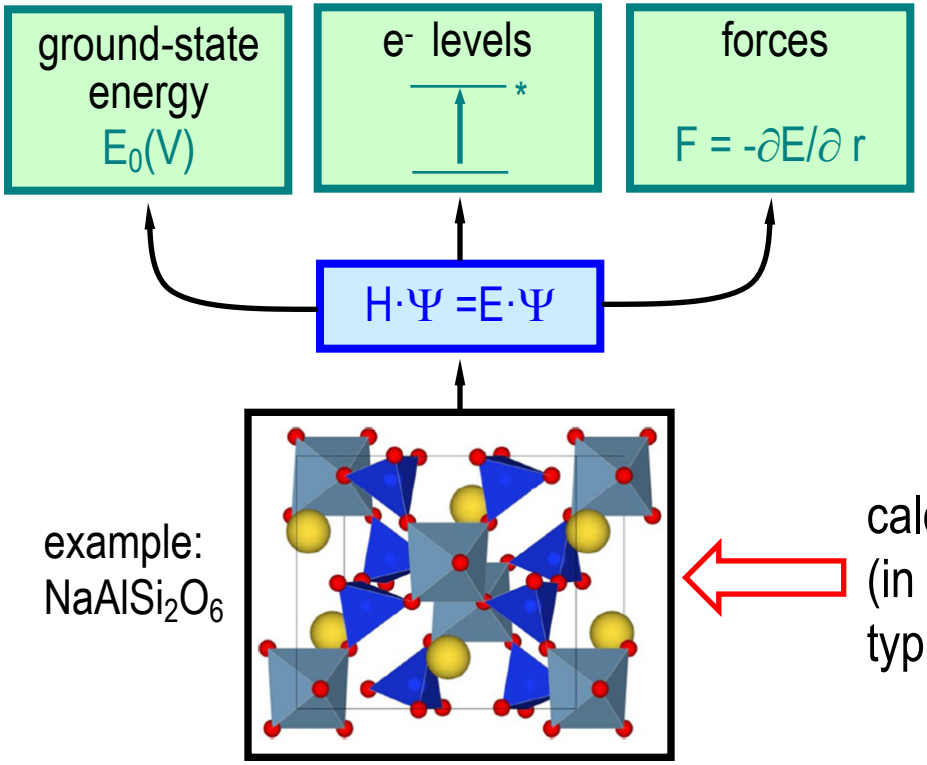
Mysen and Richet, Elsevier 2005, Silicate glasses and melts

Chumakov et al., PRL 2014, Role of disorder in the thermodynamics and atom dynamics of glasses

ab inition approach to the properties glasses

calculation of structures and properties of crystalline phases
(Stoffel & Dronskowski)

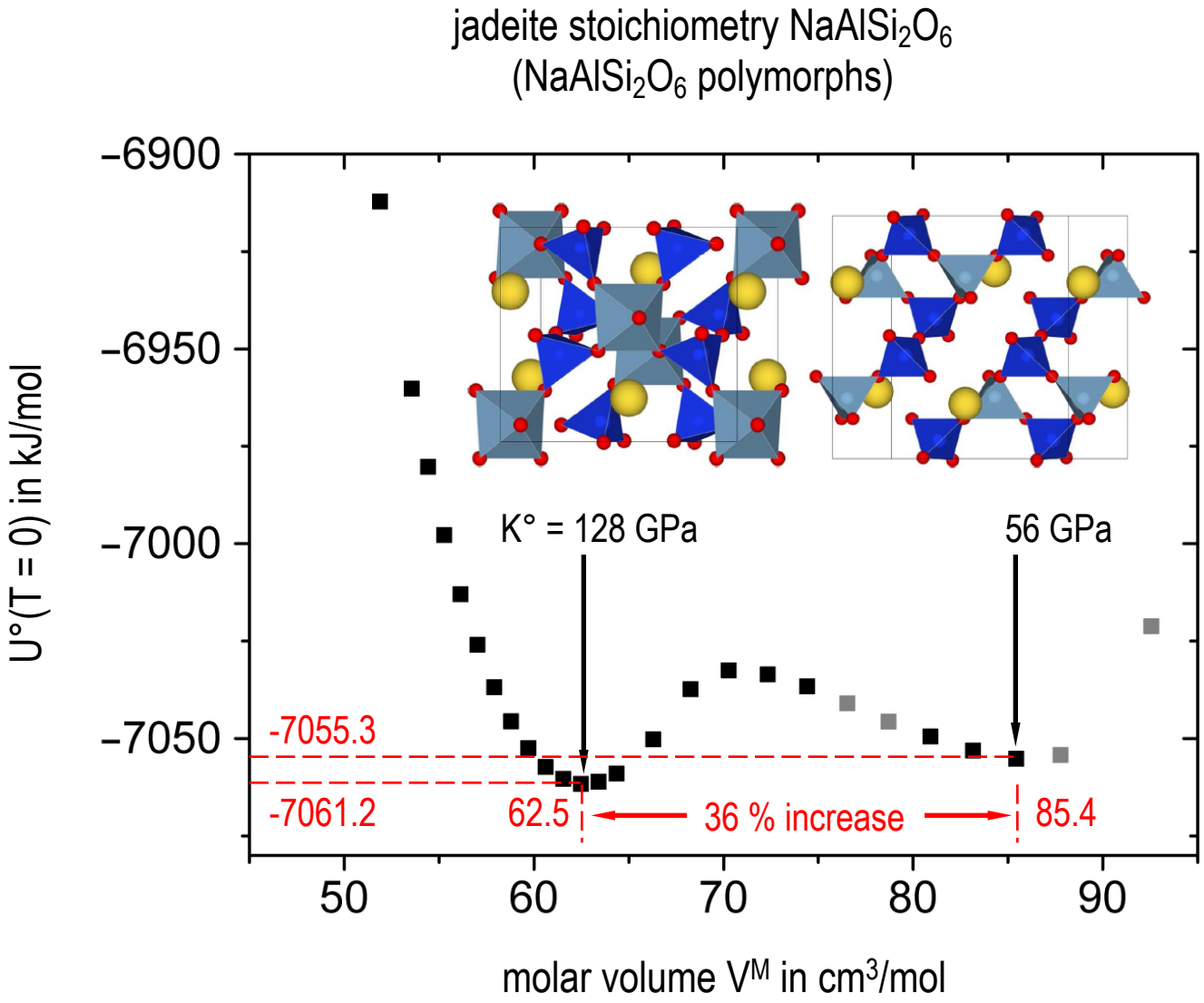
we obtain: G, H, S, c_P; K, E;
for each equilibrium structure



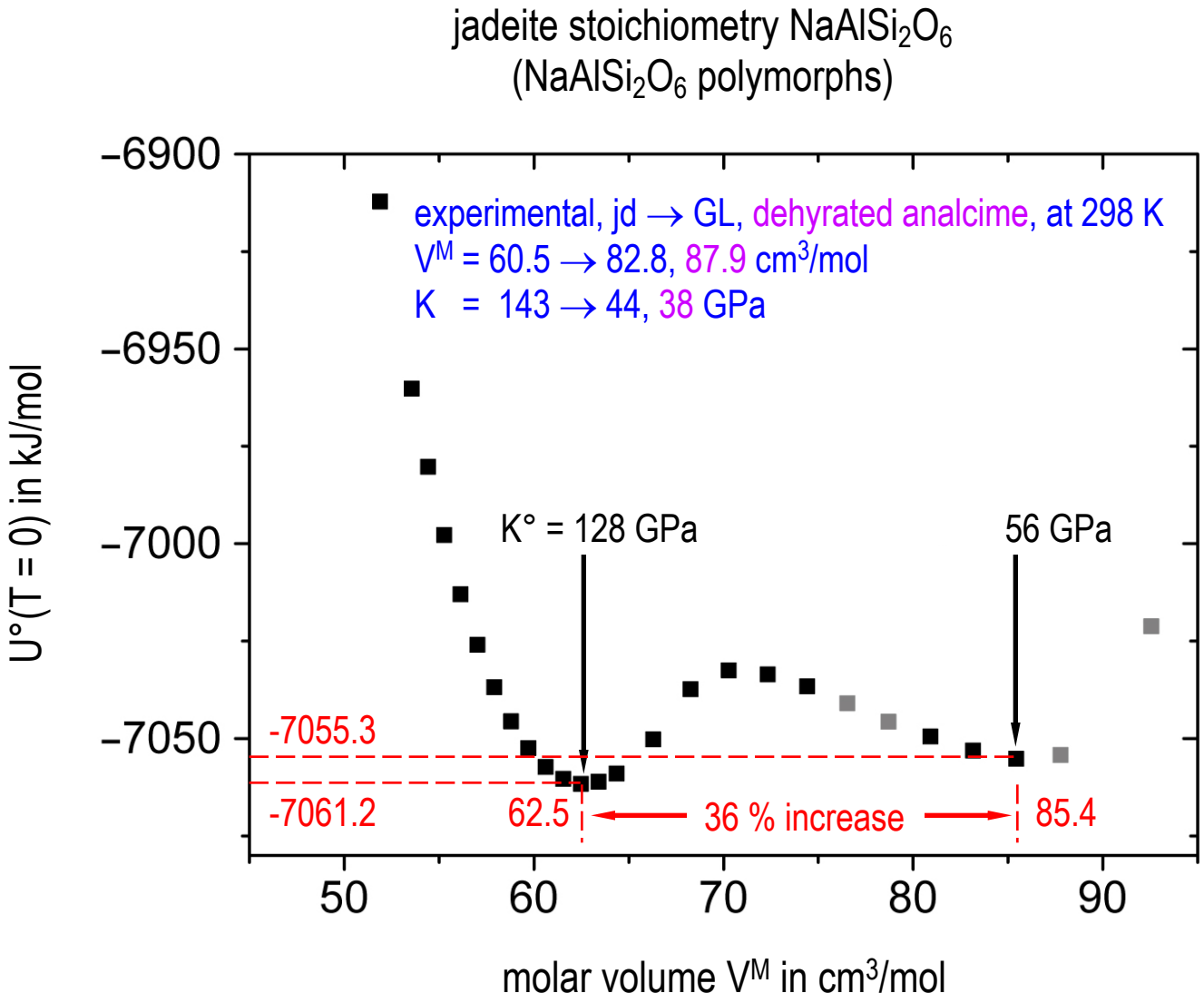
example:
$NaAlSi_2O_6$

calculated on a k-point grid
(in reciprocal space) with
typically 1000 k-points·atom

ab inition approach to the properties glasses

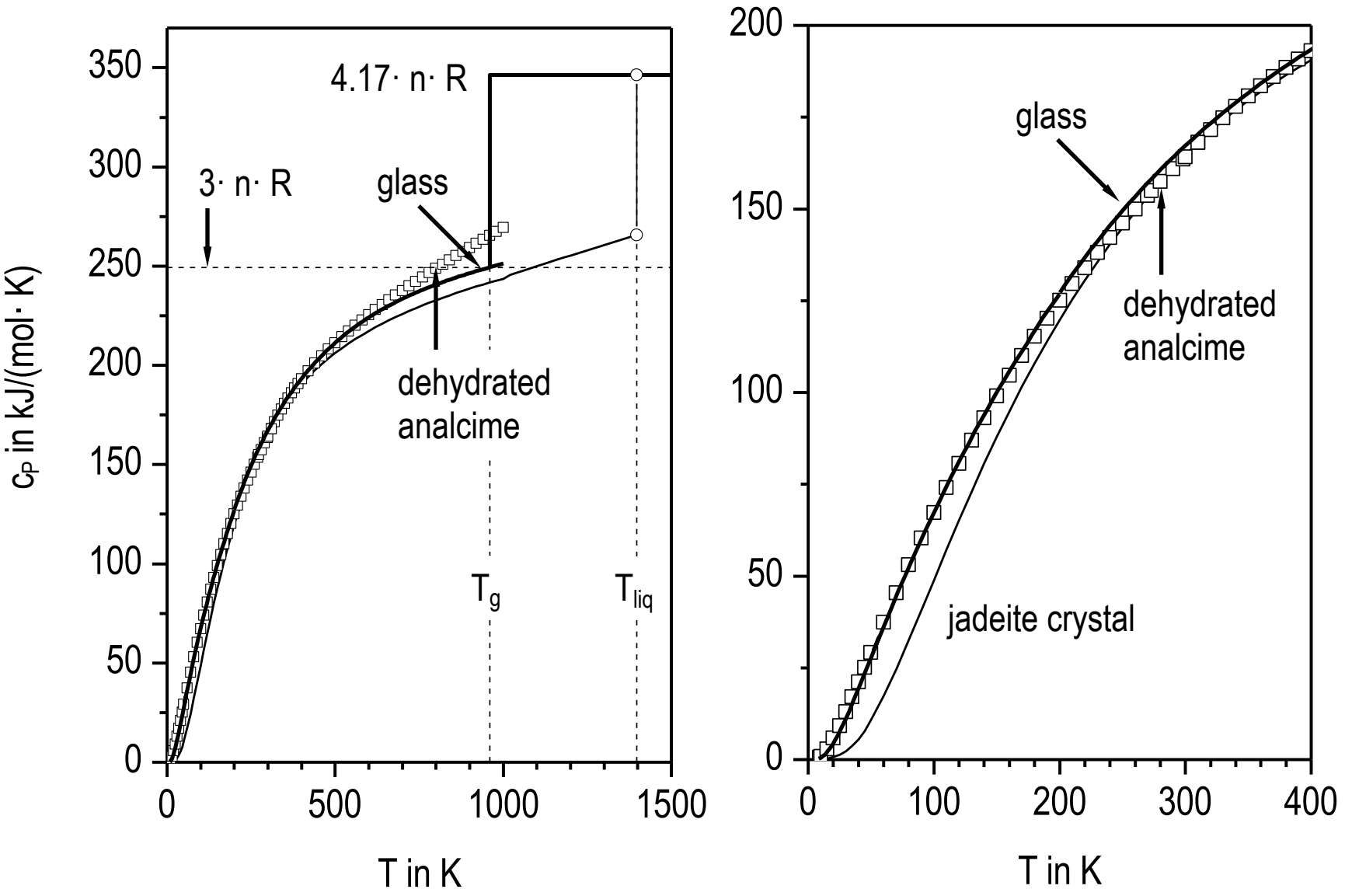


Stoffel, Philipps, Conradt, Dronskowski, ZAAC 2016



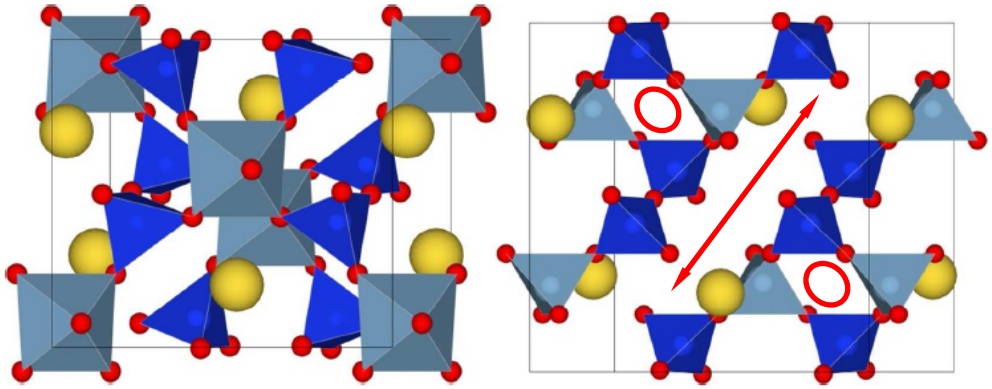
Stoffel, Philipps, Conradt, Dronskowski, ZAAC 2016

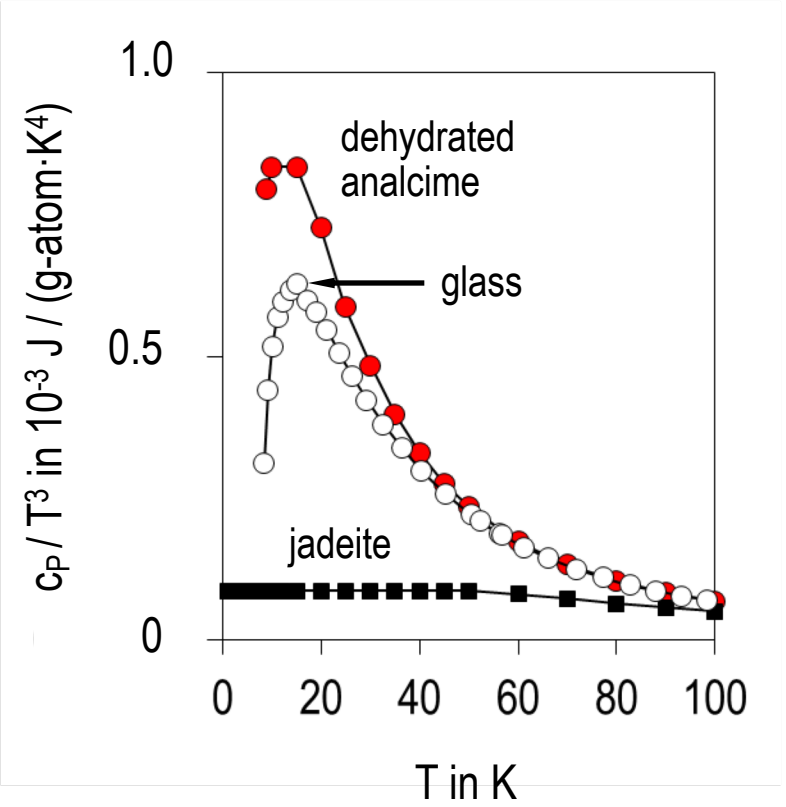
jadeite stoichiometry $NaAlSi_2O_6$
($NaAlSi_2O_6$ polymorphs)



Stoffel, Philipps, Conradt, Dronskowski, ZAAC 2016
data sources: Heminway et al., Am. Mineralog. 1999; Richet et al., Geochim. Cosmochim Acta 1993

jadeite stoichiometry $NaAlSi_2O_6$ ($NaAlSi_2O_6$ polymorphs)





jadeite (high-P phase)
corner-linked [SiO_4],
corner linked [AlO_6]

hypothetical low-P phase
corner-linked [SiO_4] and [AlO_4]
same density as jadeite glass:

crystal

$V^M(X)$ = 6.050 cm^3/g-atom

E(X) = 213 GPa

glass

8.278 cm^3/g-atom

73 Gpa

dehydrated analcime

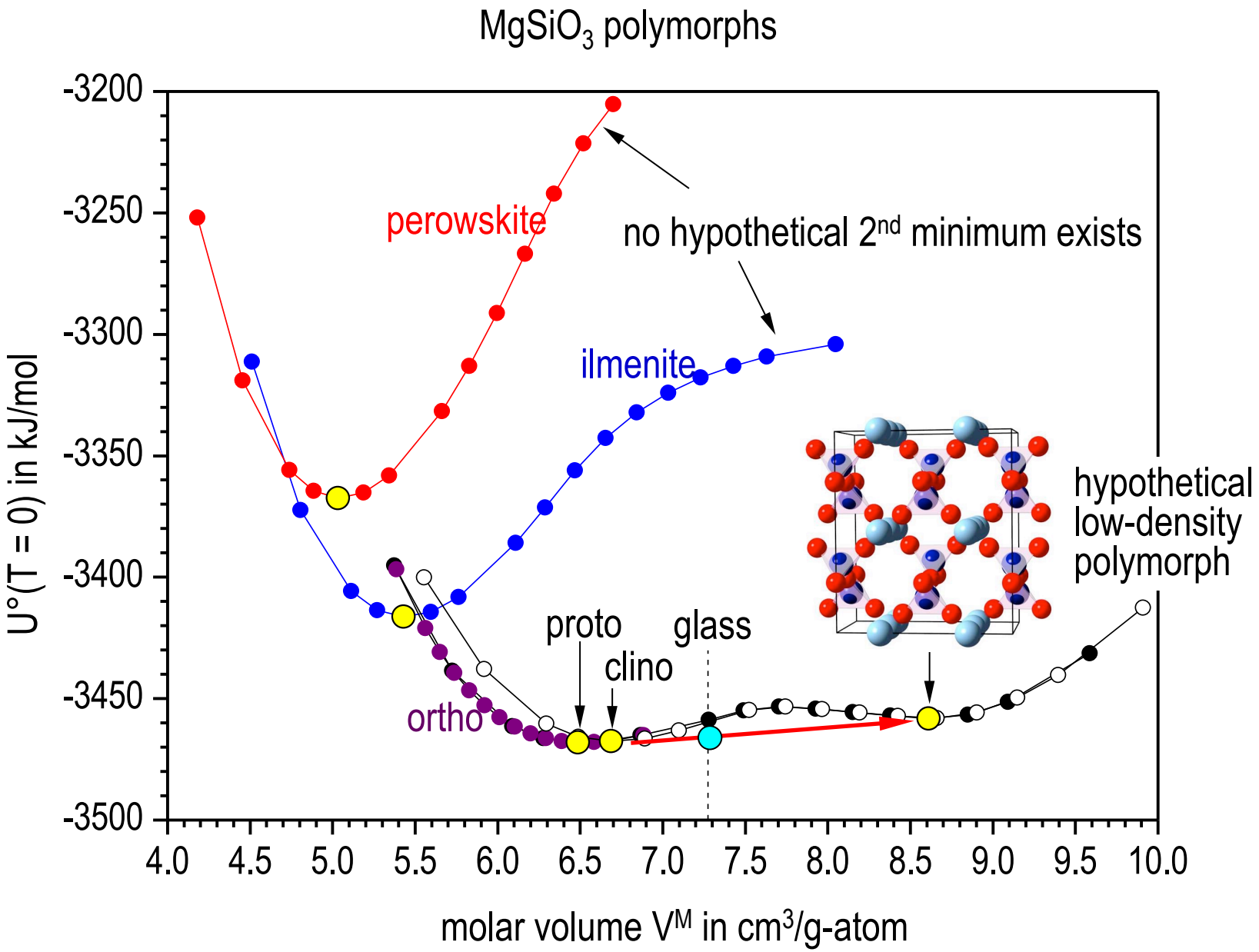
$V^M(X)$ =

8.788 cm^3/g-atom

One-Component Glasses

-

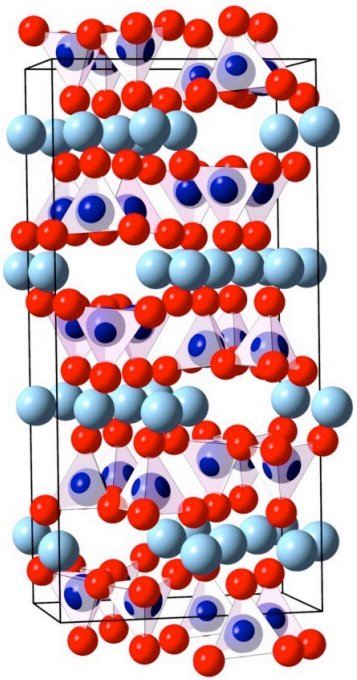
MRO based behavior



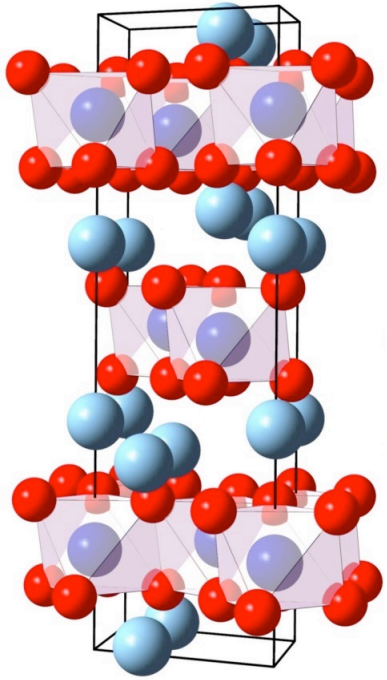
Philipps, Stoffel, Dronskowski, Conradt, Fontiers Mat. 2017

series of $MgSiO_3$ polymorphs

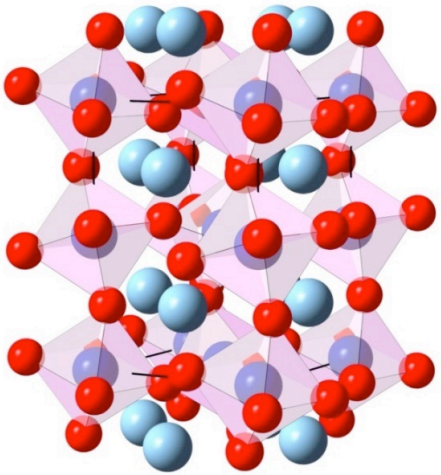
ortho, proto, clino enstatite
$[SiO_4]$ chains
corner-linked,
$[AlO_4]$



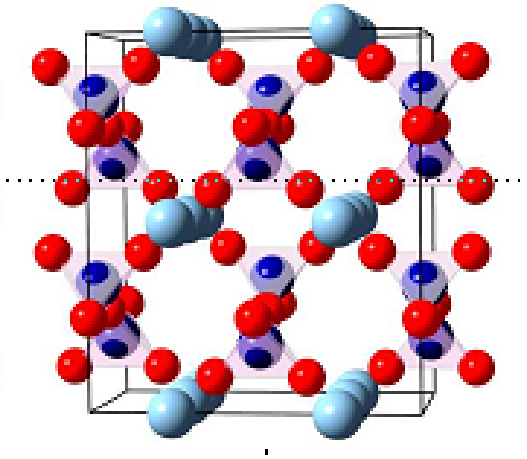
ilmenite
(high-P phase)
$[SiO_6]$ layers
edge-linked,
$[AlO_6]$



perowskite
(high-P phase)
$[SiO_6]$ 3D network
corner-linked ,
$[AlO_6]$

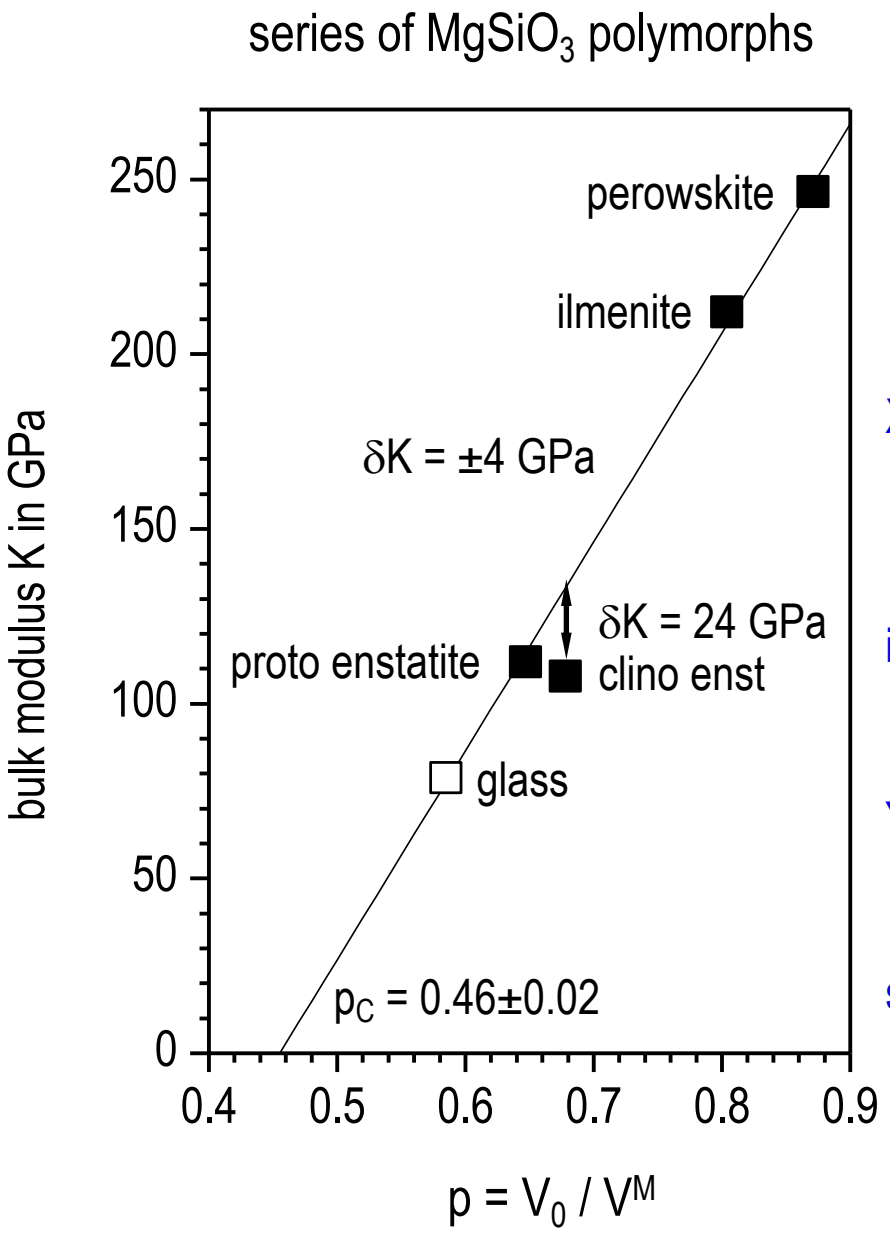


hypothetical low-density polymorph ↔ glass?
$[SiO_4]$, cristobalite-like
corner-linked,
$[AlO_4]$



