Experimental determination of thermodynamical functions of glasses

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School : Thermodynamics of Glass
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ICG-TC3
International Commission on Glass

UNION
POUR LA SCIENCE
ET LA TECHNOLOGIE
VERRIÈRES

Deutsche Glastechnische
Gesellschaft e.V.

TherMatHT GDR CNRS
Hautes températures
Thermodynamique des matériaux

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Outline

- Experimental thermodynamics on condensed phases
    - Thermodynamic potential and quantities that can be measured
    - Measurement of thermal functions
        - adiabatic calorimetry – DSC – drop calorimetry
- Thermodynamics of glass transition
    - Evolution of thermodynamic quantities at the glass transition
    - Glass description using the thermodynamic theory of irreversible processes
- Measurement of the glass transition temperature
    - Graphical methods
    - Thermodynamic methods
- Measurement of the frozen-in enthalpy

- (Measurement of the frozen-in entropy → D. Neuville lecture)

Emphasis is put on calorimetric techniques with temperature as the intensive variable which is controlled

Experimental thermodynamics on condensed phases

Thermodynamic potential for condensed phases

$$G(T, p, n_i, \ldots) = U + pV - TS = H - TS = \sum_i \mu_i n_i$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p, n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T, n_i} dp + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{p, T, n_{j \neq i}} dn_i$$

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i$$

- **A system under isothermal, isobaric conditions minimizes its Gibbs energy at equilibrium**
- **G is the most practical thermodynamic potential for condensed phases** because its natural variables p, T and n_i can be
  - **measured** (thermometer, barometer, balance)
  - **controlled** (which is not the case of V for condensed phases)

What can be measured ?