$V°/V^M$ =	0.647 to 0.670	0.807	0.871	0.500; the glass: 0.585
K =	112 to 108	212	245	the glass: 79 GPa

Philipps, Stoffel, Dronskowski, Conradt, Fontiers Mat. 2017



$$V_0 = \frac{4\pi}{3} \cdot N_A \cdot \sum \left(x_{an} \cdot r_{an} + x_{cat} \cdot r_{cat} \right)$$

X axis:

$$\frac{V_0}{V^M} = \frac{V_0}{M} \cdot \rho \propto \rho$$ (normalized density)

intercept p_C = percolation limit

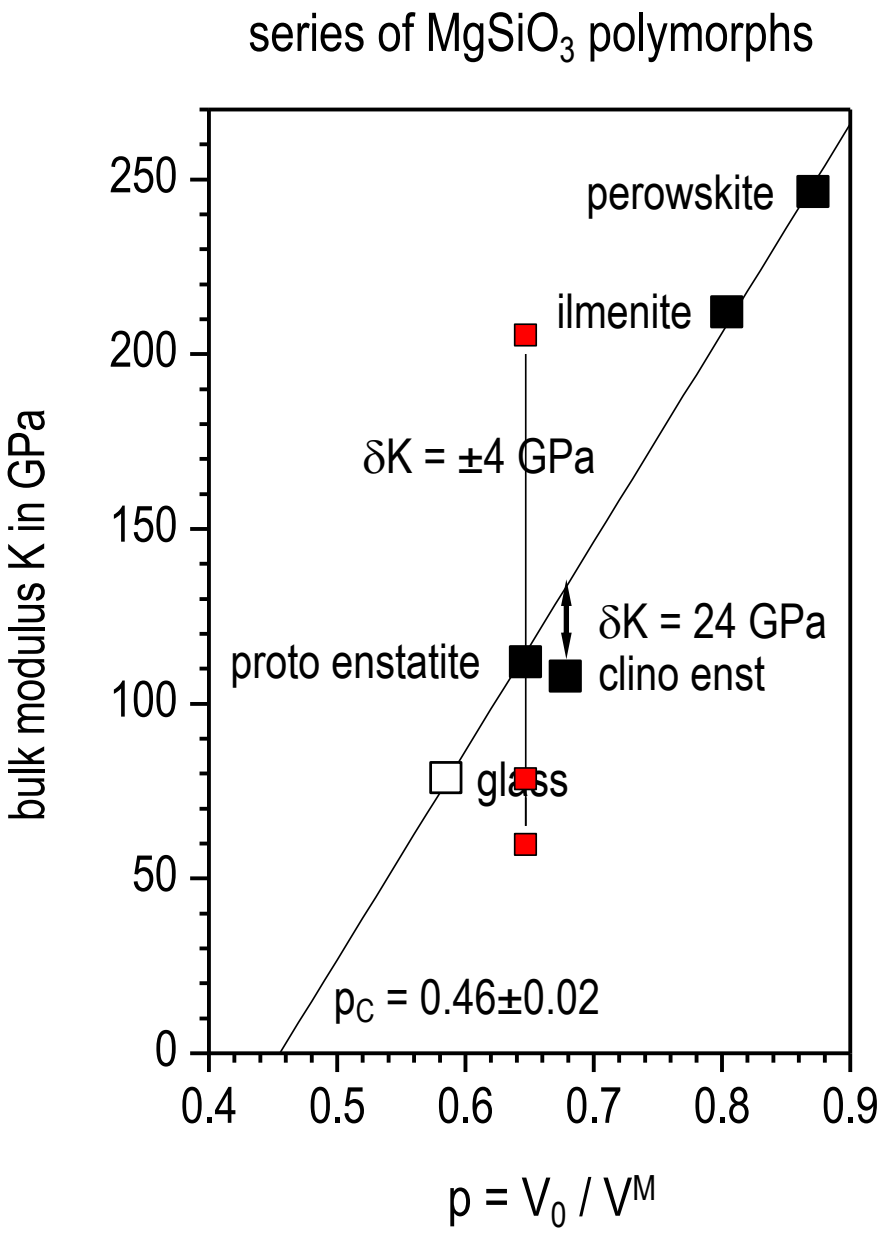
Y axis:

$$K = b \cdot (\rho - \rho_C)$$

slope b in [m^2/s^2]

Philipps, Stoffel, Dronskowski, Conradt, Fontiers Mat. 2017

glasses formed at 1 bar are commeasurable with randomly oriented polycrystalline low-density polymorphs



$$V_0 = \frac{4\pi}{3} \cdot N_A \cdot \sum \left(x_{an} \cdot r_{an} + x_{cat} \cdot r_{cat} \right)$$

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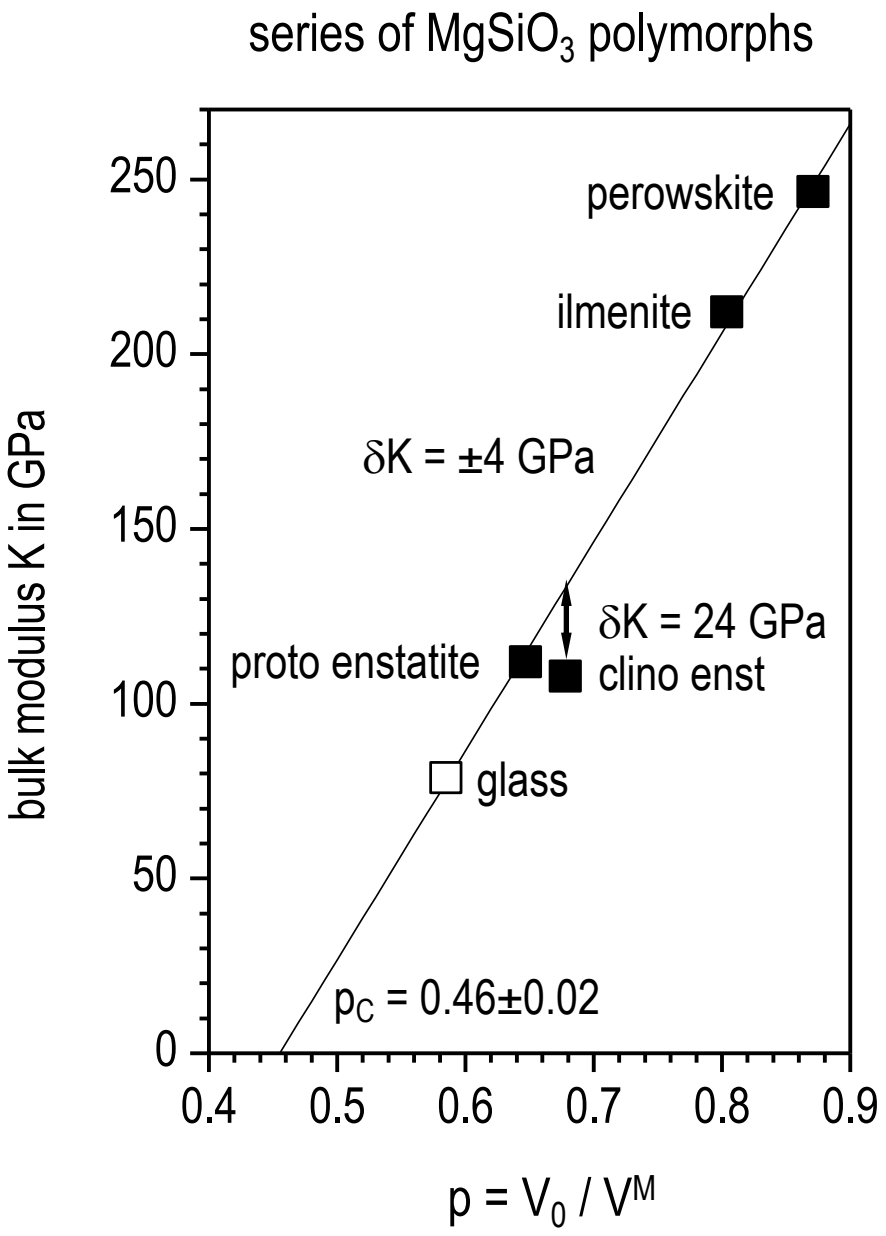
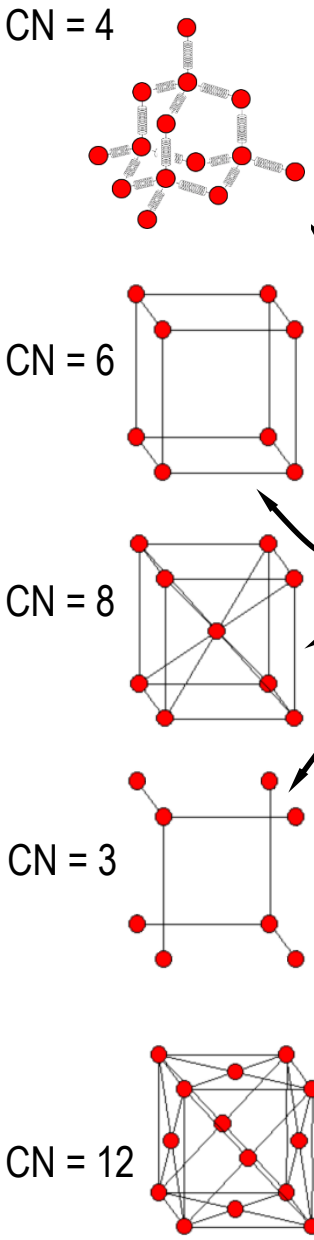
Philipps, Stoffel, Dronskowski, Conradt, Fontiers Mat. 2017



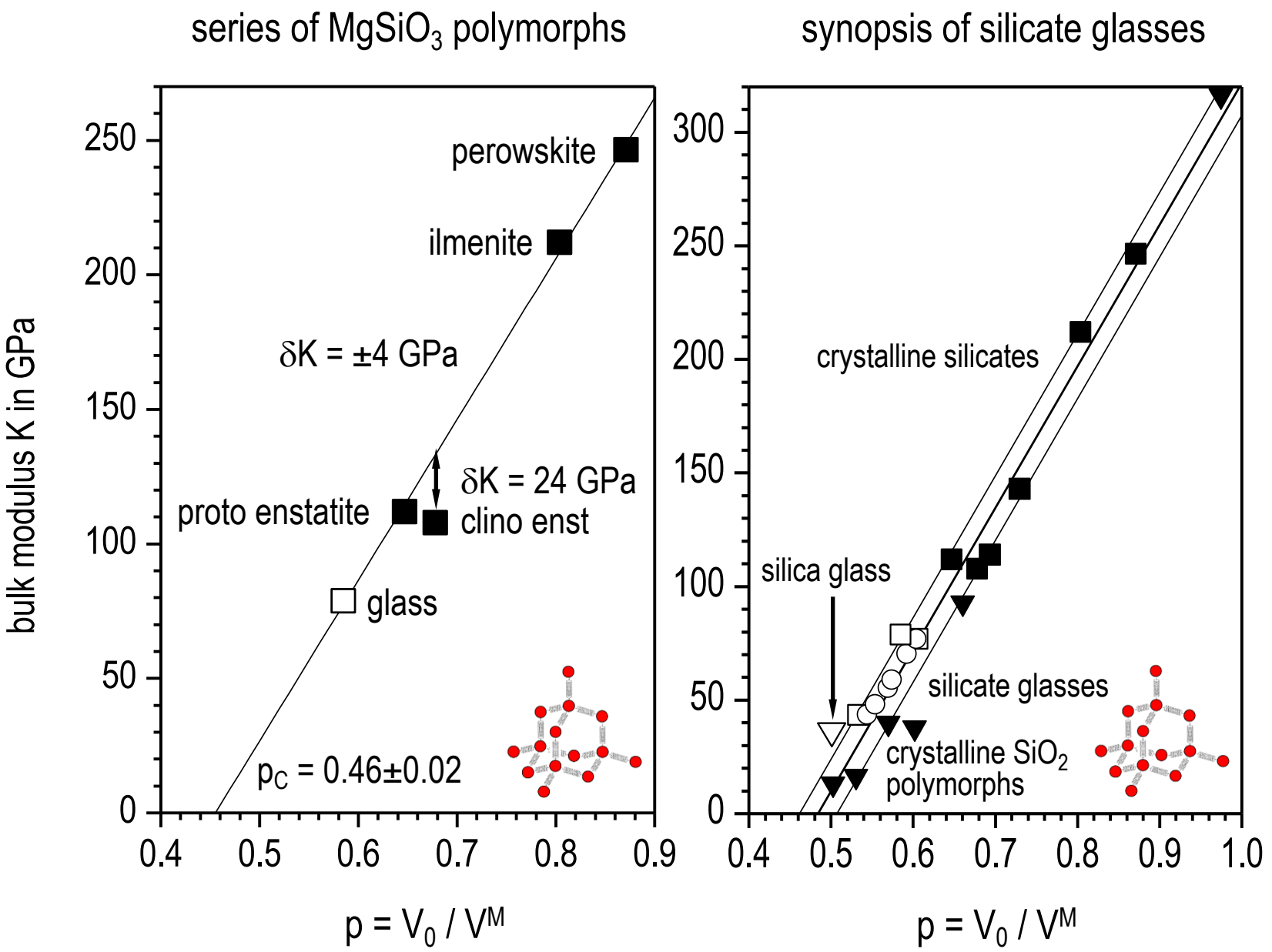


critical thersholds p_c for site percolation of dense materials

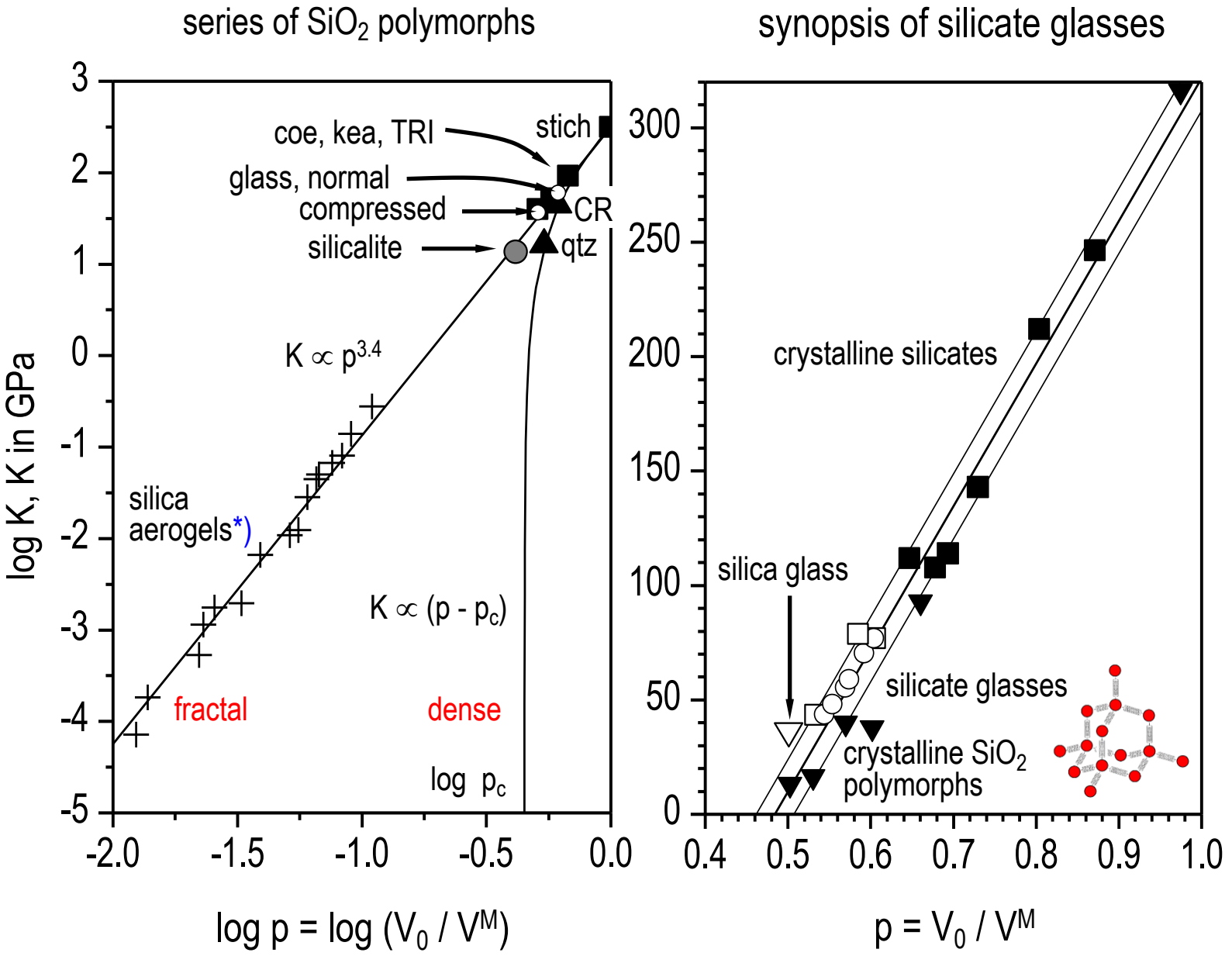
3D lattices	p_C
diamond *)	0.430
cubic primitive	0.312
bcc, or cubic primitive with 3 neighbors	0.246
fcc	0.198

*) corner linked tetrahedra (diamond, ice); randomness of one of the nearest neigbors: → 0.47

Philipps, Stoffel, Dronskowski, Conradt, Fontiers Mat. 2017

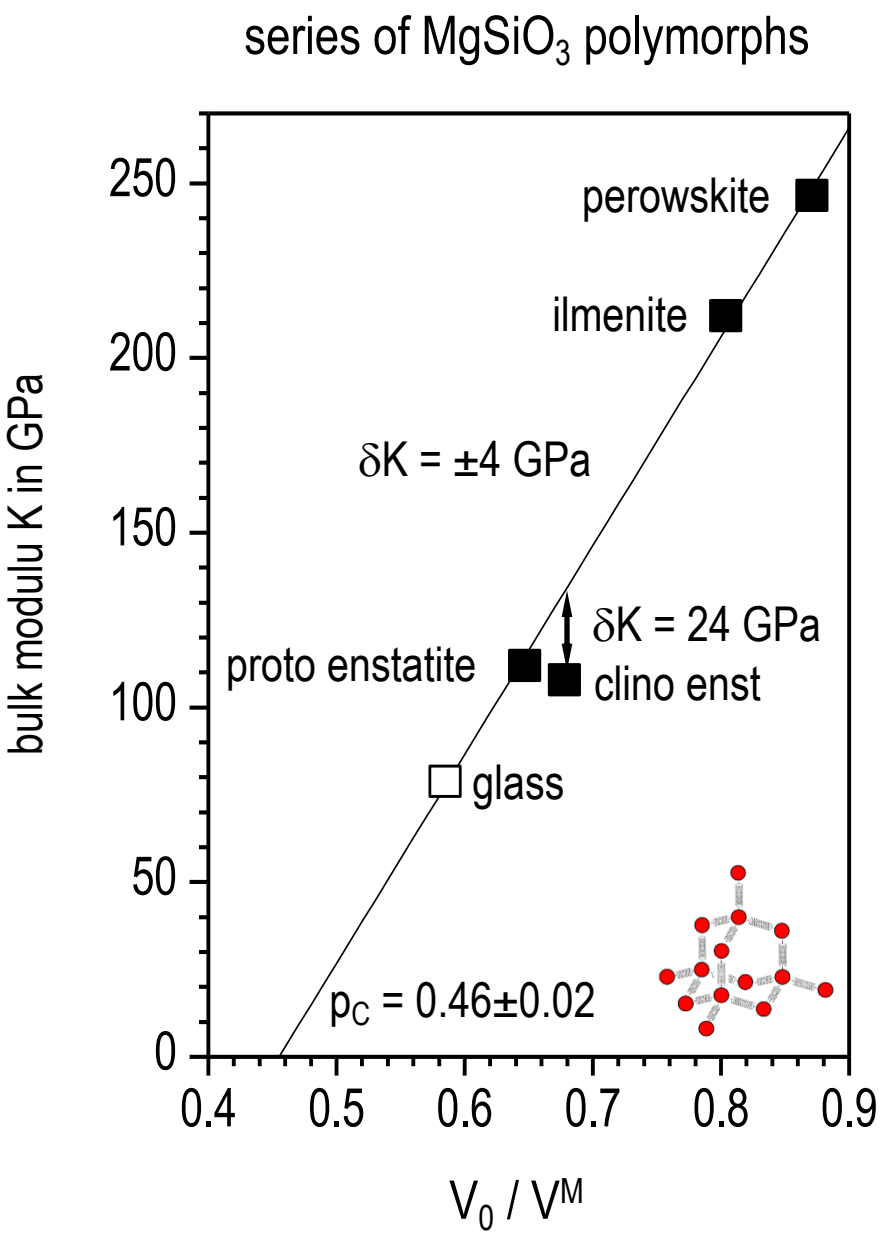


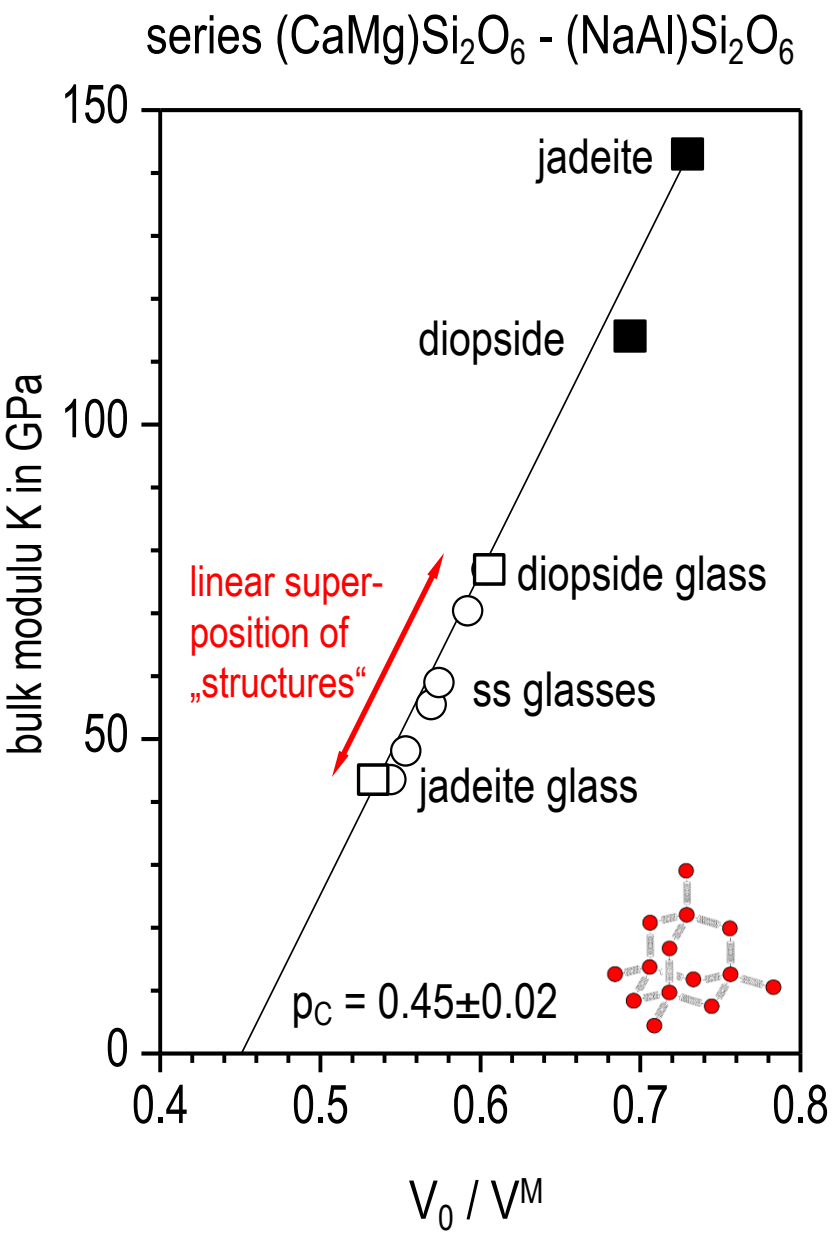
Philipps, Stoffel, Dronskowski, Conradt, Fontiers Mat. 2017



*) data: Woignier & Phalippou, HAL archieves ouvertes 1889

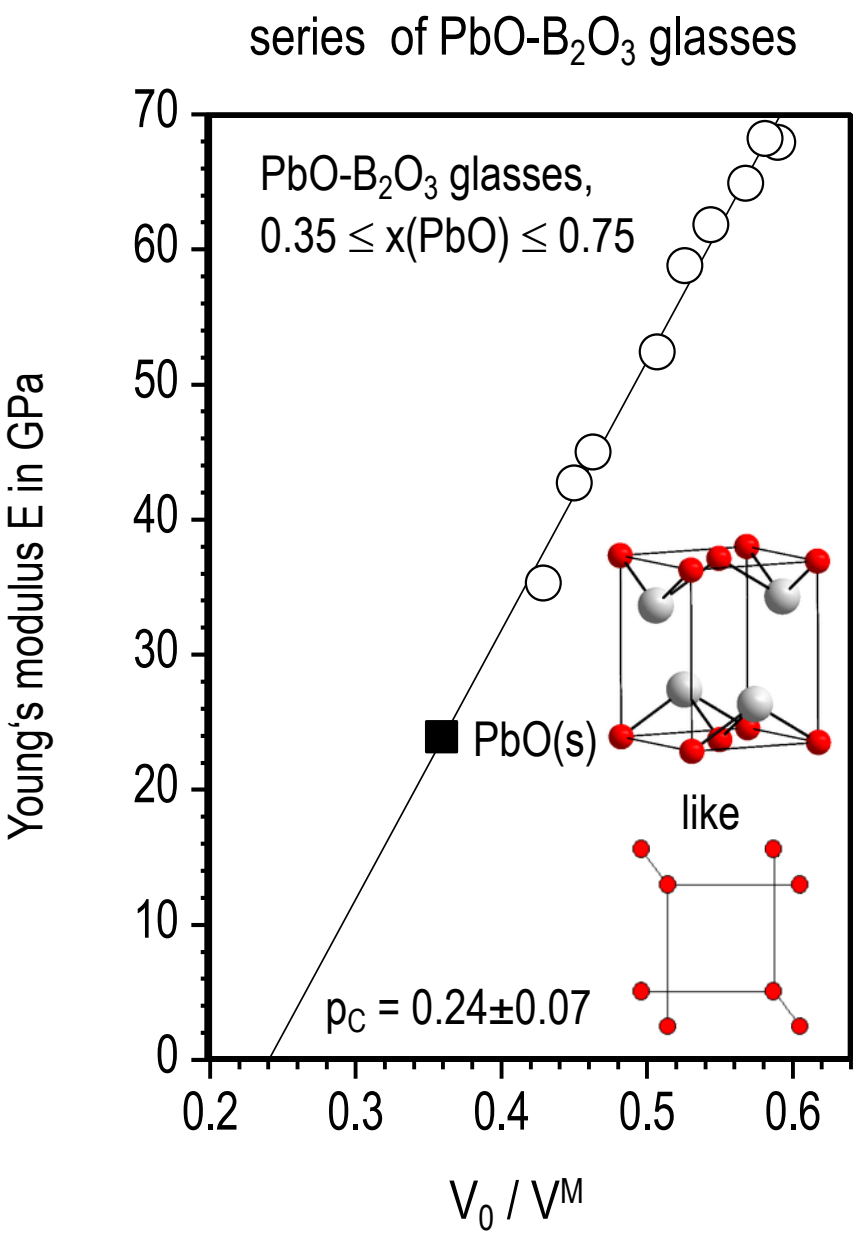
Multi-Component Glasses



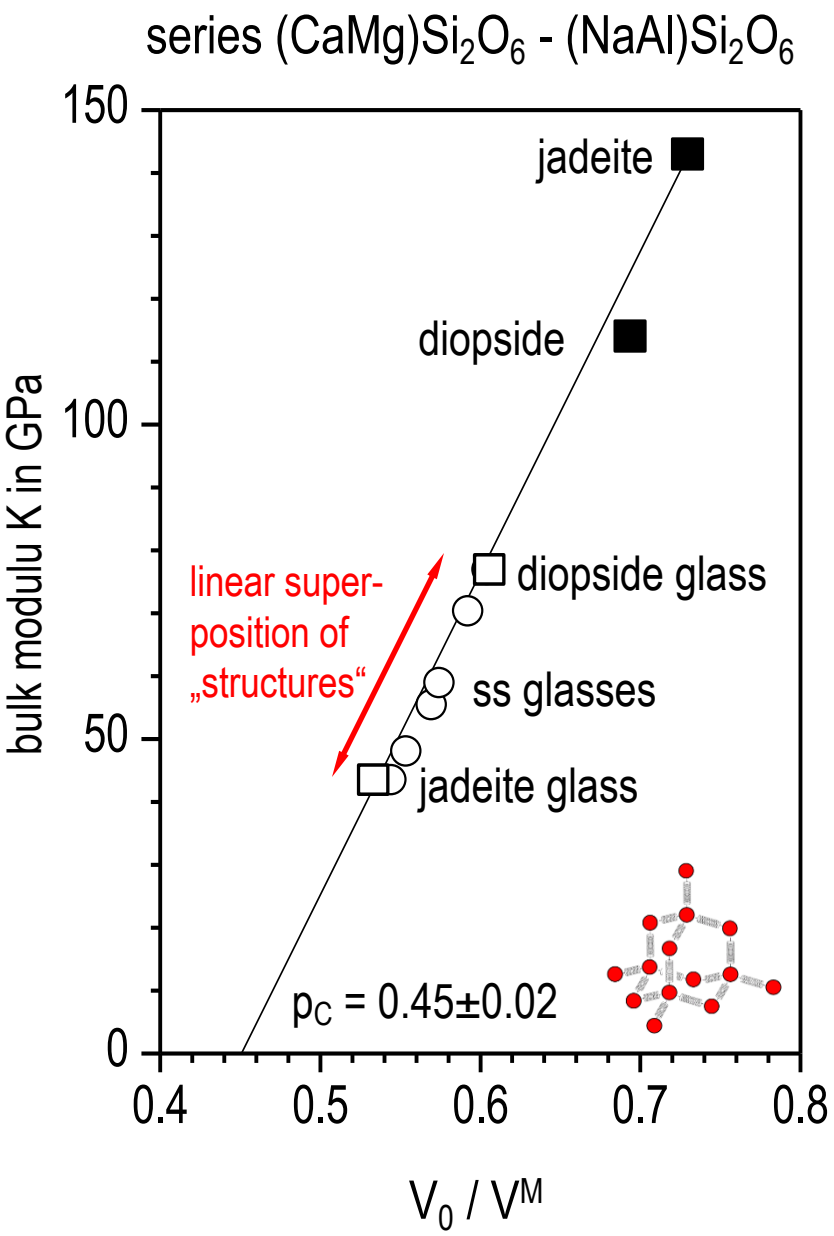


Philipps, Stoffel, Dronskowski, Conradt, Fontiers Mat. 2017

data: Jindal et al., Ceram. Int. 2011

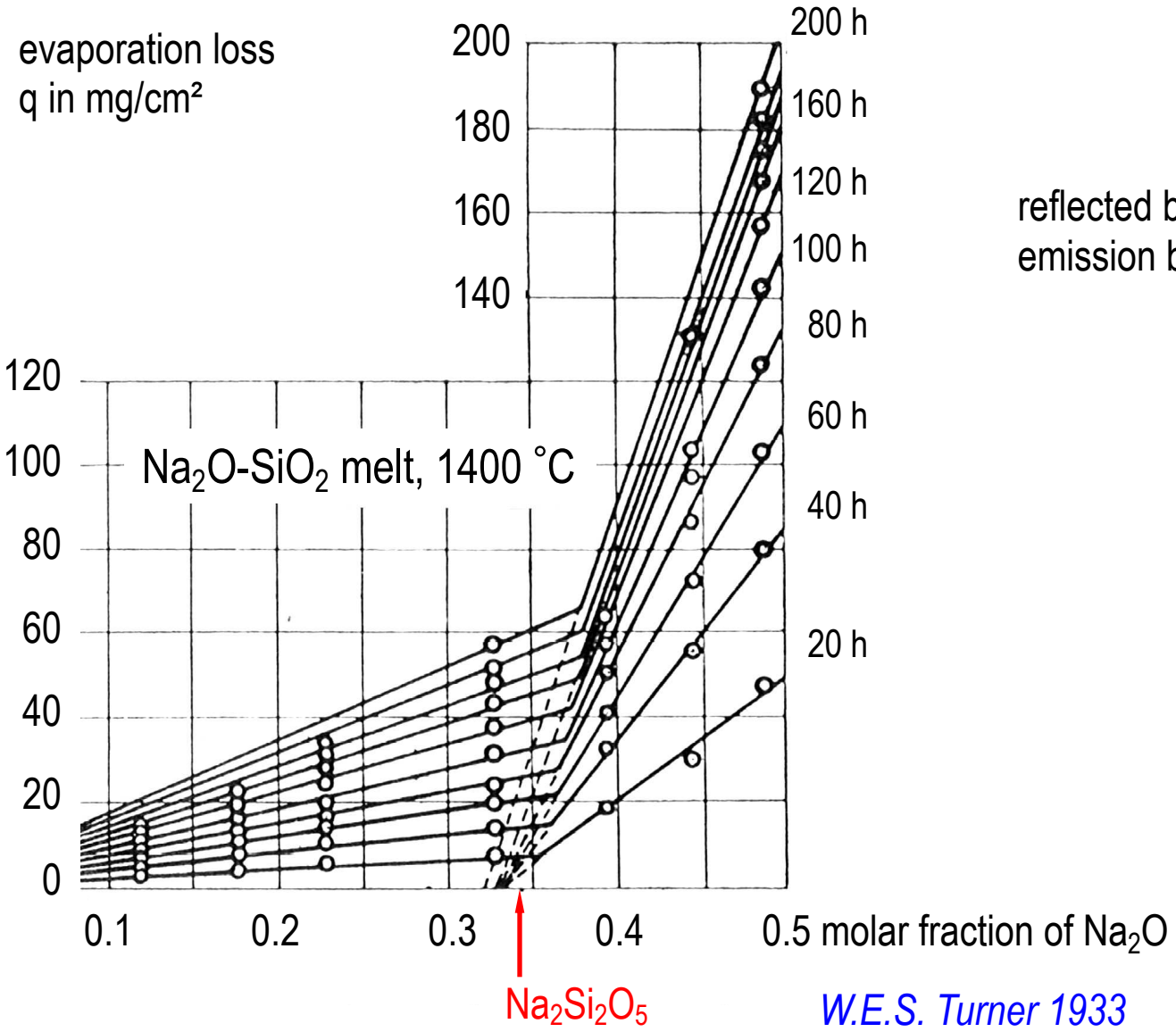


data: Mohajerani et al., JNCS 2013



data: Jindal et al., Ceram. Int. 2011

speciation of Na_2O-SiO_2 melt at 1400 °C

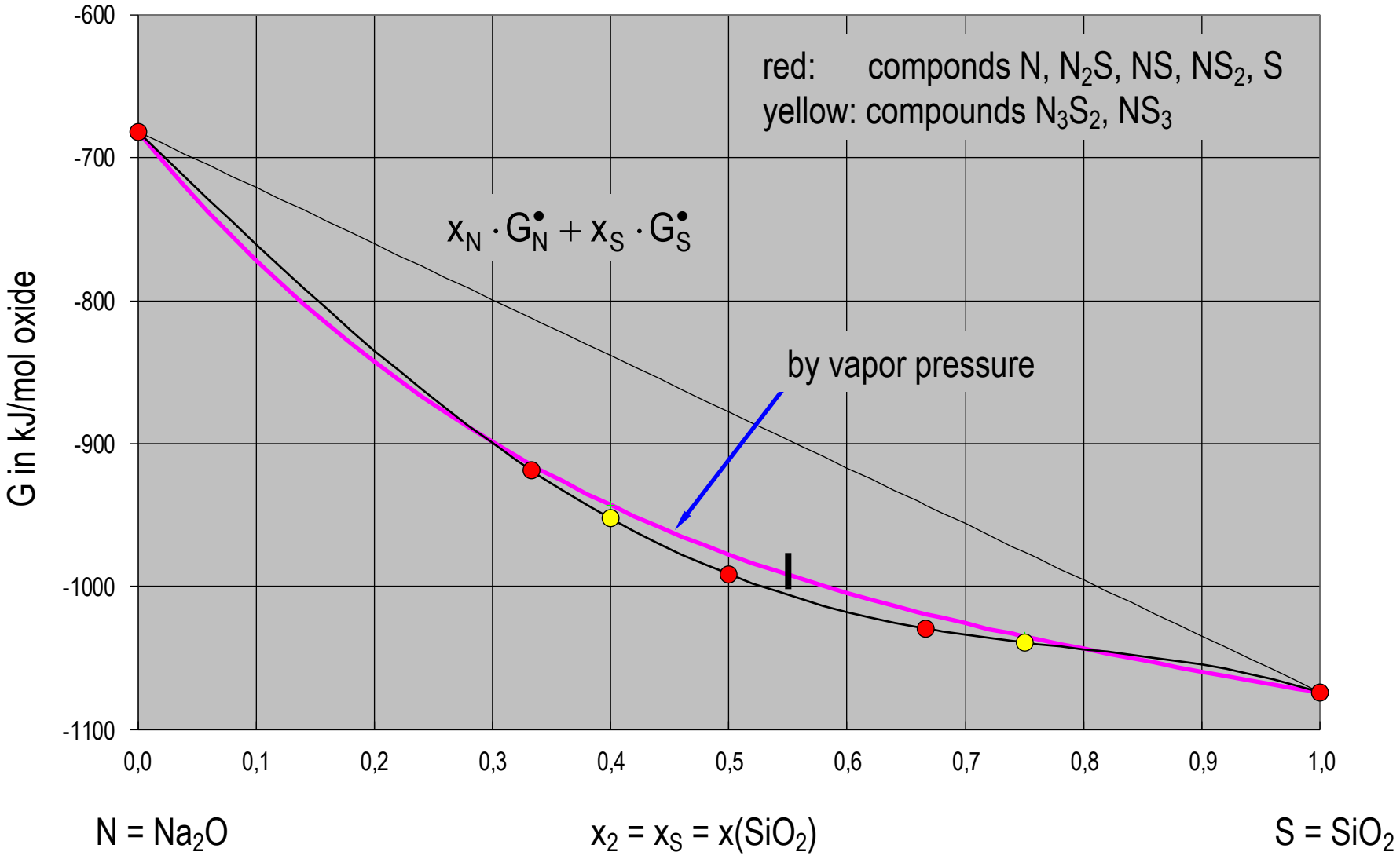


reflected by:
emission behavior

W.E.S. Turner 1933

G data of sodium silicates N_2S, N_3S_2, NS, NS_2, N_3S_8 in their liquid state allow one to model the entire G(x) curve.

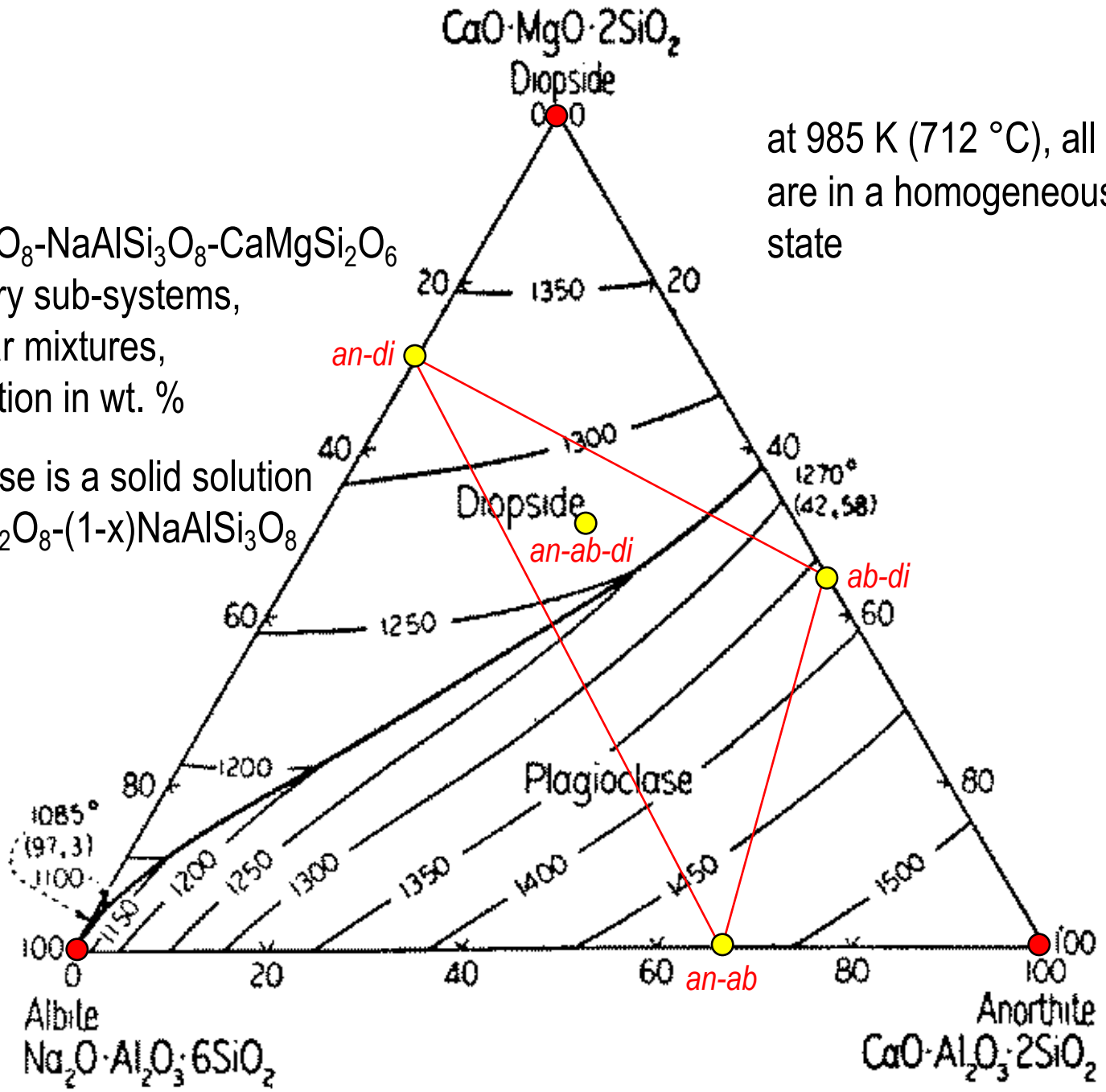
Paradigm: mixing energy ⇔ compound formation energy.



system:
an-ab-di,
$CaAl_2Si_2O_8$-$NaAlSi_3O_8$-$CaMgSi_2O_6$
and binary sub-systems,
equimolar mixtures,
presentation in wt. %

plagioclase is a solid solution
$xCaAl_2Si_2O_8$-$(1-x)NaAlSi_3O_8$

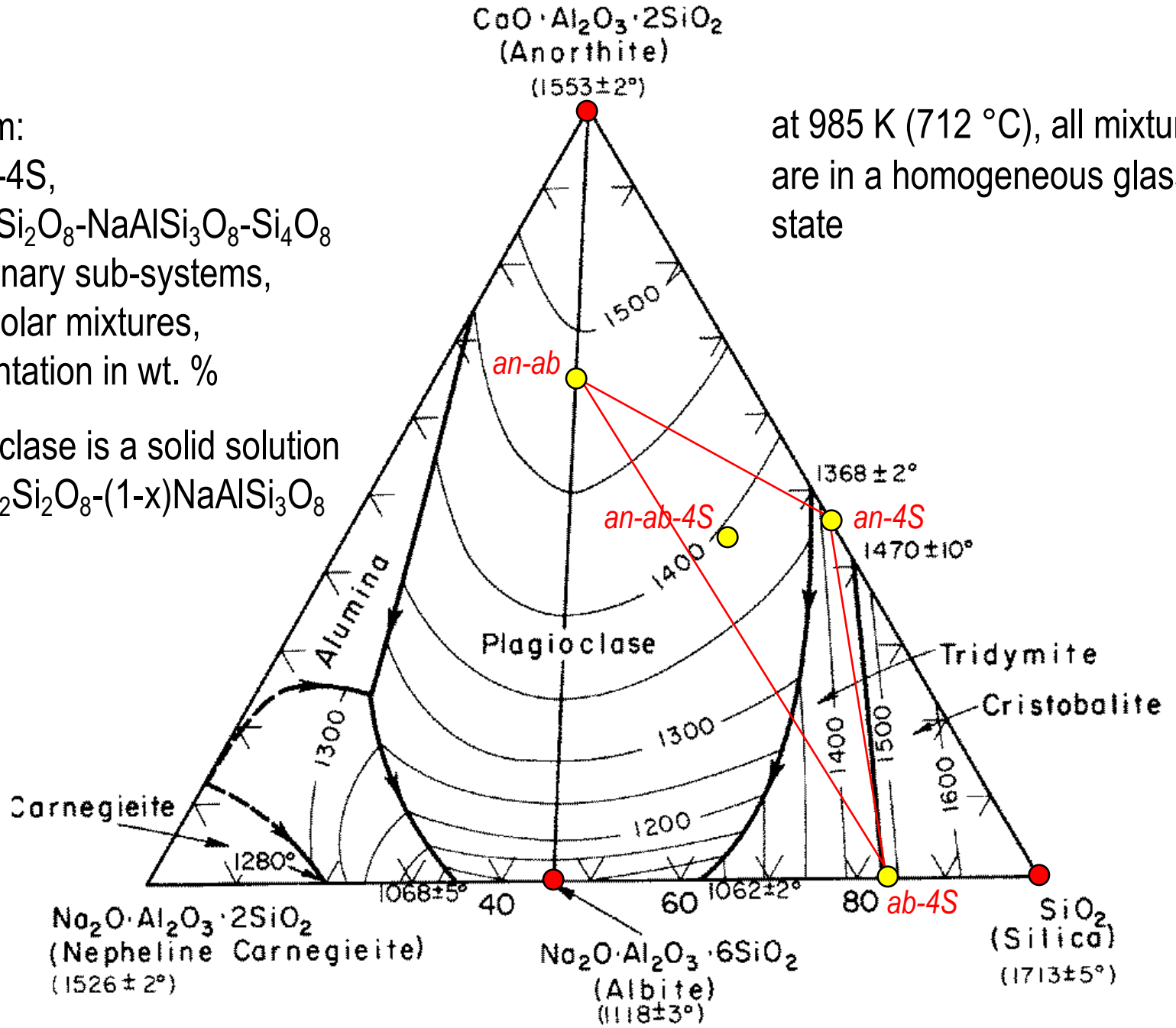
at 985 K (712 °C), all mixtures are in a homogeneous glassy state



system:
an-ab-4S,
$CaAl_2Si_2O_8$-$NaAlSi_3O_8$-Si_4O_8
and binary sub-systems,
equimolar mixtures,
presentation in wt. %

plagioclase is a solid solution
$xCaAl_2Si_2O_8$-$(1-x)NaAlSi_3O_8$

at 985 K (712 °C), all mixtures are in a homogeneous glassy state



equimolar binary and ternary glasses; components k = an, di, ab, 4S; $\Sigma n_k = 1$ mol;
H^{MIX} determined at 712 °C in liquid $2PbO \cdot B_2O_3$
by Navrotsky et al. Geochim. Cosmochim. Acta 44 (1980)

glass	$\Sigma n_k \cdot H_k$ [kJ/mol] glass	$\Sigma n_{ox} \cdot H_{ox}$ [kJ/mol] data	H^{MIX}_{ox} [kJ/mol] $H_{gl} - H_{ox}$	H^{MIX} [kJ/mol] exp	$S^{MIX,id}_k$ [J/mol·K] calc
an-di	-3441.8	-3414.0	-27.8	-6.8	-5.7
an-ab	-3792.3	-3750.5	-41.8	-8.6	-5.7
ab-di	-3304.9	-3235.5	-69.4	+5.9	-5.7
4S-an	-3680.3	-3694.0	+13.7	-2.2	-5.7
4S-ab	-3543.3	-3515.5	-27.9	±0.0	-5.7
an-ab-di	-3513.0	-3466.6	-46.3	-5.2	-9.0
4S-an-ab	-3672.0	-3653.3	-18.7	-6.2	-9.0

heat of mixing negligible against heat of formation;

$S^{MIX,id}_k = RT \cdot \Sigma \ln(x_k)$

equimolar binary and ternary glasses; components k = an, di, ab, 4S; $\Sigma n_k = 1$ mol;
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4S-an-ab	-3672.0	-3653.3	-18.7	-6.2	-9.0

heat of mixing negligible against heat of formation;

$S^{MIX,id}_k = RT \cdot \Sigma \ln(x_k)$

component k	formula	$d \approx V^{1/3}$(unit cell) [Å]
an	$CaAl_2Si_2O_8$	8.7
di	$CaMgSi_2O_6$	7.6
ab	$NaAlSi_3O_8$	8.7
4S	Si_4O_8	8.8

entropy of mixing negligible against entropy of formation;

2 unit cells in each direction $\Rightarrow$
$S^{MIX} < 0.034 \cdot S^{MIX,id}_k$

$V^m(atoms) = (M/\rho) / N_A$

V^m(atoms in formula) = 1.7E-28 m^3
V^m(8 unit cells) = 4.9E-27 m^3

macroscopic properties of multi-component glasses are obtained

via linear superposition of the properties of their constitutional components as given by the phase diagram

the set of k corresponds to an energetic minimum

Gibbs energy:

$$G = \sum_k n_k \cdot G_k^{\bullet} + \underbrace{H^{MIX}}_{\approx 0} - T \cdot \underbrace{S^{MIX}}_{\approx 0} \approx \sum_k n_k \cdot G_k^{\bullet}$$

any macroscopic property P based on phonon DVS:

$$P = \sum_k n_k \cdot P_k^{\bullet}$$

macroscopic properties of multi-component glasses are obtained

via linear superposition of the properties of their constitutional components as given by the phase diagram

the set of k corresponds to an energetic minimum

Gibbs energy:

$$G = \sum_k n_k \cdot G_k^{\bullet} + H^{MIX} - T \cdot S^{MIX} \approx \sum_k n_k \cdot G_k^{\bullet}$$

($H^{MIX} \approx 0$, $S^{MIX} \approx 0$)

any macroscopic property P based on phonon DVS:

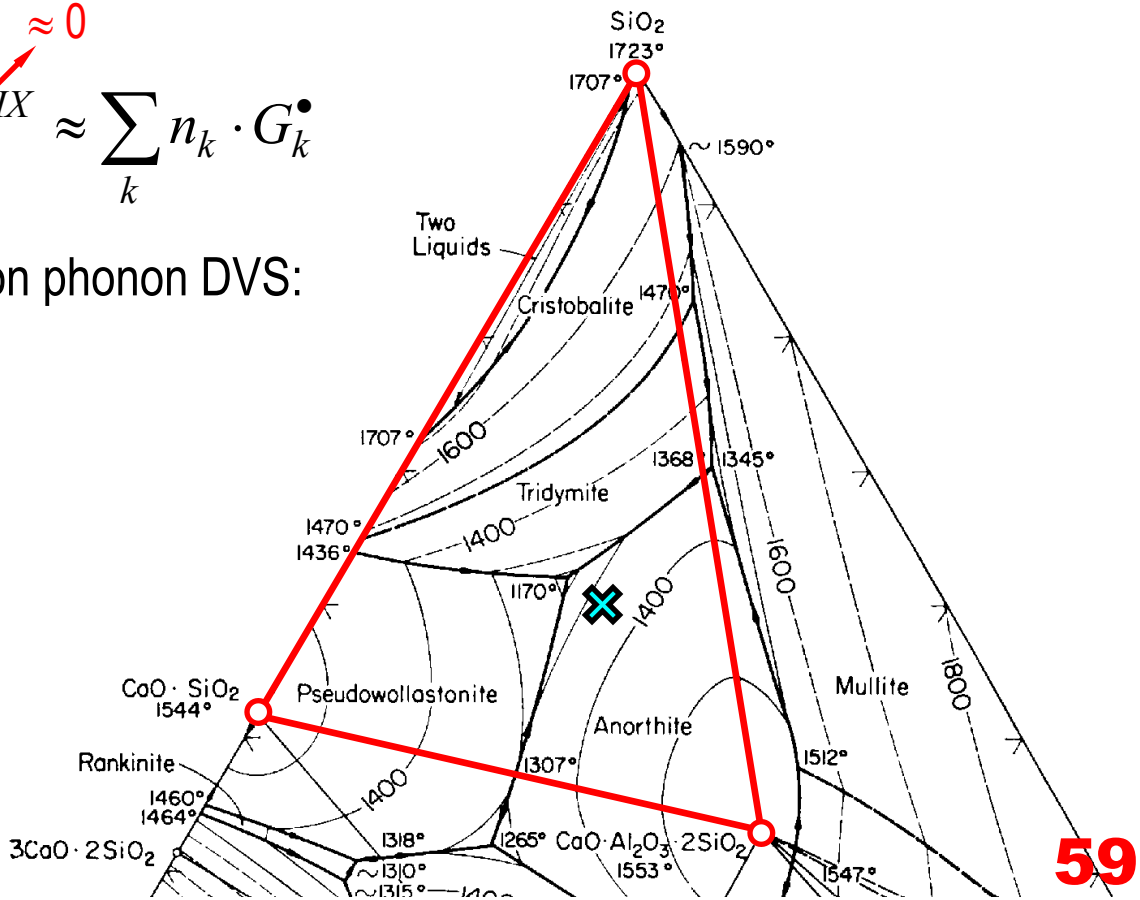
$$P = \sum_k n_k \cdot P_k^{\bullet}$$

Example

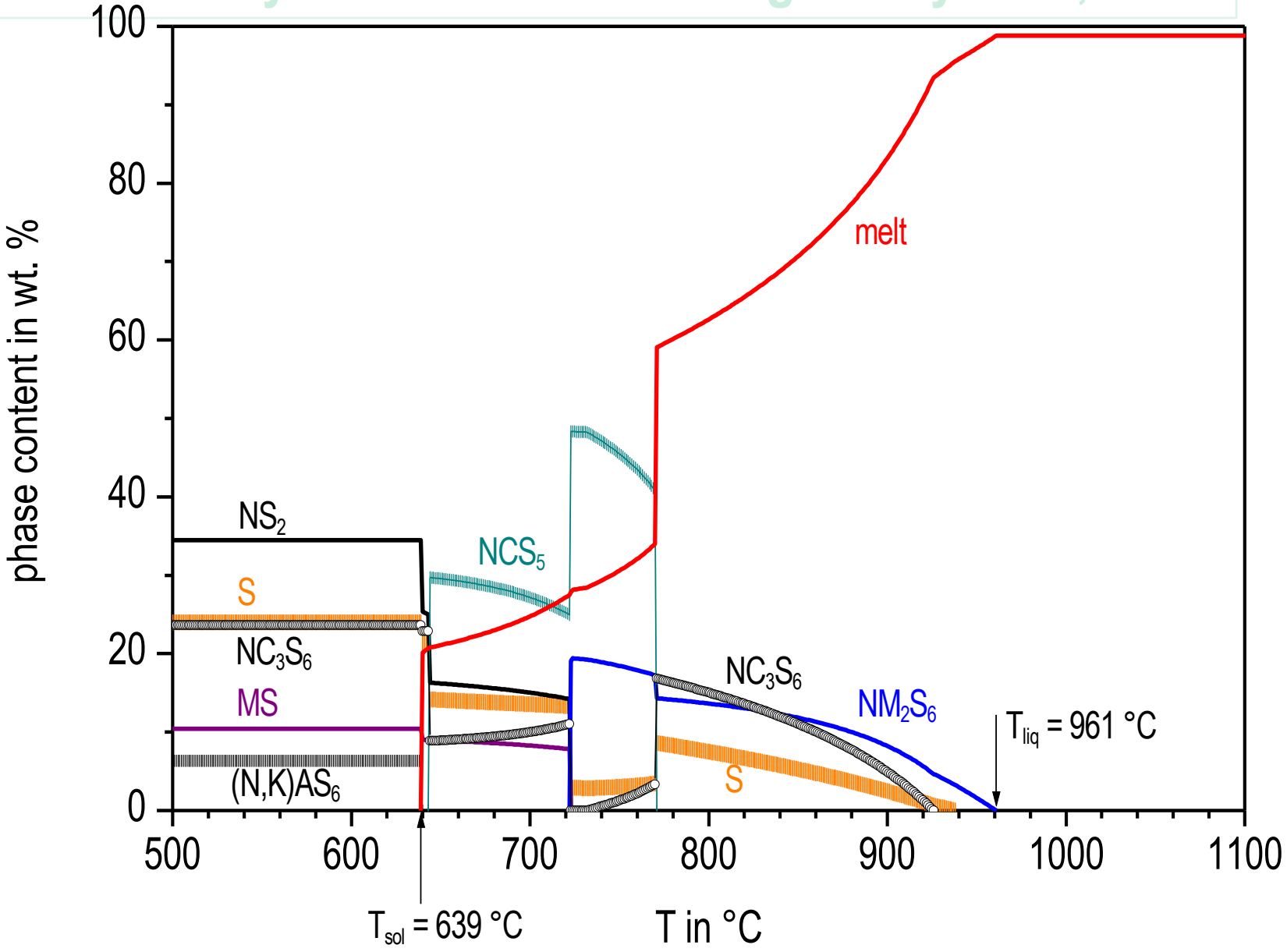
Oxides: CaO, Al_2O_3, SiO_2

Constitututional conponents for composition ✖ :

SiO_2, $CaO \cdot SiO_2$, $CaO \cdot Al_2O_3 \cdot SiO_2$



glass DGG-1



$$H^{\circ}_{glass} = \sum_k n_k \cdot (H^{\circ}_k + H^{vit}_k)$$

$$H^{\circ}_{1673,liq} = \sum_k n_k \cdot H^{\circ}_{1673,liq,k}$$

$$S^{\circ}_{glass} = \sum_k n_k \cdot (S^{\circ}_k + S^{vit}_k)$$

$$S^{\circ}_{1673,liq} = \sum_k n_k \cdot S^{\circ}_{1673,liq,k}$$

$$c_{P,liq} = \sum_k n_k \cdot c_{P,liq,k}$$

$$H_{T,liq} = H^{\circ}_{1673,liq} + c_{P,liq} \cdot (T - 1673)$$

$$S_{T,liq} = S^{\circ}_{1673,liq} + c_{P,liq} \cdot \ln(T / 1673)$$

$$\Delta H_{T,liq} = H_{T,liq} - H^{\circ}_{glass}$$

$$MOD = \sum_k y_k \cdot MOD_k$$

density,
thermal expansion coefficient,
chemical potentials of oxides, ...

Components vs. Species

Paradigm "component" versus "species":

A component is a **stoichiometric unit** allowing to express the chemical **composition** of a system in an **irreducible** way.

Example: The composition (by mol)
16.667 Na_2O 8.333 Al_2O_3 75 SiO_2
may also be expressed
as
33.333 $Na_2O{\cdot}2SiO_2$ 33.333 $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ 33.333 SiO_2
or
25 $Na_2Si_2O_5$ 50 $NaAlSi_3O_8$ 25 SiO_2
or
in 1000 other ways.

The total number of components is restricted; it has to follow Gibbs' phase rule.

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or
25 $Na_2Si_2O_5$ 50 $NaAlSi_3O_8$ 25 SiO_2
or
in 1000 other ways.

The total number of components is restricted; it has to follow Gibbs' phase rule.

A species is a structural entity.

In condensed phases, it is a SRO entity.

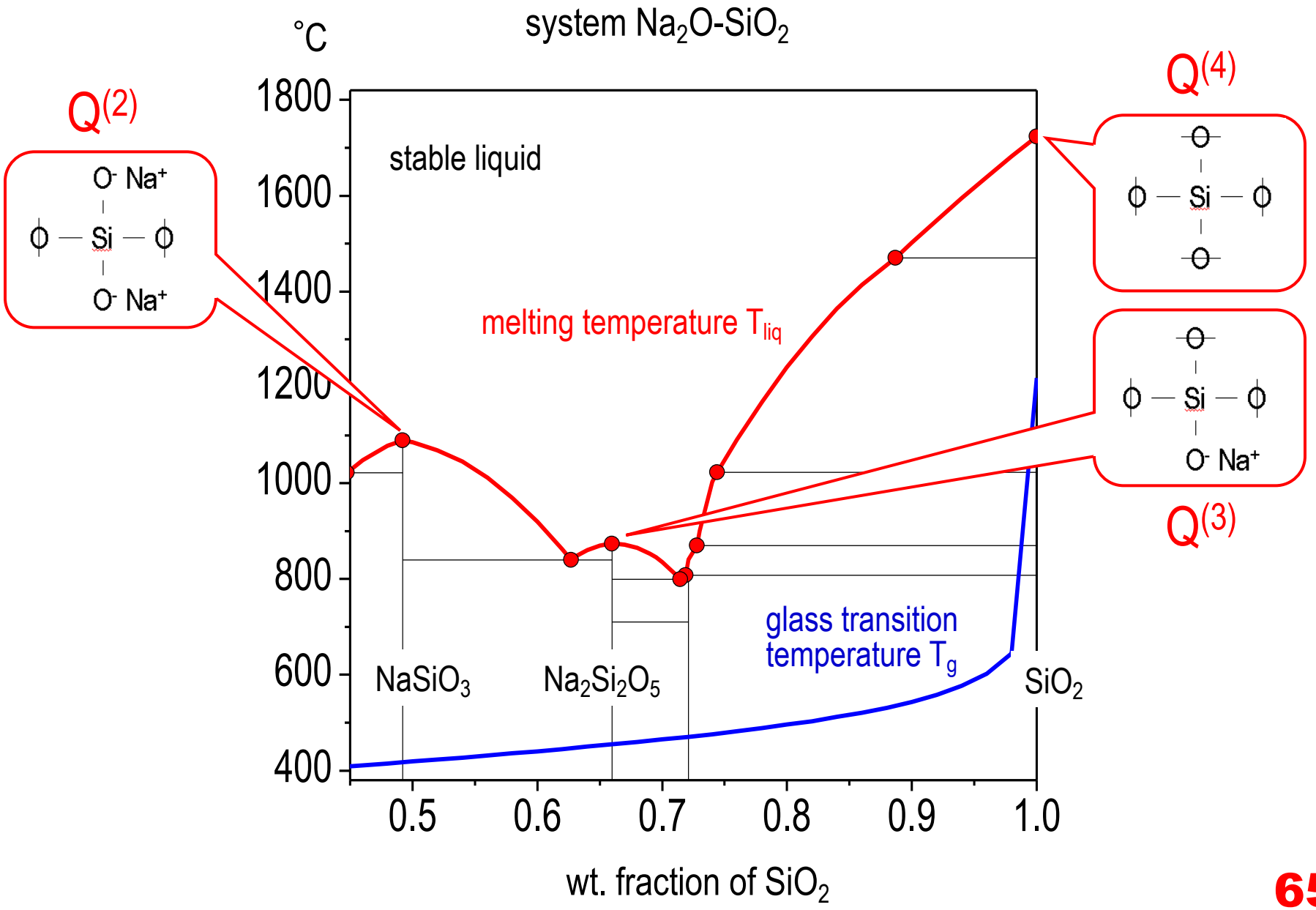
Example: SO_3 dissolved in water is present as H_2SO_4, HSO_4^-, SO_4^{2-}.

In gases, a species is a real molecule.

Example: Evaporated $PbCl_2$ is present as Pb(g), PbCl(g), Pb_2Cl_2(g), Cl_2(g).

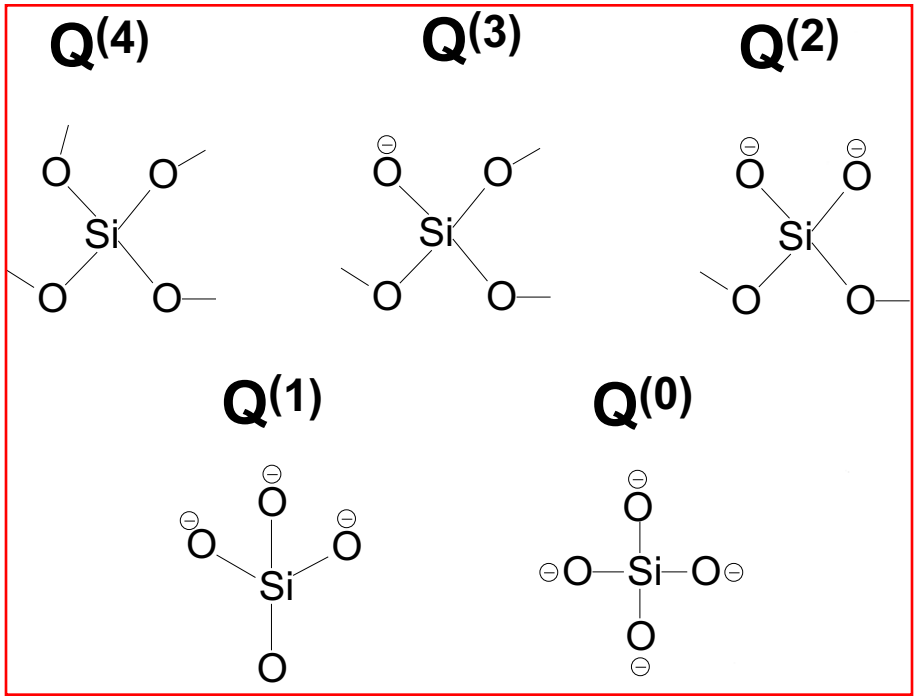
The total number of species may be very large.

Paradigm "component" versus "species": The phase diagram presents components

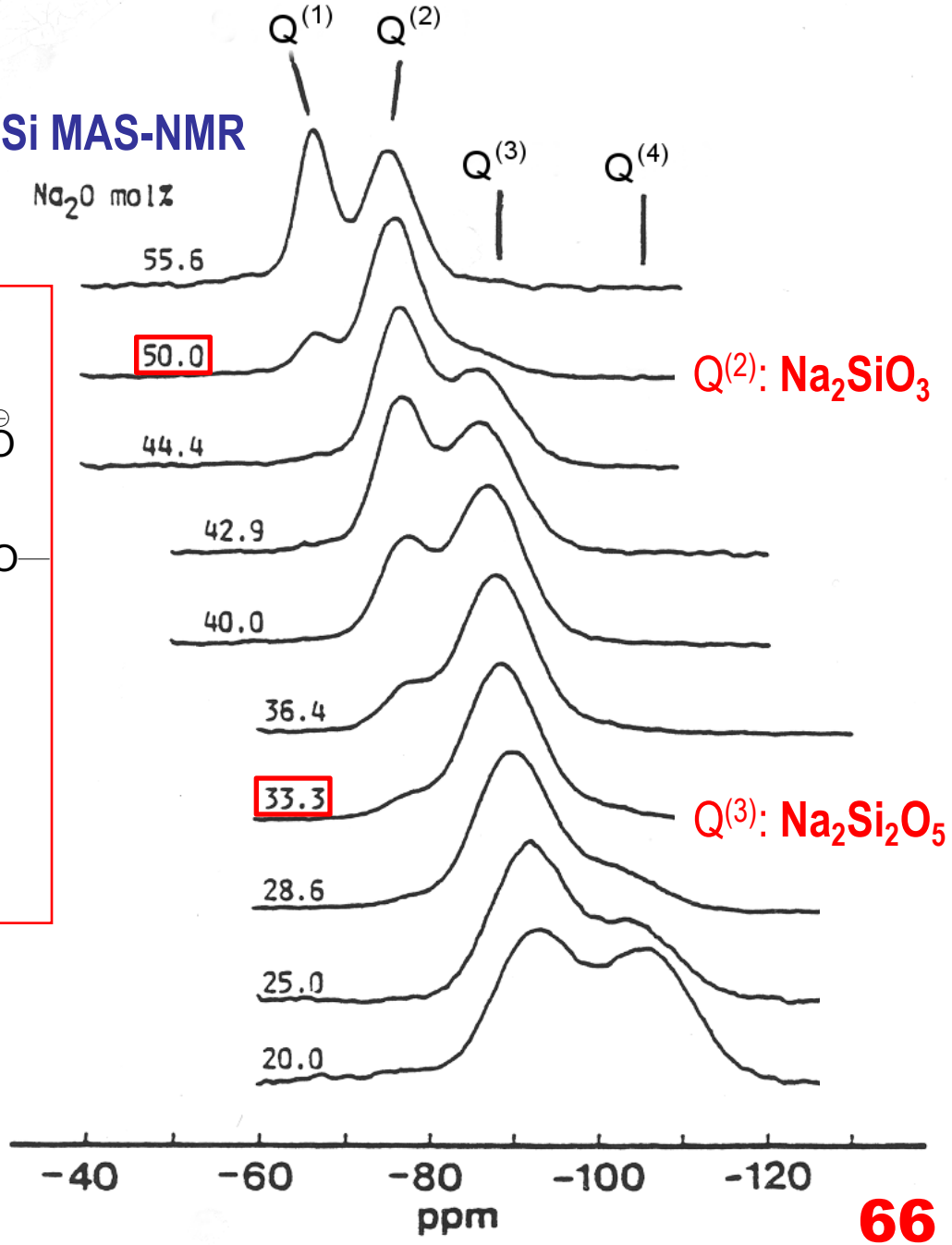


Paradigm "component" versus "species":

Spectroscopic methods identify **species**

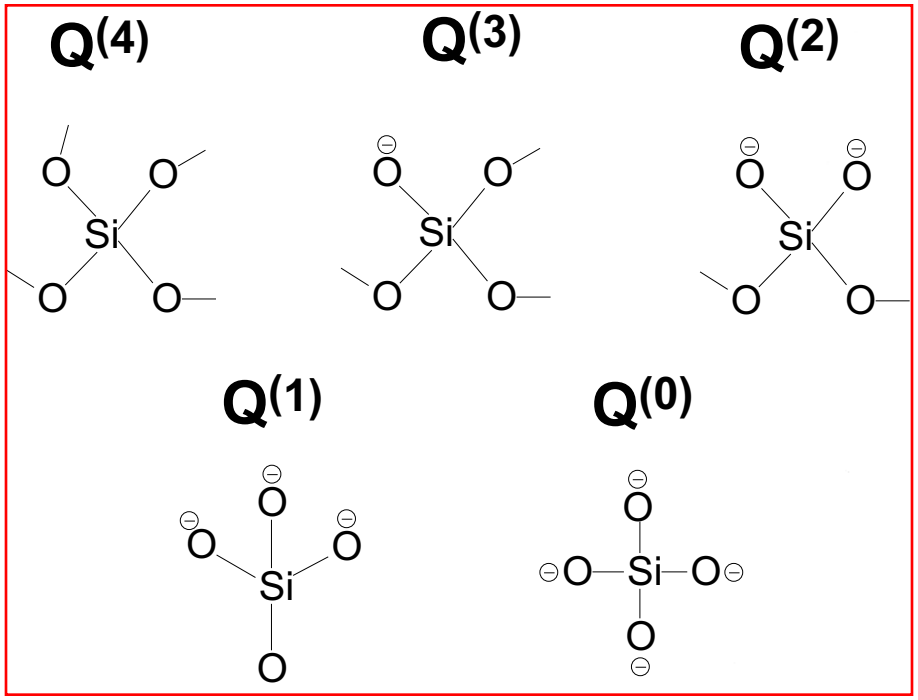


local structure of silicate glass,
borrowed from Prof. Jinjun Ren's lecture



Paradigm "component" versus "species":

Obviously, **species** have some relation to the phase diagram



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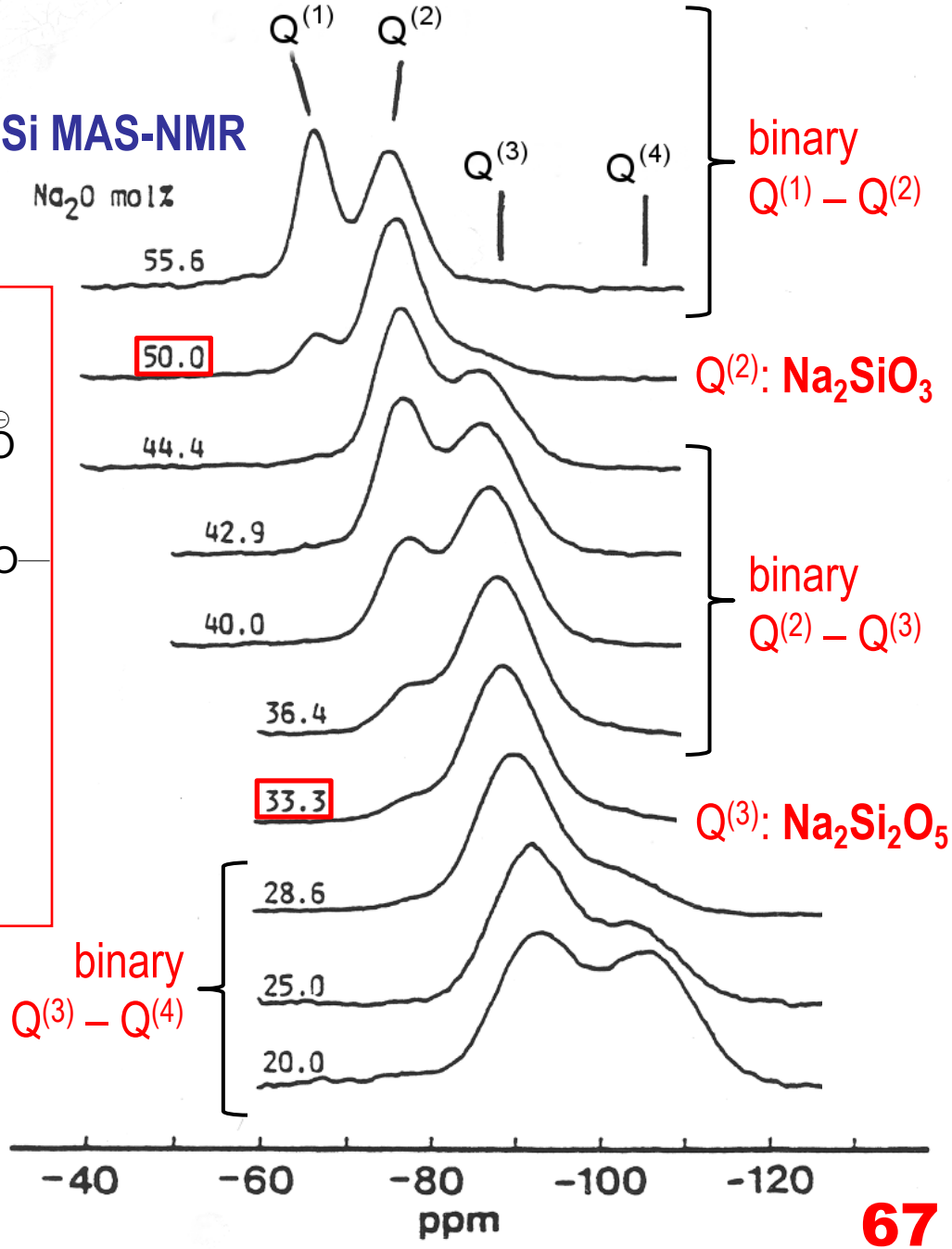
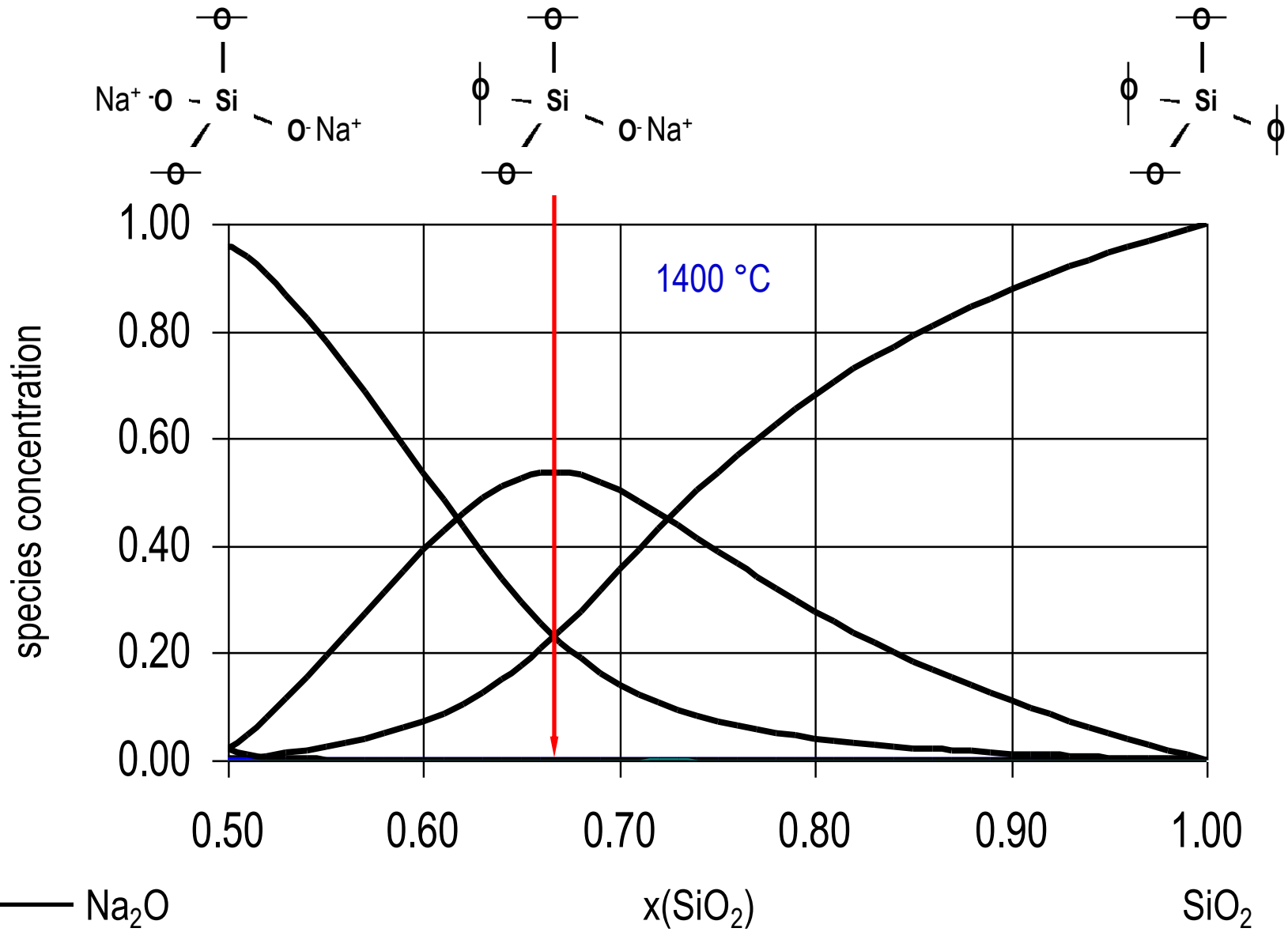


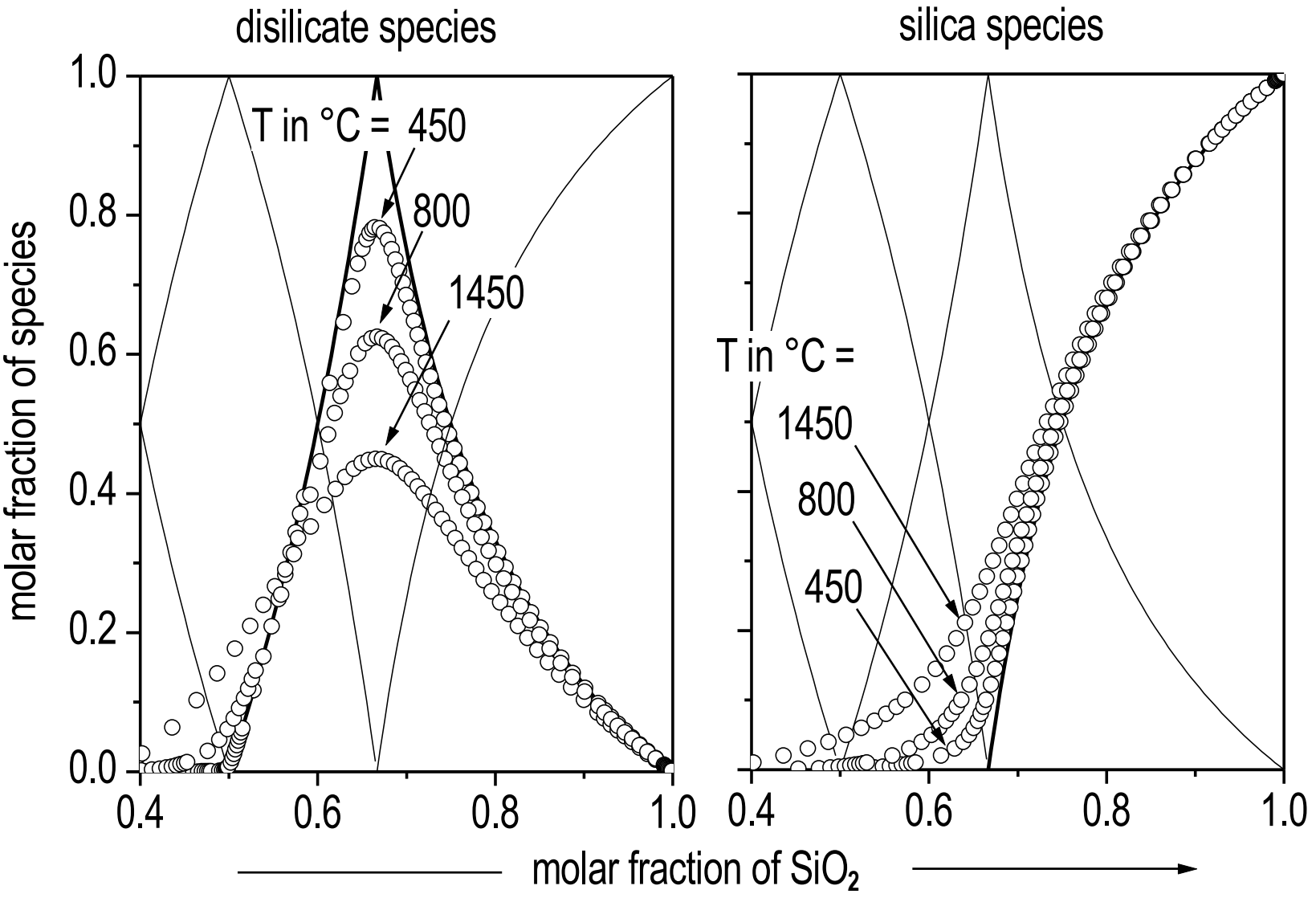
Paradigm "component" versus "species":

the one-component liquid system NS_2(liq) contains species 23 SiO_2, 23 Na_2SiO_3, 54 $Na_2Si_2O_5$ (by mol)

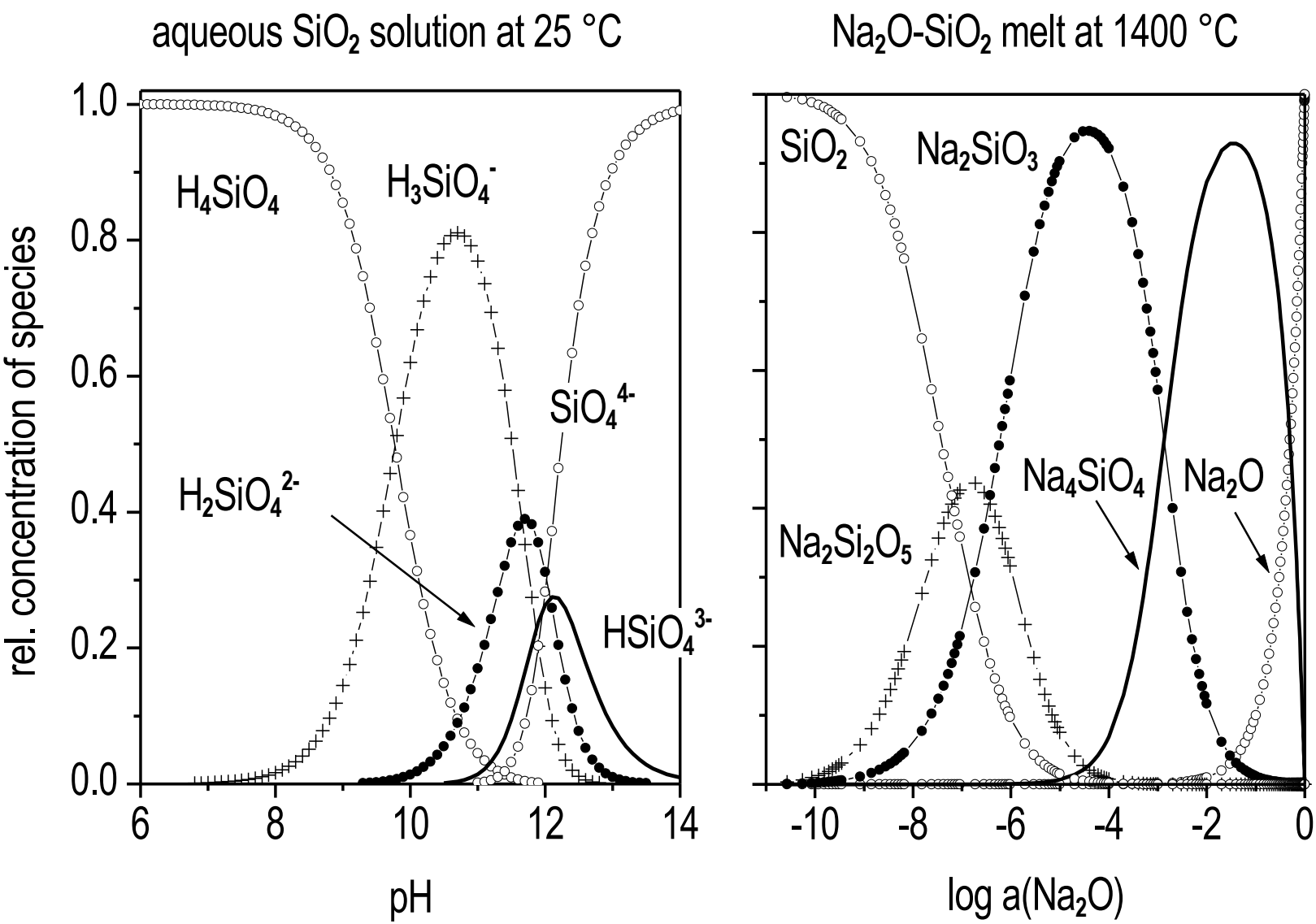


Paradigm "component" versus "species":

species distribution is temperature dependent



Paradigm "component" versus "species": Analogy to aqueous solutions

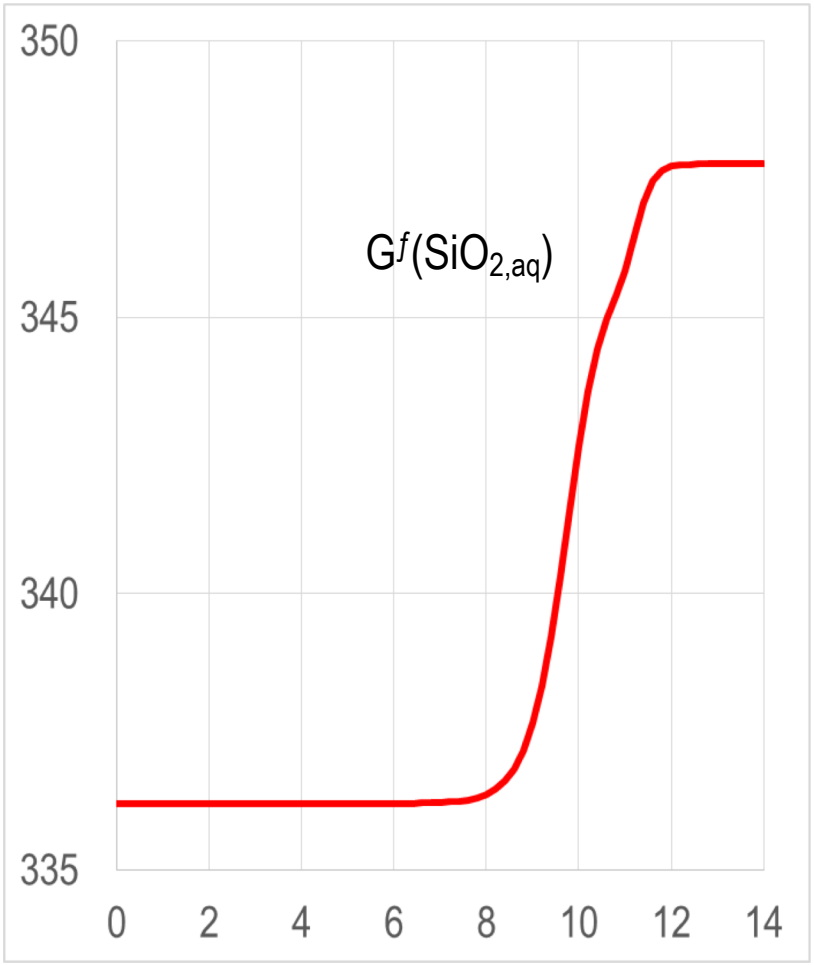


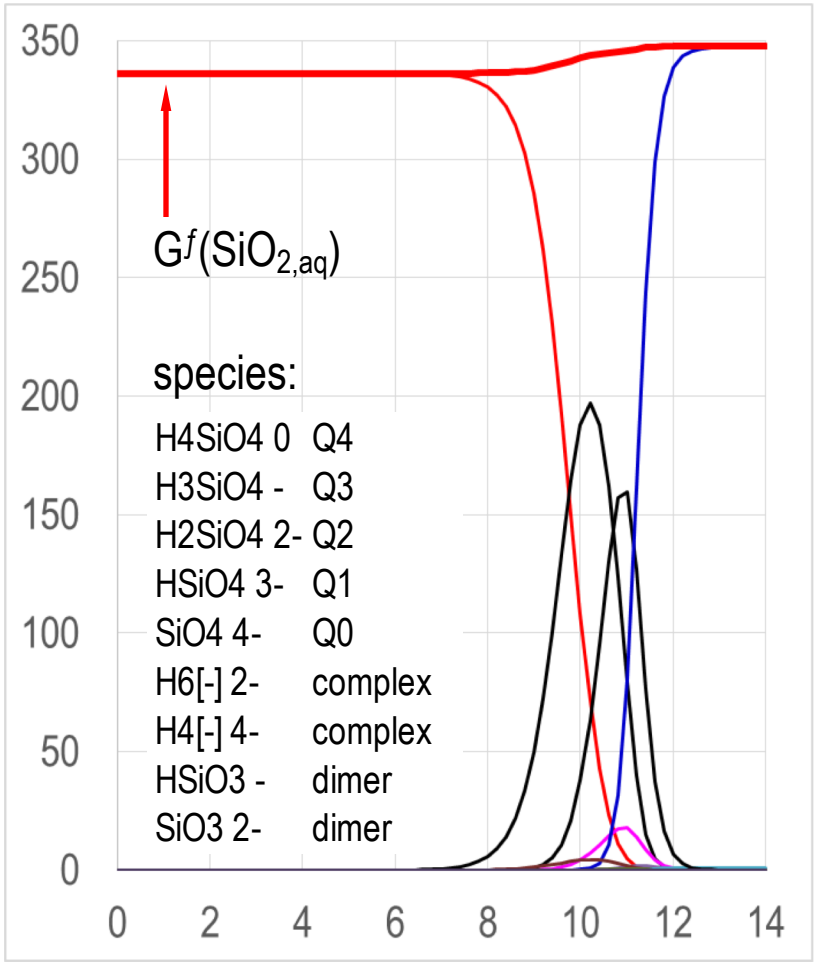
Conradt, JNCS 345 & 346 (2004)

Paradigm "component" versus "species": Analogy to aqueous solutions

This is the Gibbs energy of the component $SiO_{2,aq}$ as a function of pH

Thin lines are the weighted contributions $x_i \cdot G^f_i$ of species i; their sum is equal to $G^f(SiO_{2,aq})$





$-G^f$ in kJ per 100 g SiO_2

pH

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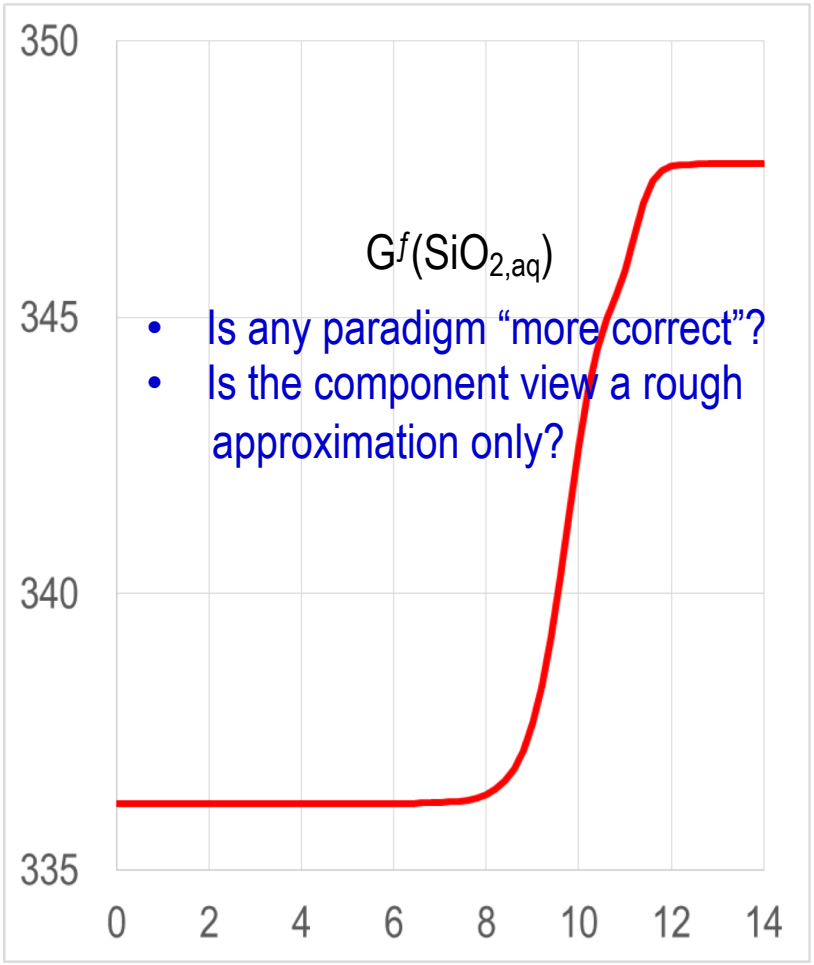

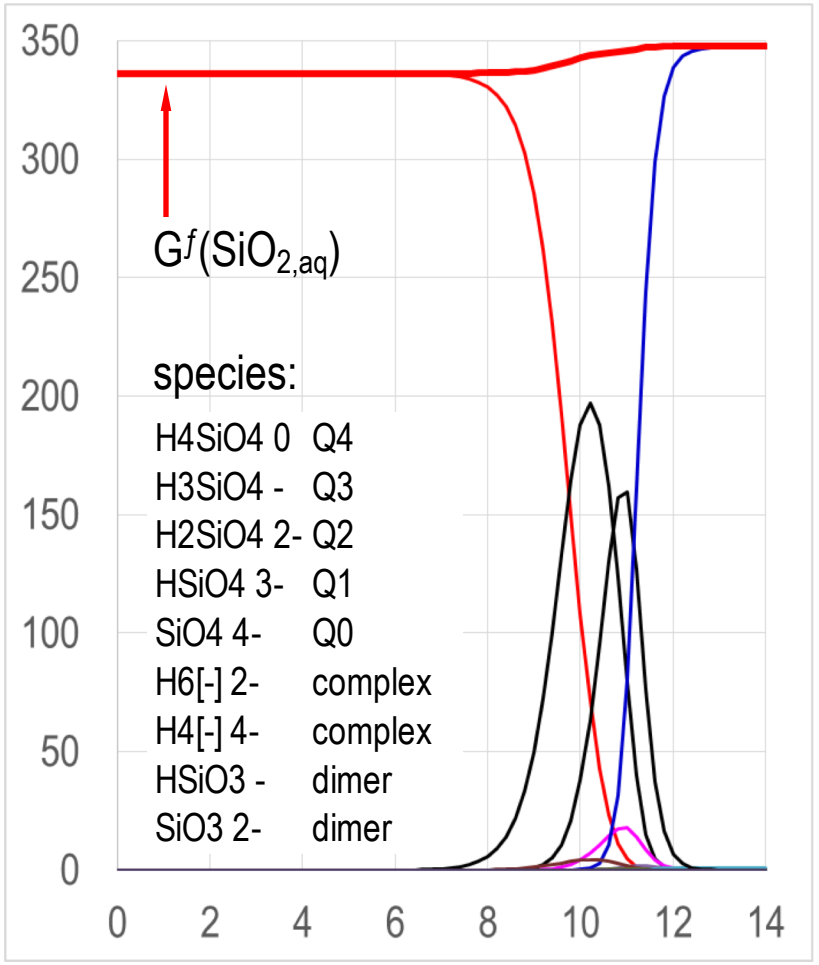

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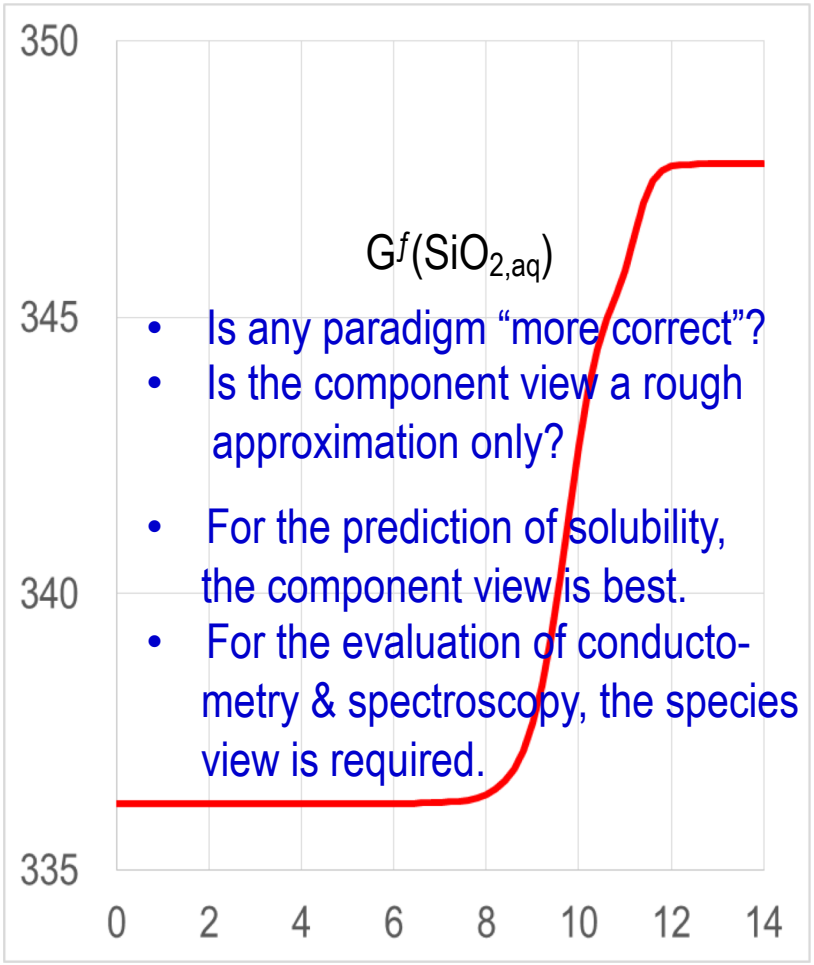

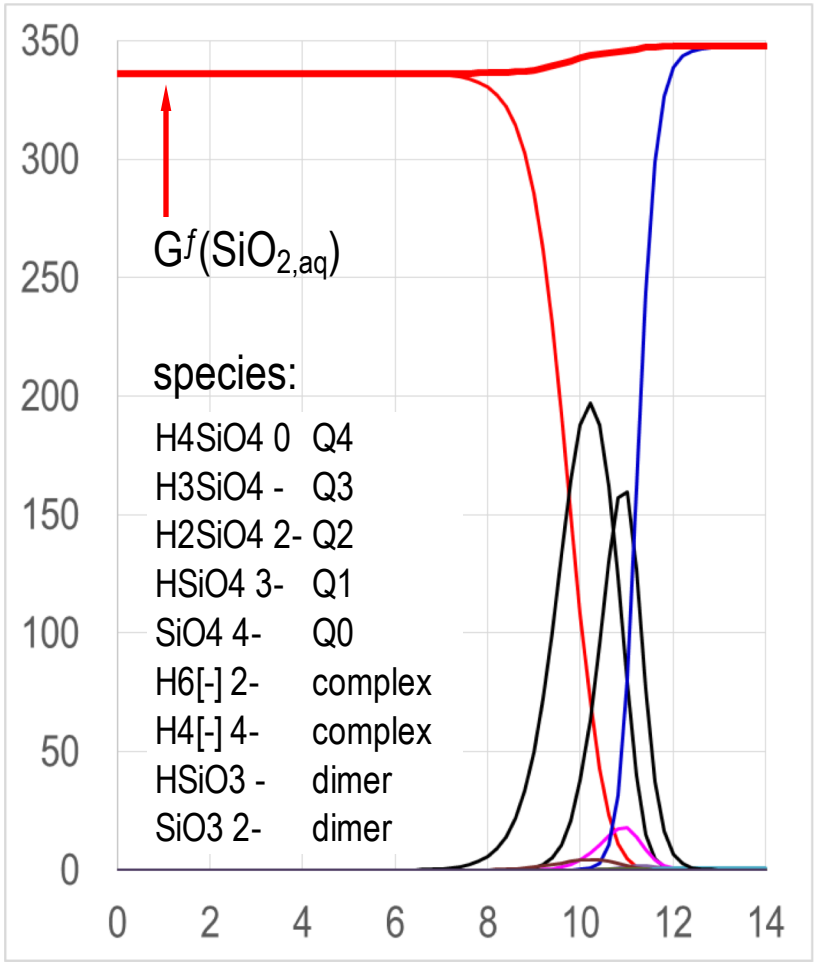

pH

The Technological Harvest

$$H^{\circ}_{glass} = \sum_k n_k \cdot (H^{\circ}_k + H^{vit}_k)$$

$$H^{\circ}_{1673,liq} = \sum_k n_k \cdot H^{\circ}_{1673,liq,k}$$

$$S^{\circ}_{glass} = \sum_k n_k \cdot (S^{\circ}_k + S^{vit}_k)$$

$$S^{\circ}_{1673,liq} = \sum_k n_k \cdot S^{\circ}_{1673,liq,k}$$

$$c_{P,liq} = \sum_k n_k \cdot c_{P,liq,k}$$

$$H_{T,liq} = H^{\circ}_{1673,liq} + c_{P,liq} \cdot (T - 1673)$$

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$$MOD = \sum_k y_k \cdot MOD_k$$

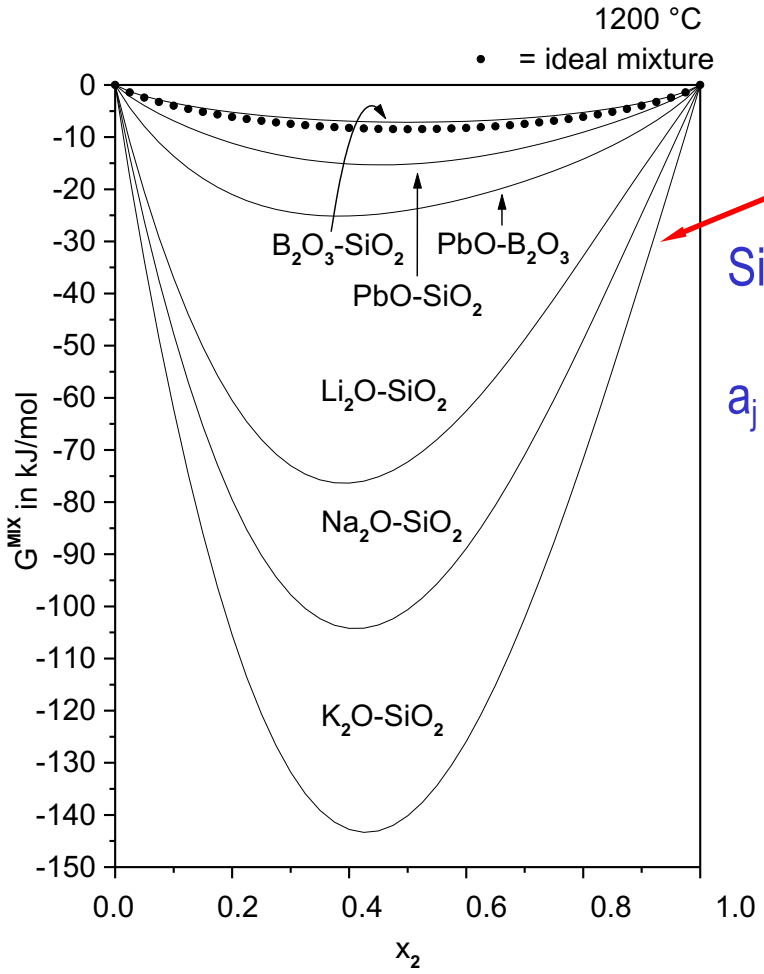
density,
thermal expansion coefficient,
chemical potentials of oxides, ...

This concept calls for a technological harvest.

Total Gibbs energy G of a mixture of oxides j :

$$G = \sum_j n_j \cdot G_j^{\bullet} + \sum_j n_j \cdot G_j^{MIX} = \sum_j n_j \cdot G_j^{\bullet} + RT \cdot \sum_j n_j \cdot \ln a_j = \vec{n}_j^{\,T} \cdot \left(\vec{G}_j^{\bullet} + \vec{G}_j^{MIX} \right)$$

a_j = activity j; the vector element of the G^{MIX} vector is $G_j^{MIX} = RT \cdot \ln a_j$



Silicates are extremely non-ideal mixtures of their oxides;

$a_j \approx x_j$ is far from reality; a_j is smaller by 1E-2 to 1E-10.

Total Gibbs energy G of a mixture of oxides j :

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Total Gibbs energy G of the same mixture, is presented by constitutional components k (as read from phase diagrams) by

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Change of the basis of components from oxides j to compounds k:

$$\vec{n}_j = M \cdot \vec{n}_k \Rightarrow \vec{n}_k = M^{-1} \cdot \vec{n}_j \quad \text{or} \quad \vec{n}_k^{\,T} = \vec{n}_j^{\,T} \cdot (M^{-1})^T \qquad (M^{-1})^T = (M^T)^{-1}$$

M is the coefficient matrix:

	S	NC_3S_6	NS_2
SiO_2	1	6	2
CaO	0	3	0
Na_2O	0	1	1

Total Gibbs energy G of a mixture of oxides j :

$$G = \sum_j n_j \cdot G_j^{\bullet} + \sum_j n_j \cdot G_j^{MIX} = \sum_j n_j \cdot G_j^{\bullet} + RT \cdot \sum_j n_j \cdot \ln a_j = \vec{n}_j^{\,T} \cdot \left(\vec{G}_j^{\bullet} + \vec{G}_j^{MIX} \right)$$

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Inserting n_k yields

$$G \approx \vec{n}_k^{\,T} \cdot \vec{G}_k^{\bullet} = \left(\vec{n}_j \cdot (M^{-1})^T \right) \cdot \vec{G}_k^{\bullet} = \vec{n}_j \cdot \left((M^{-1})^T \cdot \vec{G}_k^{\bullet} \right) = \vec{n}_j \cdot \vec{Z}_j^{\bullet}$$

$$\Rightarrow \vec{Z}_j^{\bullet} = \vec{G}_j^{\bullet} + \vec{G}_j^{MIX} = \vec{G}_j^{\bullet} + + RT \ln a_j$$

ICG Thermodynamic school – Erlangen May 2012, 2019

experiments:

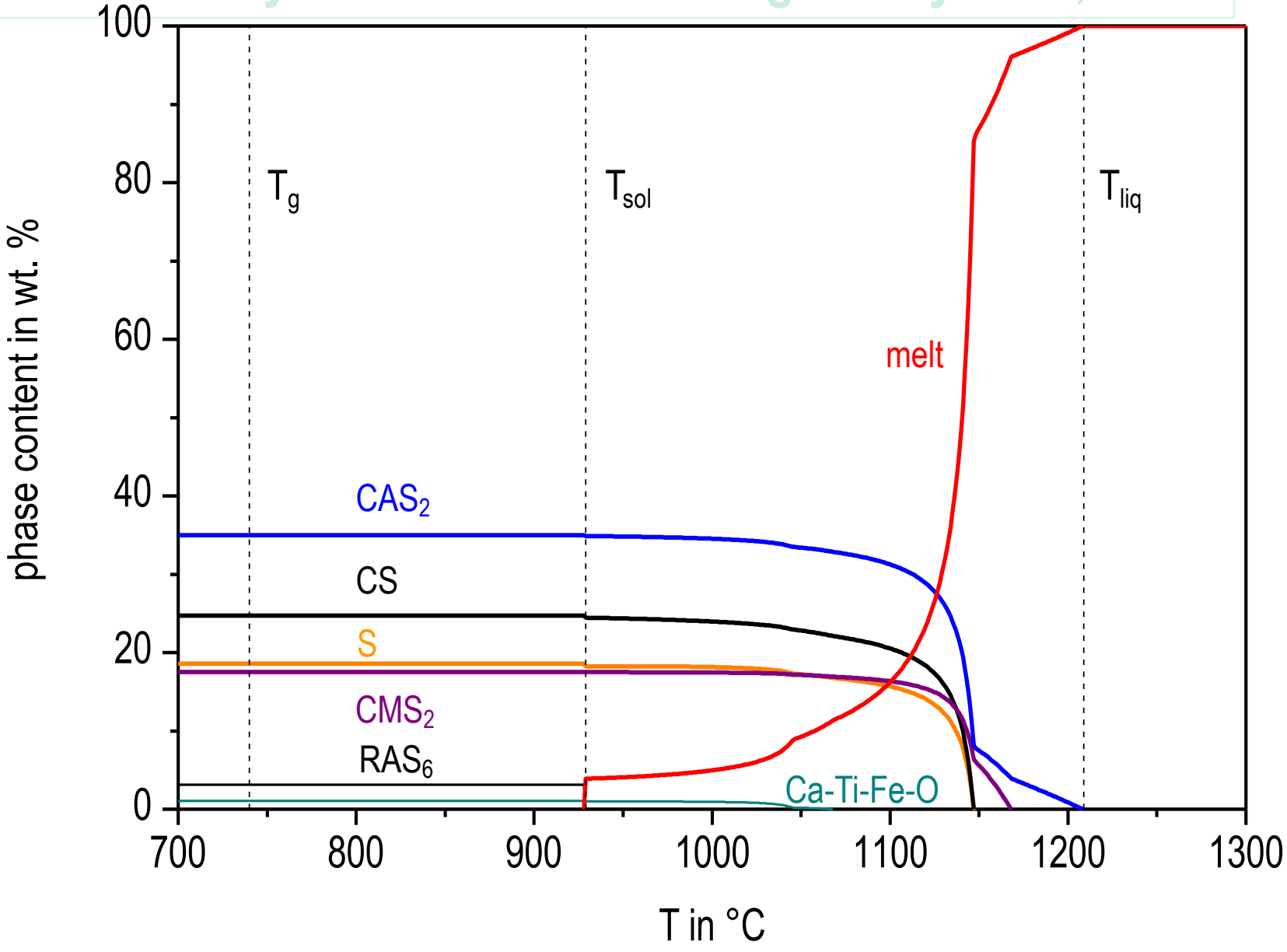
Simon Bartolomey, Ph.D. candidate
Katharina Philipps, Ph.D. candidate
Hans-Jürgen Roth, M.Sc. student
Malte Sander, M.Sc. student
Lina Heuser, M.Sc. Student

calculations:

the winter term 2015-16
M.Sc. glass course:

Lina Heuser, Marlene Weimer, Malte Sander, Jannik Beers, Martin Lauff, Fabian Kruschewski, Athanasios Papadimitrion, Lars Mühlenbeck

ECR glass®



ECR glass®

	g/100g	g/mol	mol/100g	mol el
SiO2	59.92	60.084	0.9973	2.9918
TiO2	0.34	79.898	0.0043	0.0128
Al2O3	12.88	101.961	0.1263	0.6316
Fe2O3	0.30	159.691	0.0019	0.0094
FeO	0.12	71.846	0.0017	0.0033
MgO	3.12	40.311	0.0774	0.1548
CaO	22.79	56.079	0.4064	0.8128
Na2O	0.04	61.979	0.0006	0.0019
K2O	0.49	94.203	0.0052	0.0156
SUM	100.00		1.6210	4.6340

1.1564 $3 \cdot n \cdot R$ J/(g·K)

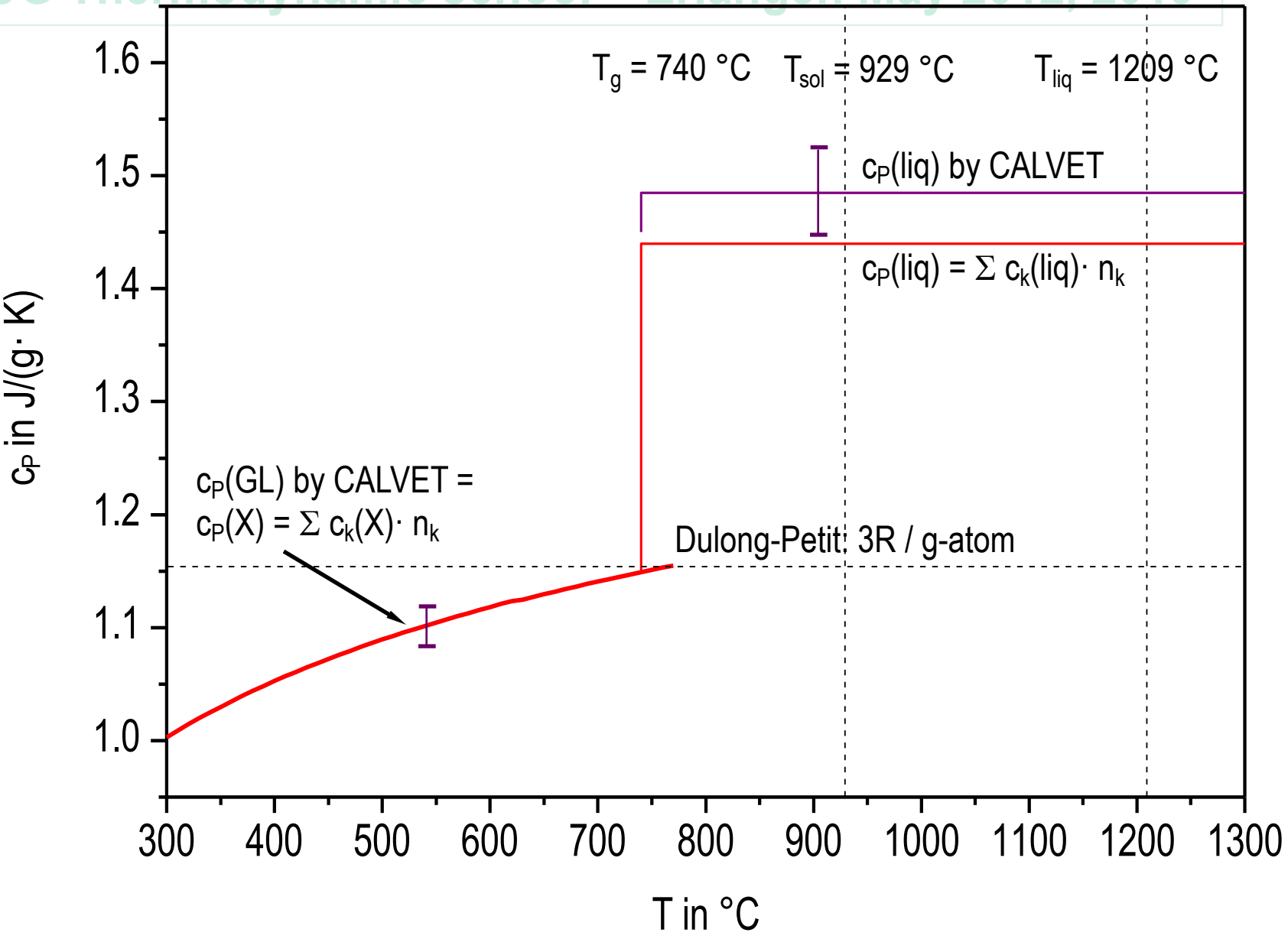
	g/100g	g/mol	mol/100g
Fe2O3	0.02	159.691	0.0001
FeO·Fe2O3	0.39	231.537	0.0017
CaO·TiO2	0.58	135.977	0.0043
K2O·Al2O3·6SiO2	2.90	556.668	0.0052
Na2O·Al2O3·6SiO2	0.34	524.444	0.0006
CaO·MgO·2SiO2	16.76	216.558	0.0774
CaO·Al2O3·2SiO2	33.52	278.208	0.1205
CaO·SiO2	23.73	116.163	0.2043
SiO2	21.76	60.084	0.3622
SUM	99.99		

$3 \cdot n \cdot R = 1.156$ J/(g· K)

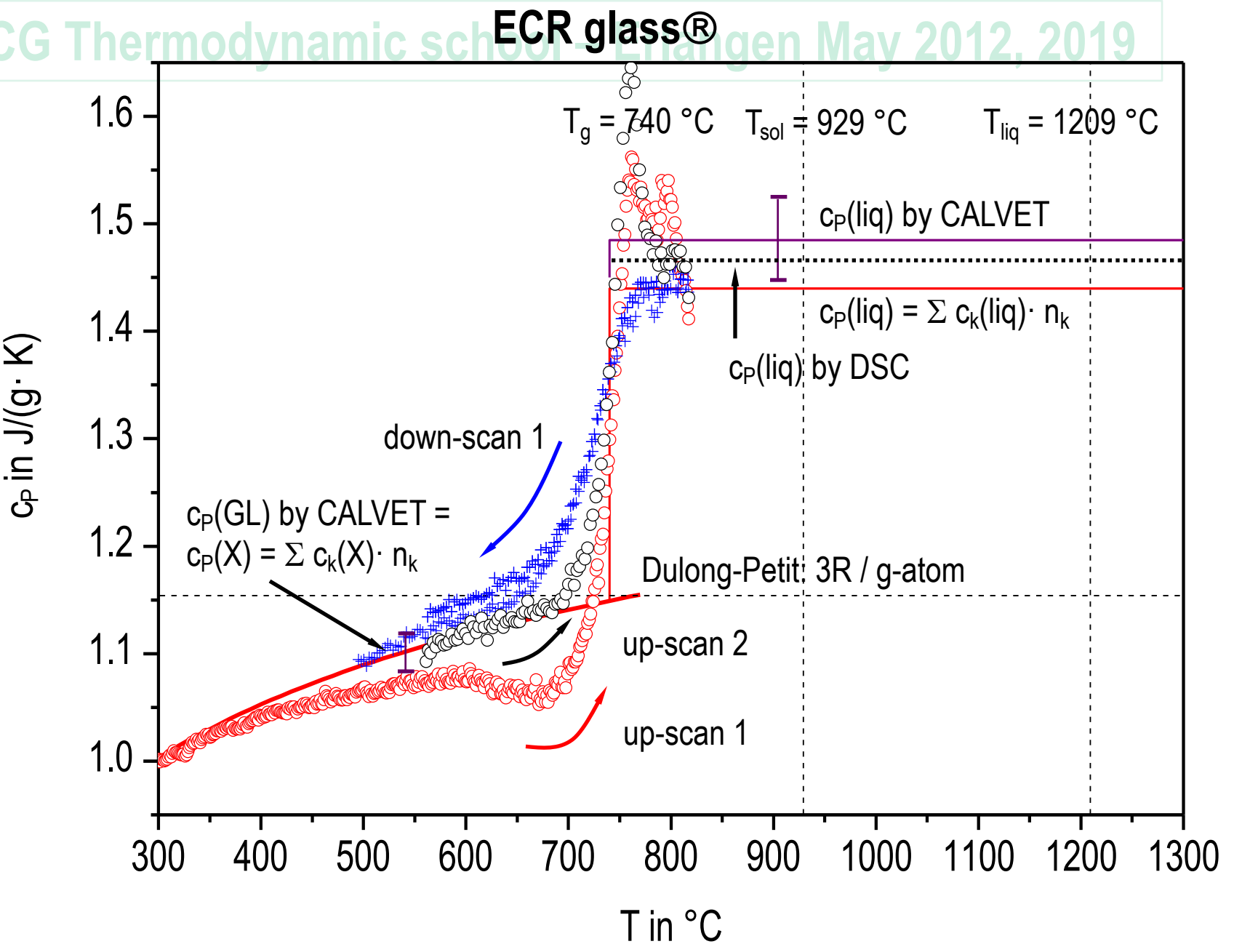
$S^{vit} = 0.1216$ J/(g· K)

$H^{vit} = 332.9$ J/g

ECR glass®



Simon Bartolomey, current Ph.D. work



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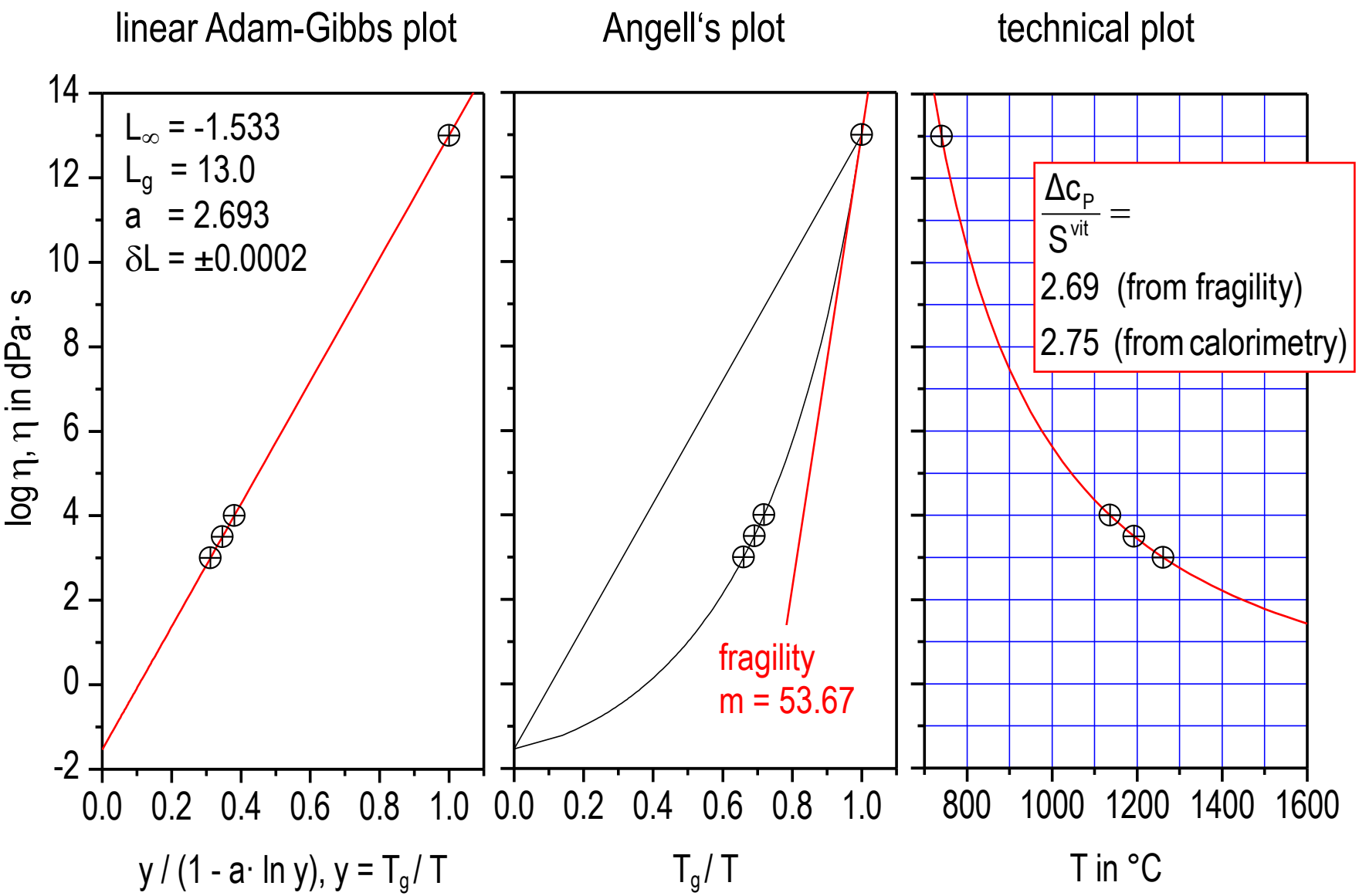
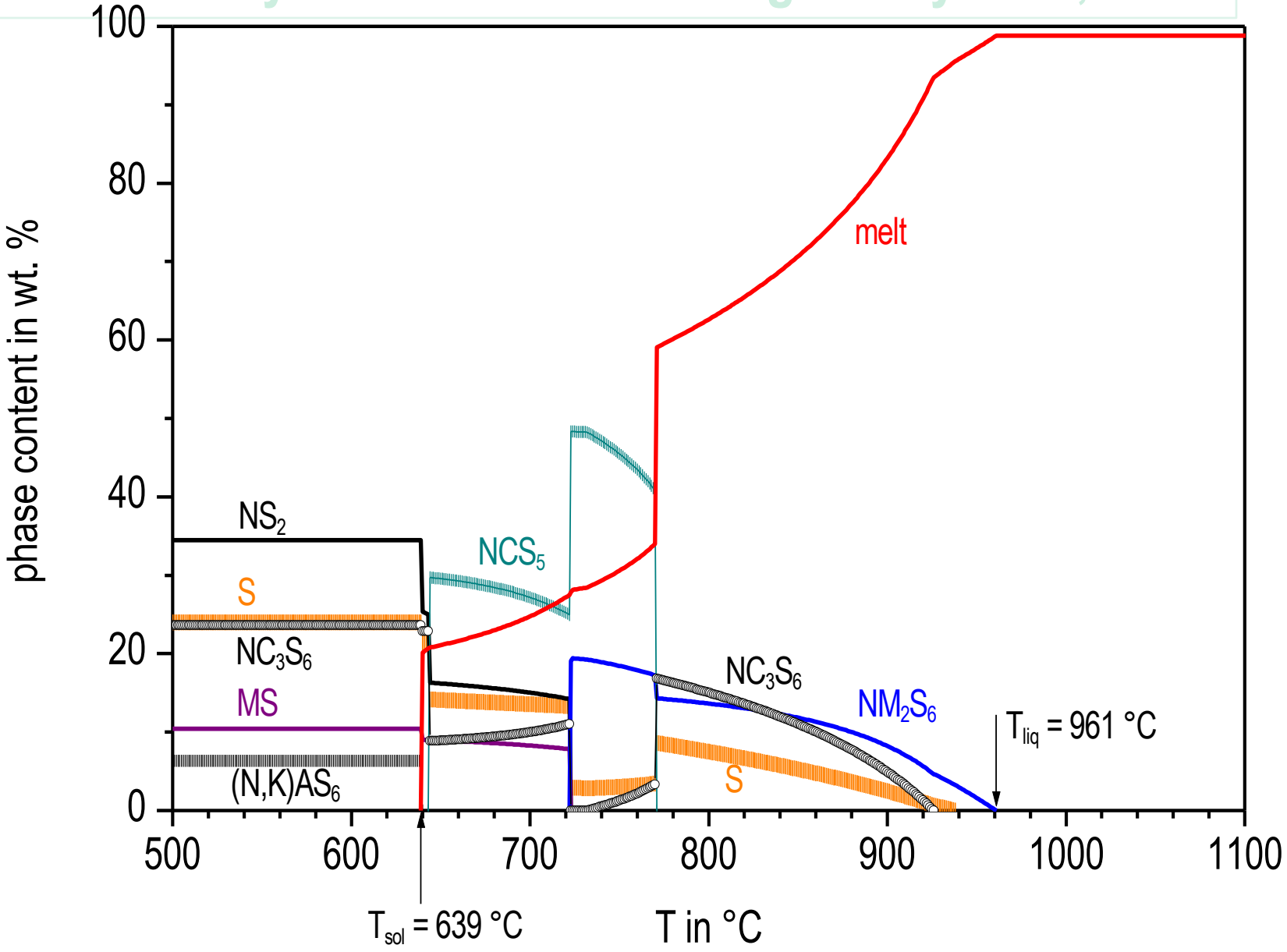

linear Adam-Gibbs plot
Angell‘s plot
technical plot
L∞ = -1.533
Lg = 13.0
a = 2.693
δL = ±0.0002
log η, η in dPa· s
y / (1 - a· ln y), y = Tg / T
Tg / T
T in °C
fragility
m = 53.67
ΔcP / Svit =
2.69 (from fragility)
2.75 (from calorimetry)

glass DGG-1



glass DGG-1

INPUT DGG1					
	g/100g	M(j)	n(j)	N	n(el)
SiO2	71.75	60.084	1.1942	3	3.5825
TiO2	0.14	79.898	0.0018	3	0.0053
Al2O3	1.23	101.961	0.0121	5	0.0603
Fe2O3	0.12	159.691	0.0008	5	0.0038
FeO	0.07	71.846	0.0010	2	0.0019
MgO	4.18	40.311	0.1037	2	0.2074
CaO	6.73	56.079	0.1200	2	0.2400
Na2O	14.96	61.979	0.2414	3	0.7241
K2O	0.38	94.203	0.0040	3	0.0121
SO3	0.44	80.061	0.0055	4	0.0220

COMPONENTS k			
	n(k)	M(k)	g/100g
CT	0.0018	135.977	0.24
Fe3O4	0.0008	231.537	0.17
FS	0.0002	131.930	0.03
MS	0.1037	100.395	10.41
KAS6	0.0040	556.668	2.25
NAS6	0.0080	524.444	4.21
Na2SO4	0.0055	142.040	0.78
NS2	0.1884	182.147	34.32
NC3S6	0.0394	590.720	23.29
S	0.4045	60.084	24.30

glass DGG-1

OXIDE ACTIVITIES			1400 °C	
	M(j)	n(j)	G°(j)	log a(j) L
TiO2	79.898	0.0000	1118.1	0.48
Al2O3	101.961	0.0392	1899.2	-3.84
Fe2O3	159.691	0.0000	1169.8	0.00
FeO	71.846	0.0000	456.8	-0.67
P2O5	141.945	0.0000	2120.0	-6.37
MnO	70.937	0.0000	550.3	-1.24
MgO	40.311	0.0496	682.0	-1.84
K2O	94.203	0.0106	701.0	-11.68
SO3	80.061	0.0000	925.0	-1.86
SiO2	60.084	1.1983	1072.8	0.00
CaO	56.079	0.1248	758.4	-3.35
Na2O	61.979	0.2259	681.5	-8.13
			0	1400

EVAPORATION

$a(Na_2O) = 10^{-8.13} = 7.4 \cdot 10^{-9}$

$\Rightarrow$

P(NaOH) = 8.8 mbar

RHEOLOGY		
cPL	1,4001	J/(g·K)
ΔcP	0,1880	J/(g·K)
Svit	0,1007	J/(g·K)

$$\frac{\Delta c_P}{S^{vit}} = 1.86 \pm 0.04$$

Young's modulus	71.9	70.2	71.0	GPa

application:

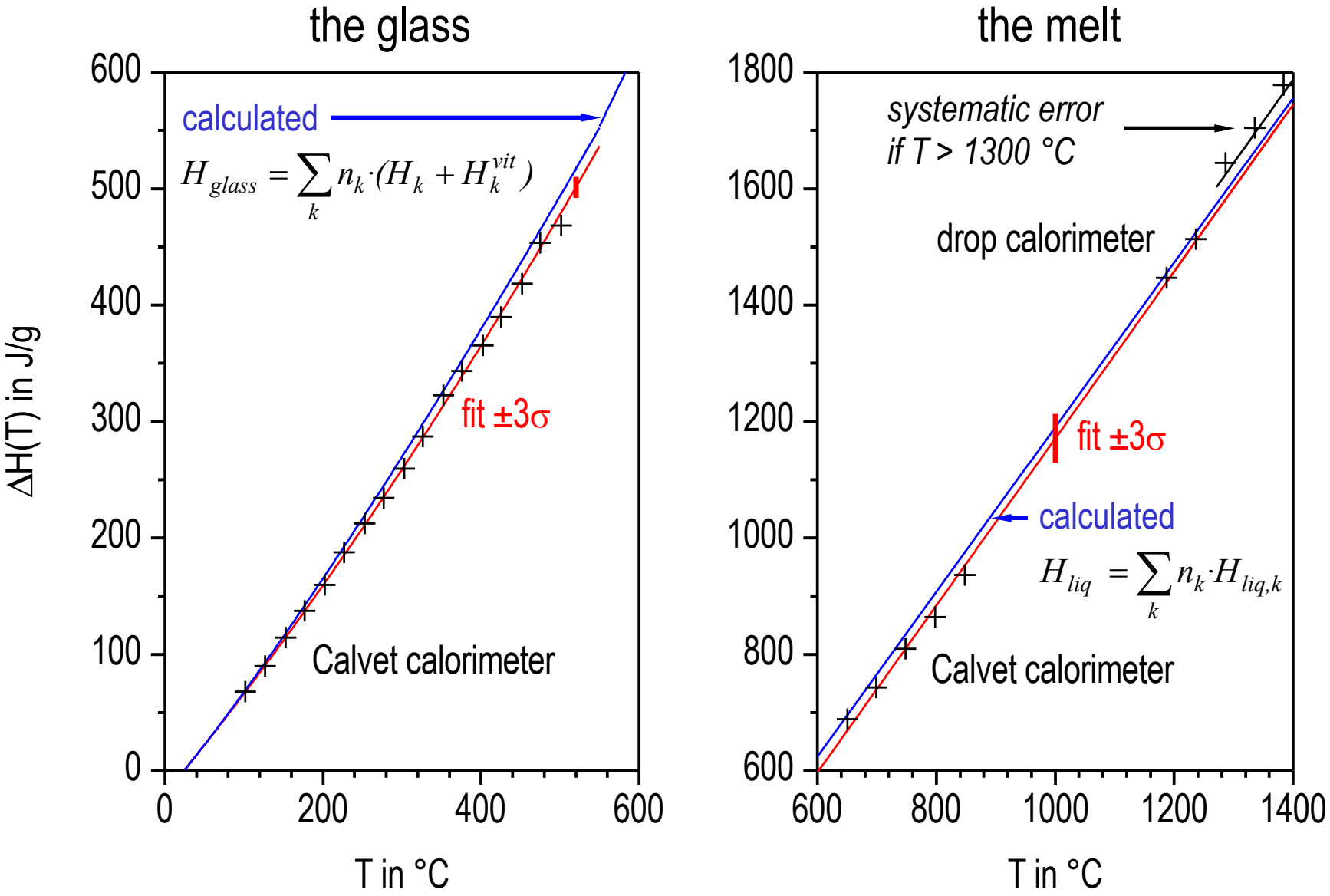
chemical durability

energy of batch-to-melt conversion

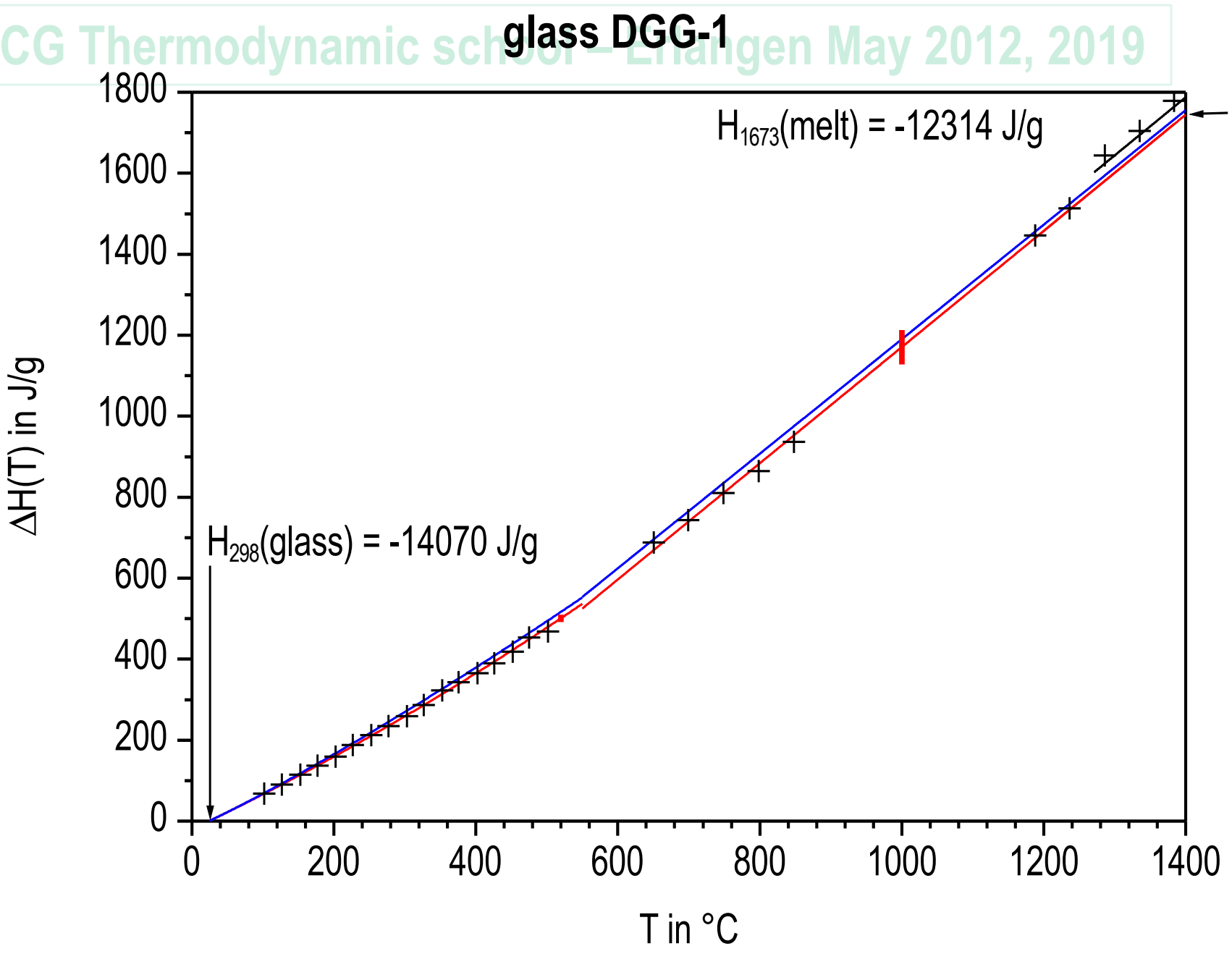
heat content of melt at pull temperature

ENERGETICS				
G*f*	1324,5	kJ/100g	25	°C
H°Glass	3908,1	kWh/t	25	°C
HT	435,3	kWh/t	1350	°C

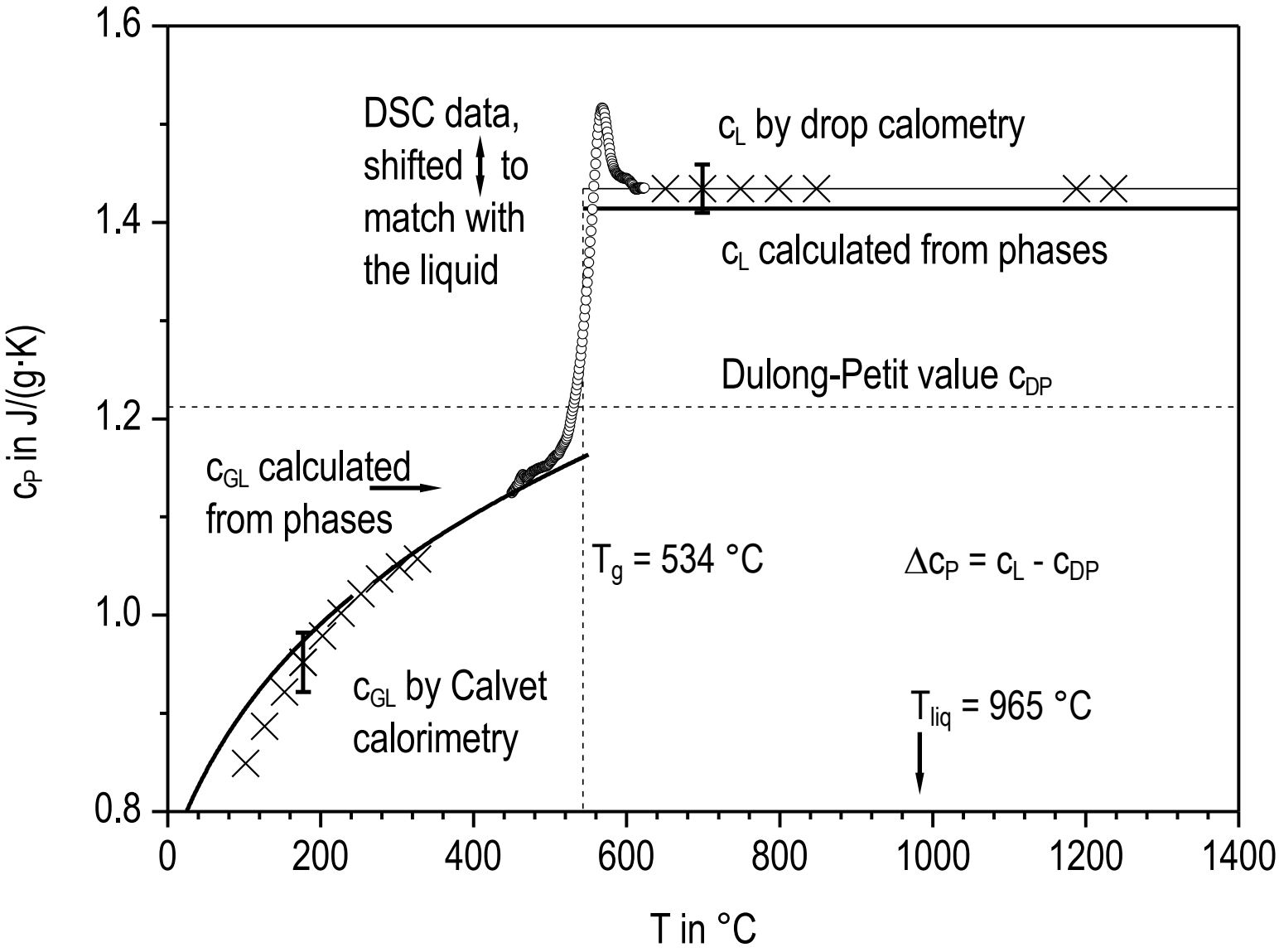
glass DGG-1



Heuser, thesis 2016

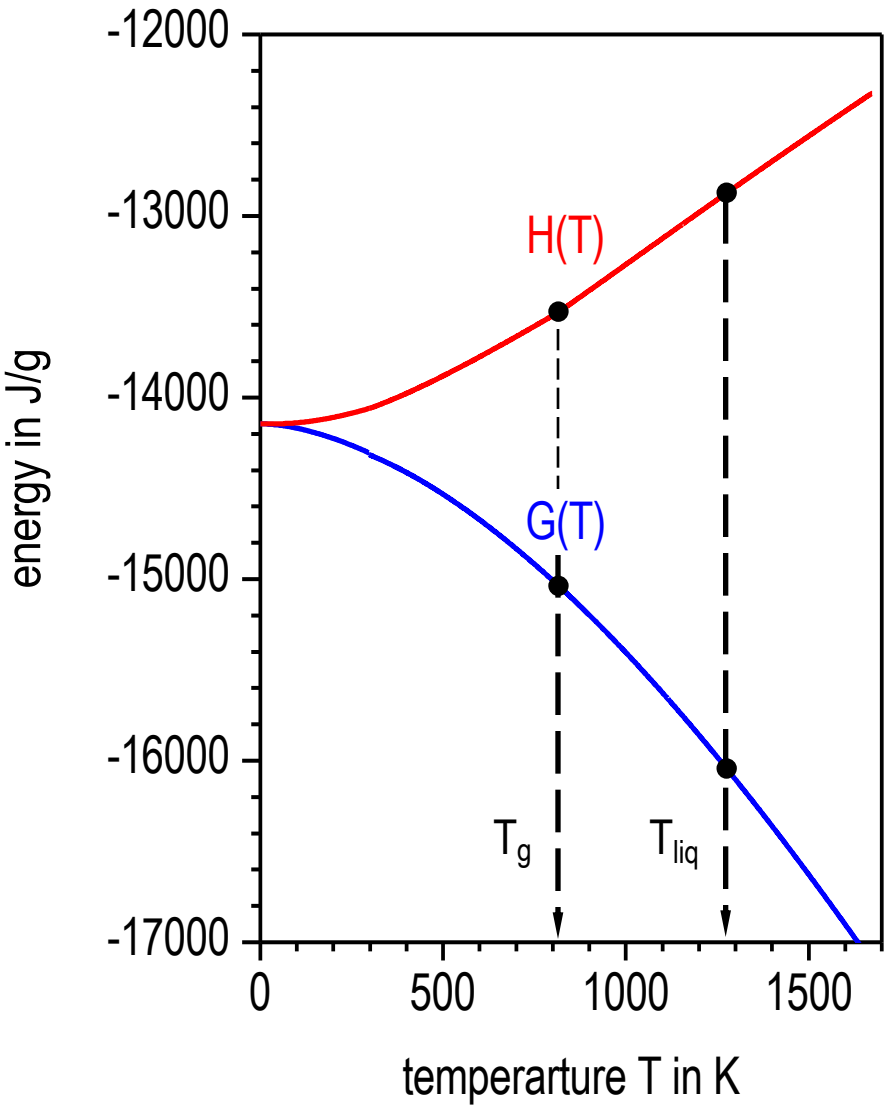


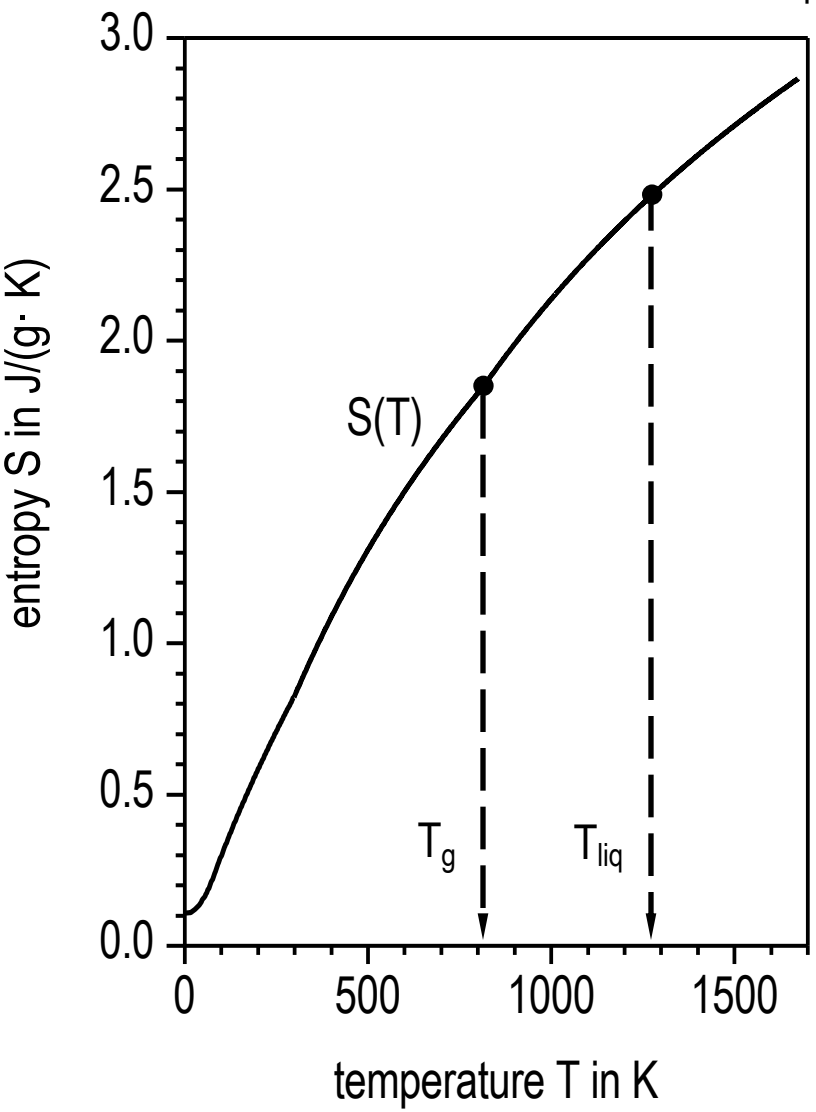
glass DGG-1


1.6
1.4
1.2
1.0
0.8
c_P in J/(g·K)
0
200
400
600
800
1000
1200
1400
T in °C
DSC data, shifted to match with the liquid
c_L by drop calometry
c_L calculated from phases
Dulong-Petit value c_{DP}
c_{GL} calculated from phases
T_g = 534 °C
$\Delta c_P = c_L - c_{DP}$
c_{GL} by Calvet calorimetry
T_{liq} = 965 °C

glass DGG-1

complete assessment of thermochemical data from T = 0 K to T > T_{liq}



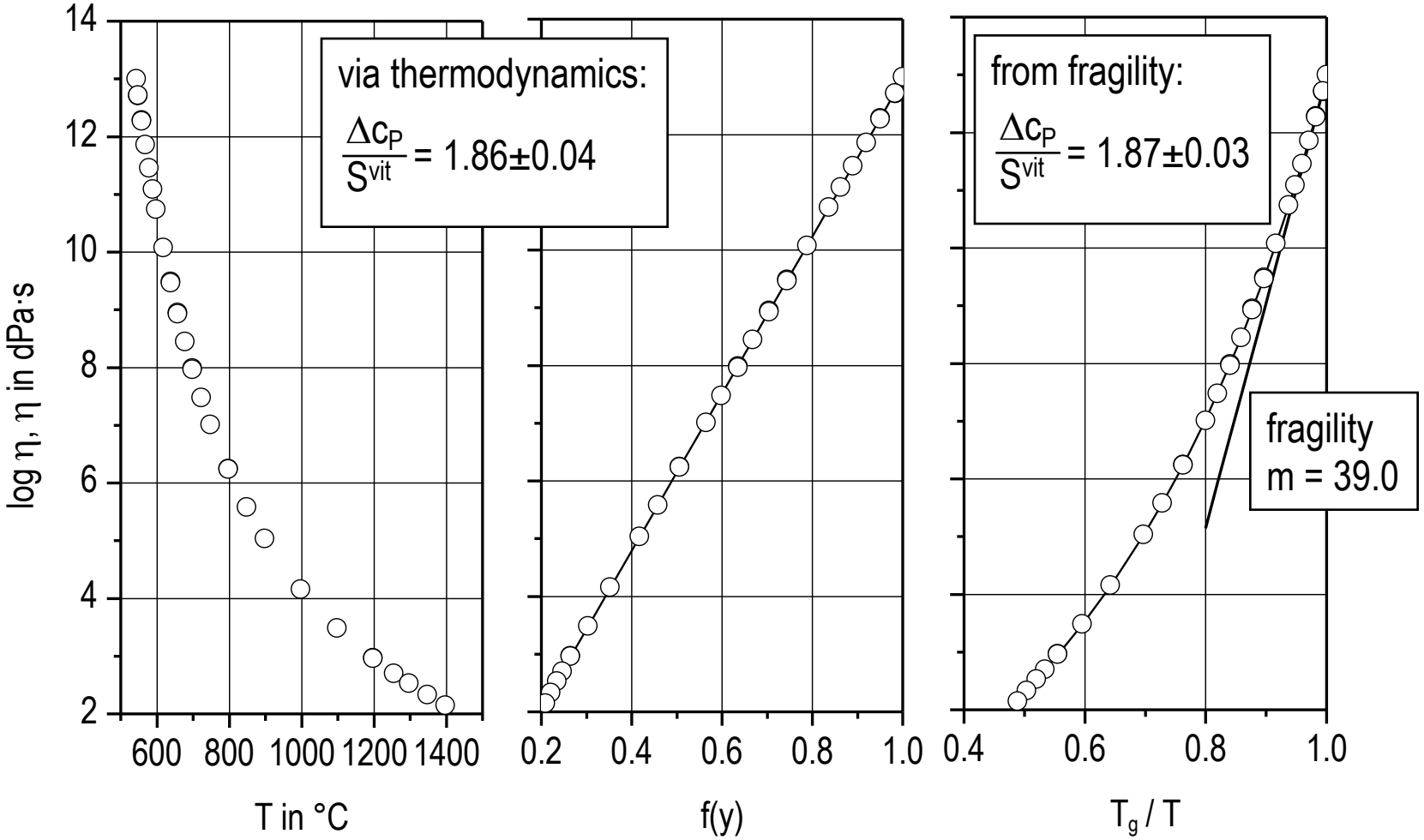


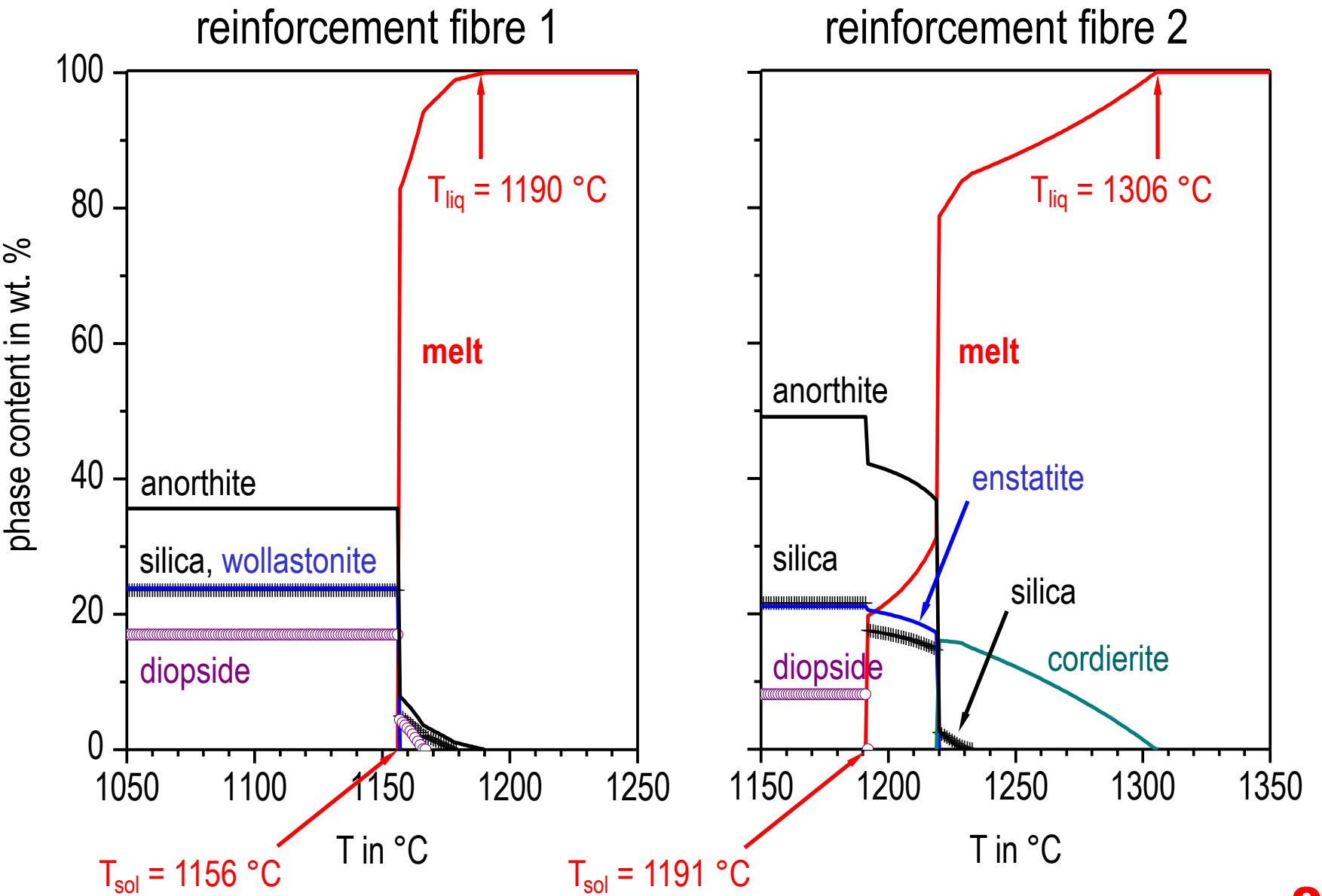
glass DGG-1

DGG-1 original data set, PTB Braunschweig

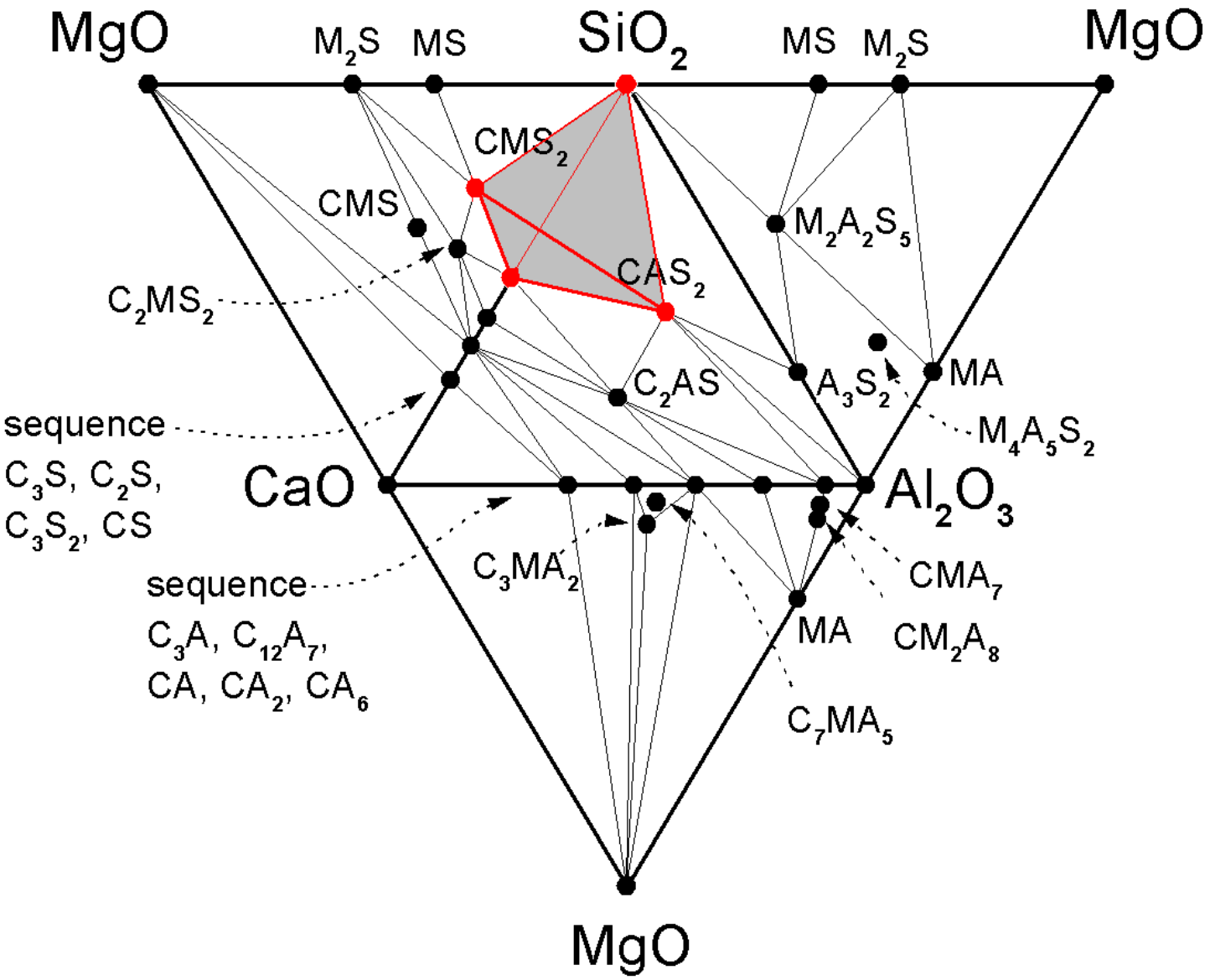
Linearized coorditate fit to Adam-Gibbs equation

Angell's plot showing the fragility slope m

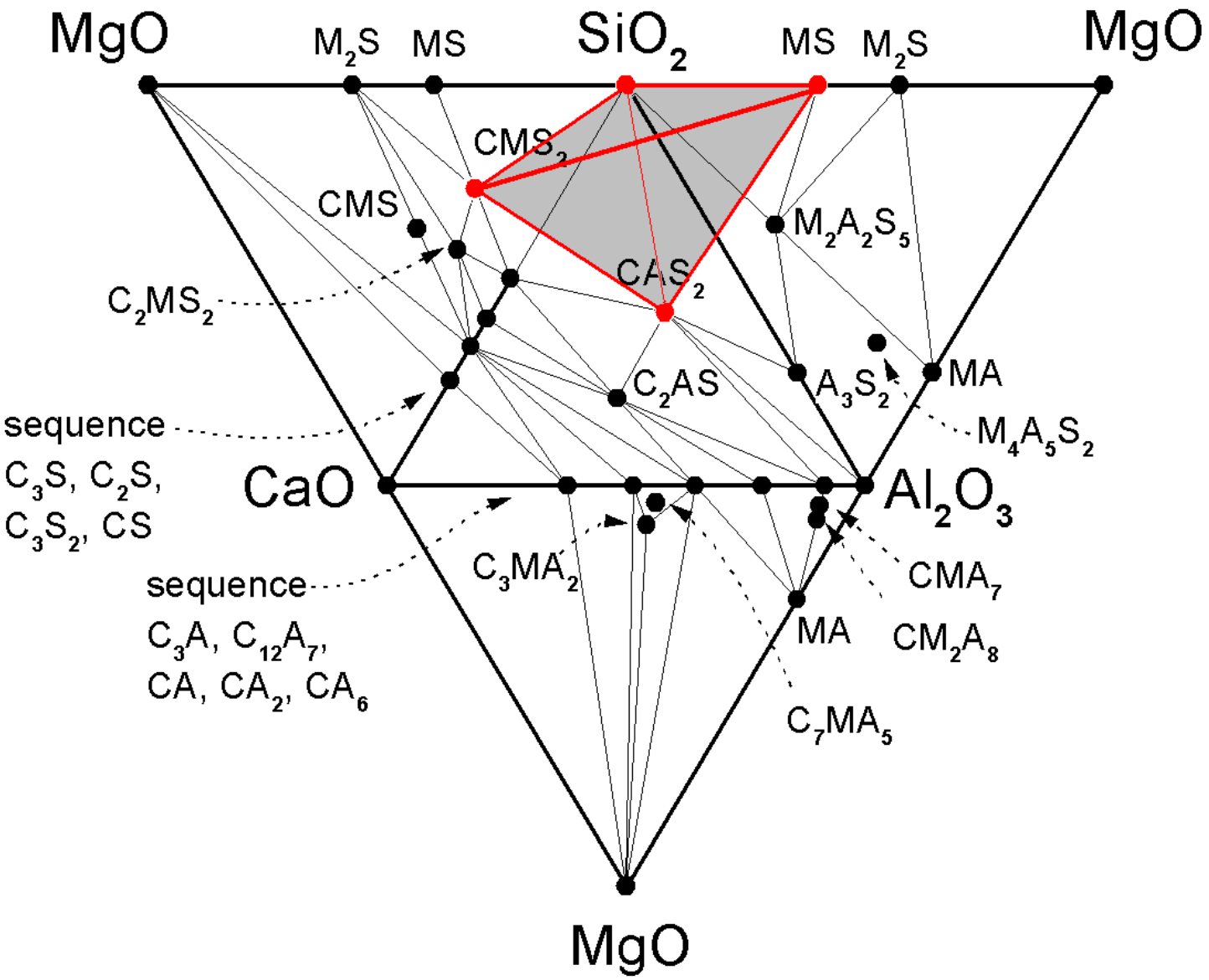



reinforcement fibre 1
reinforcement fibre 2
phase content in wt. %
100
80
60
40
20
0
1050
1100
1150
1200
1250
1300
1350
T in °C
T_liq = 1190 °C
T_liq = 1306 °C
melt
anorthite
silica, wollastonite
diopside
enstatite
silica
cordierite
T_sol = 1156 °C
T_sol = 1191 °C

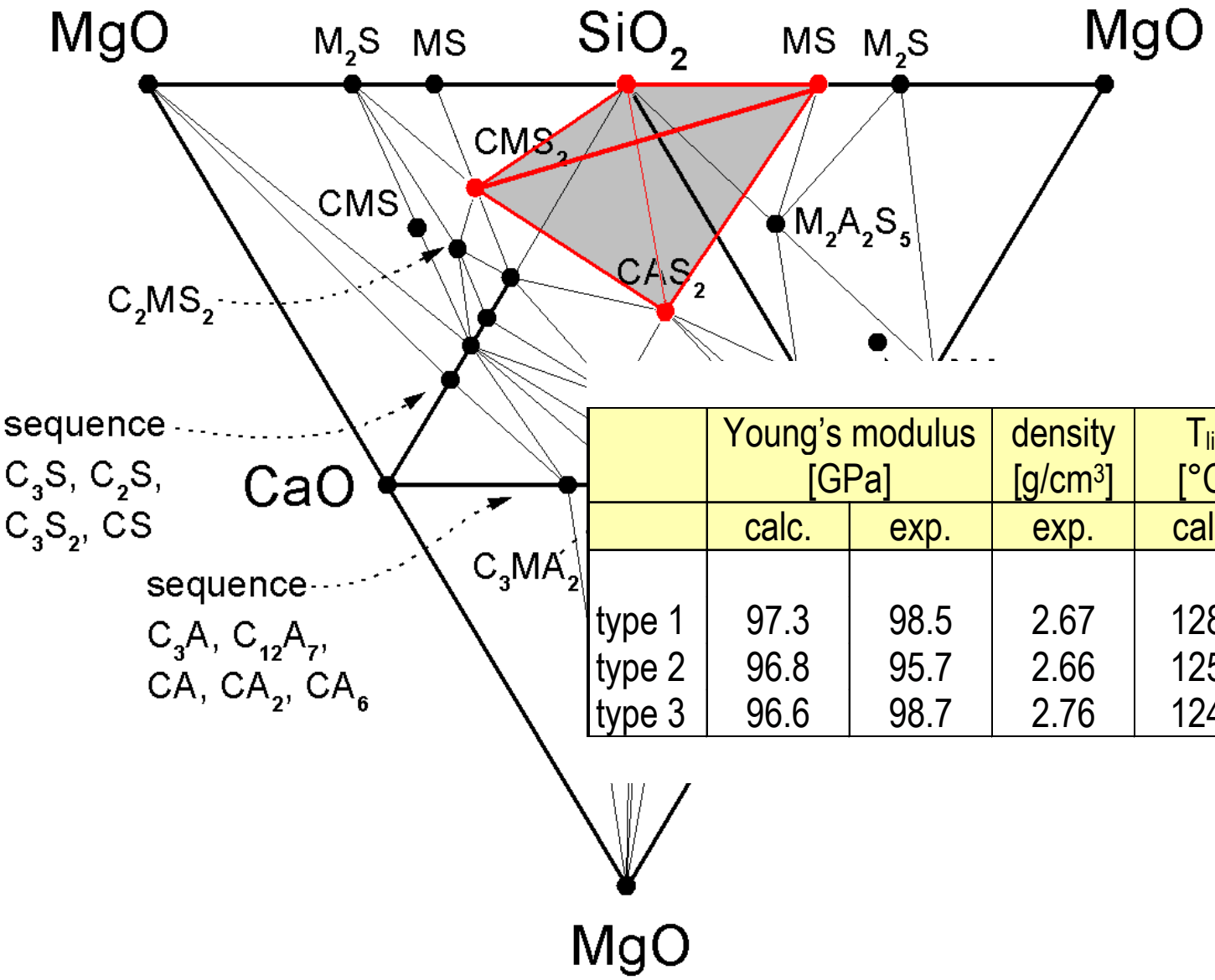
macroscopic properties of multi-component glasses; example new E-CR glass



macroscopic properties of multi-component glasses; example new E-CR glass



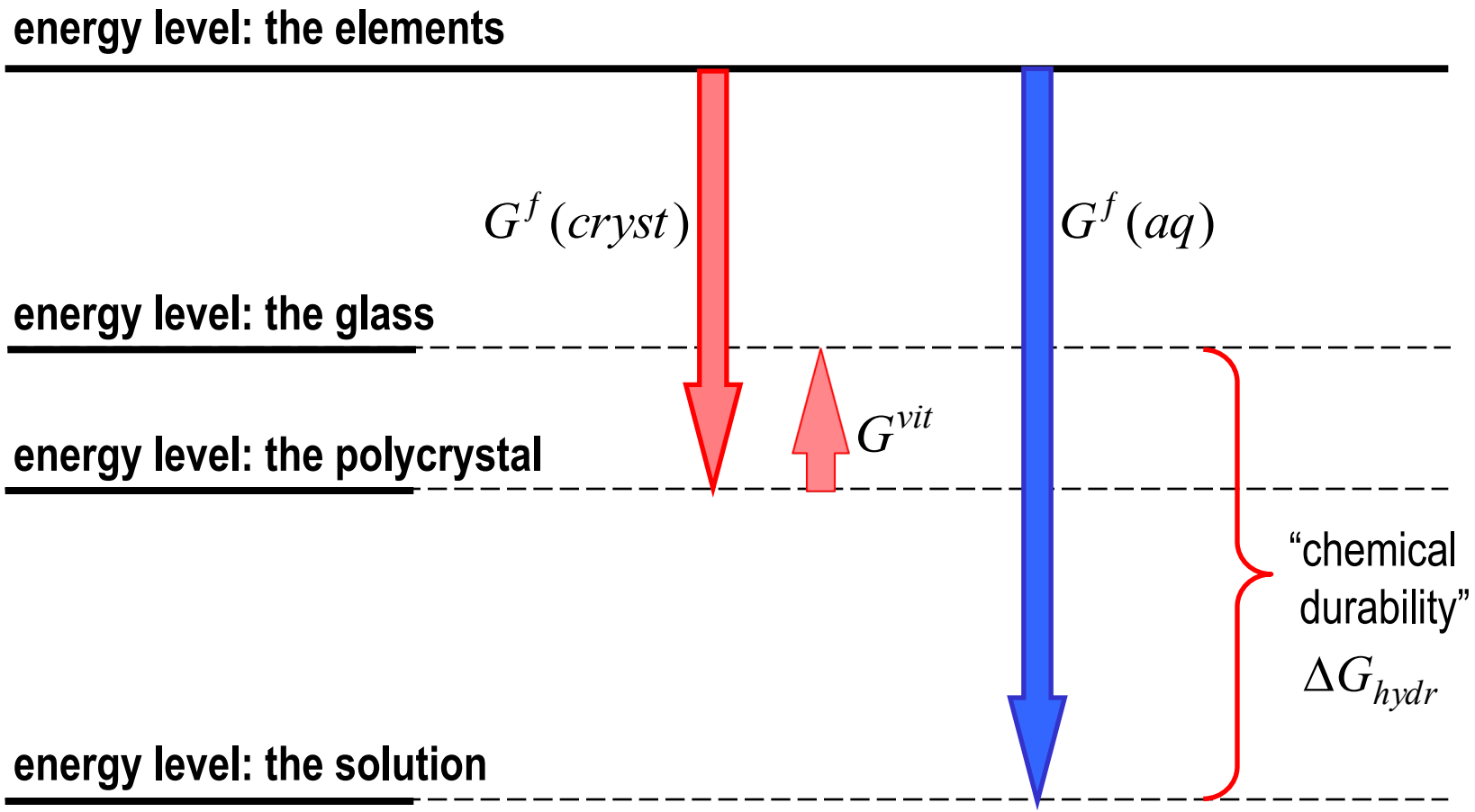
macroscopic properties of multi-component glasses; example new E-CR glass



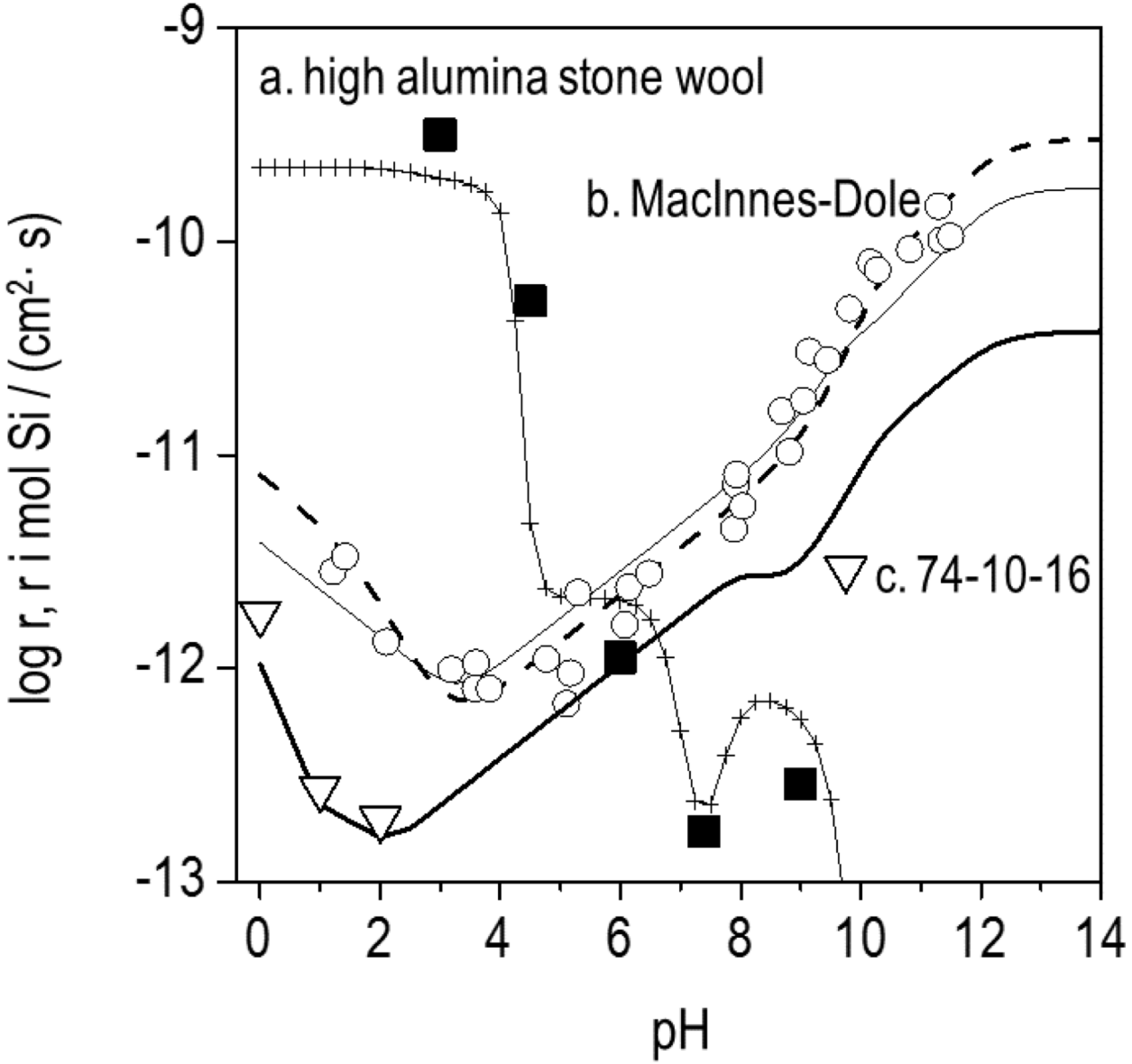
	Young's modulus [GPa]		density [g/cm³]	T_{liq} [°C]
	calc.	exp.	exp.	calc.
type 1	97.3	98.5	2.67	1286
type 2	96.8	95.7	2.66	1253
type 3	96.6	98.7	2.76	1246

hyrdolytic stability

$$\Delta G_{hydr} = G^{f}(aq) - \left(G^{f}(cryst) - G^{vit}\right)$$

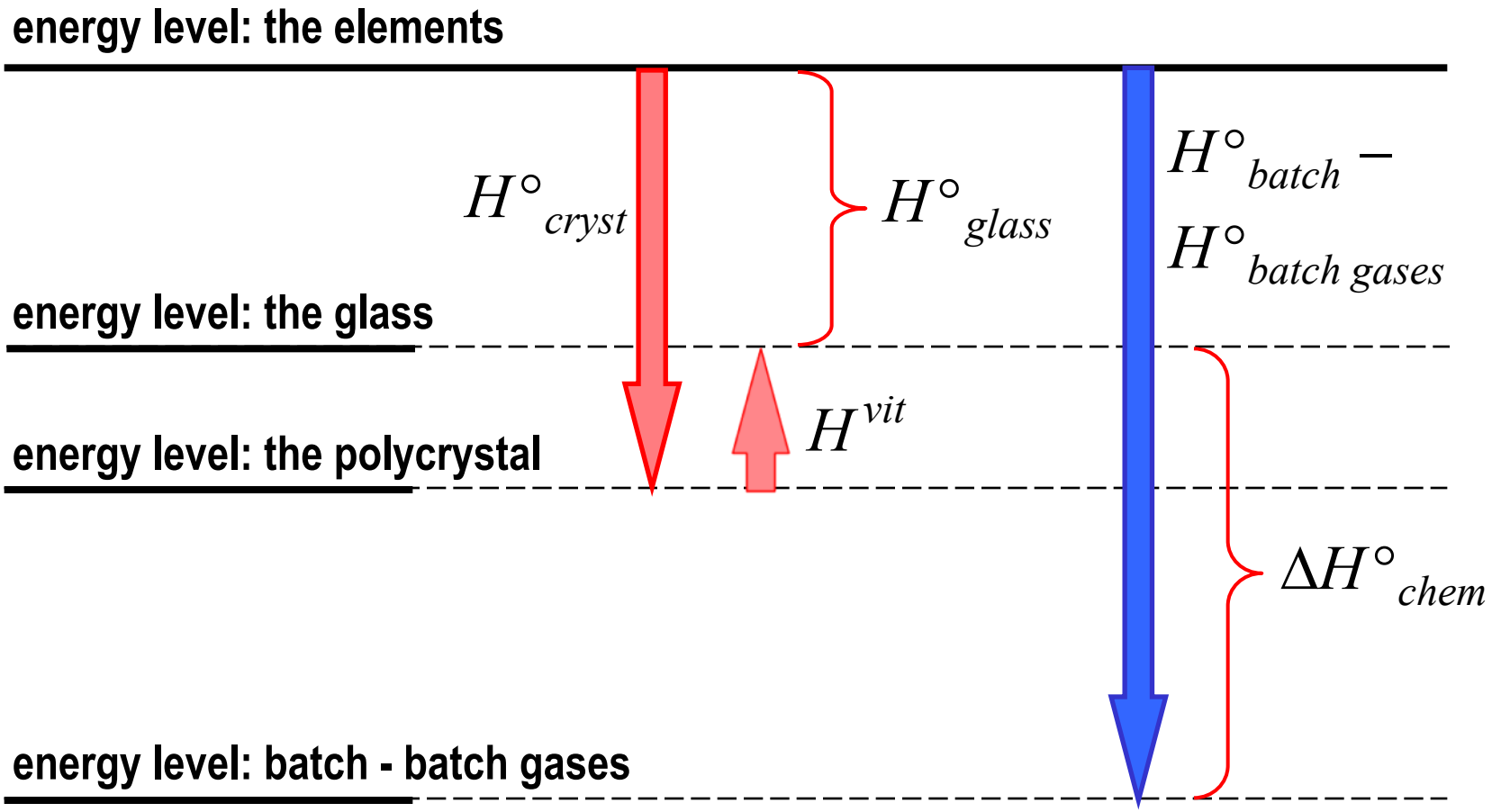


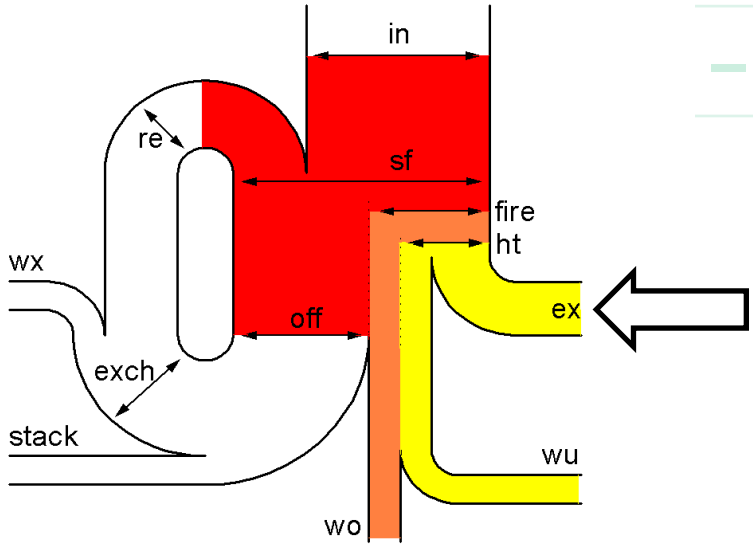
macroscopic properties of multi-component glasses; example hydrolytic stability

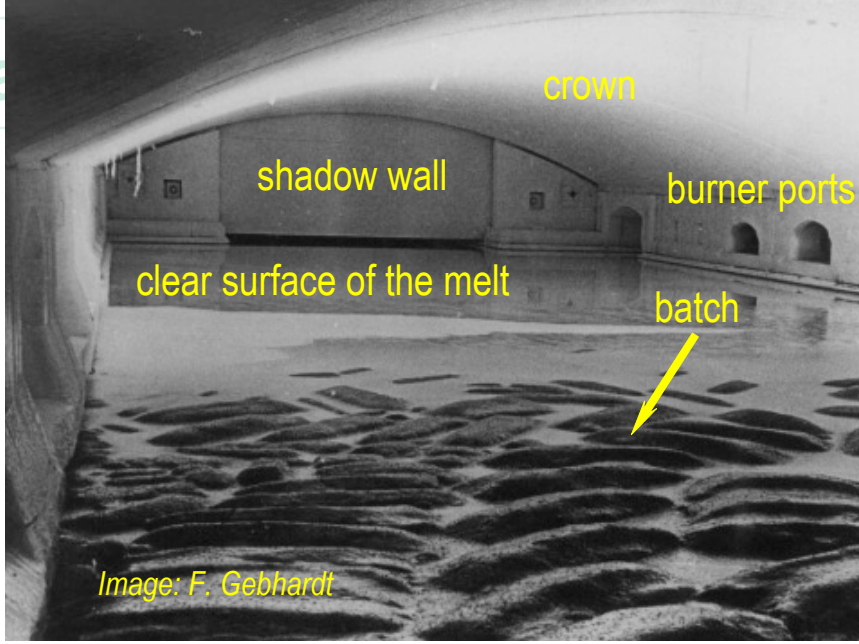


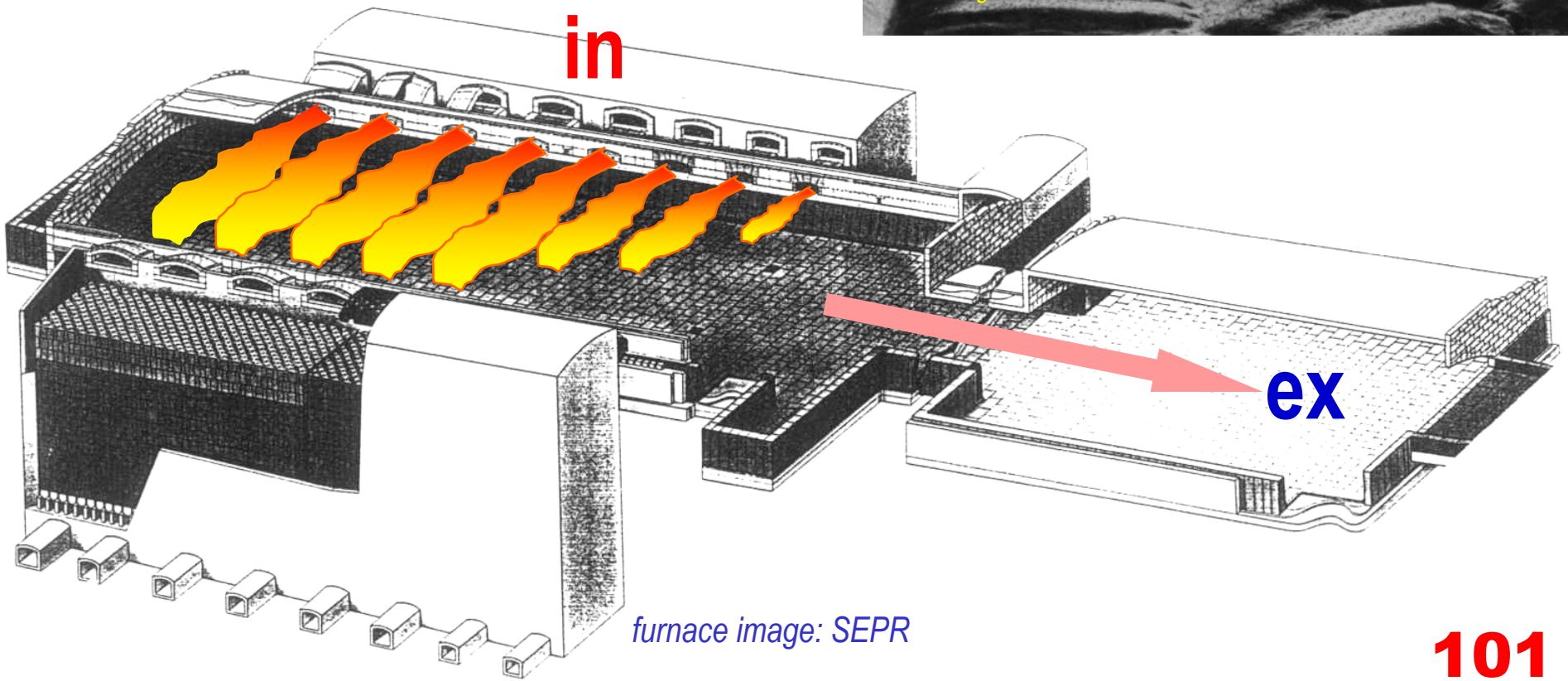
raw materials (25 °C) $\xrightarrow{\Delta H^\circ_{chem}}$ glass (25 °C) + batch gases

glass (25 °C) $\xrightarrow{\Delta H(T_{ex})}$ melt (T_{ex})









furnace image: SEPR

The End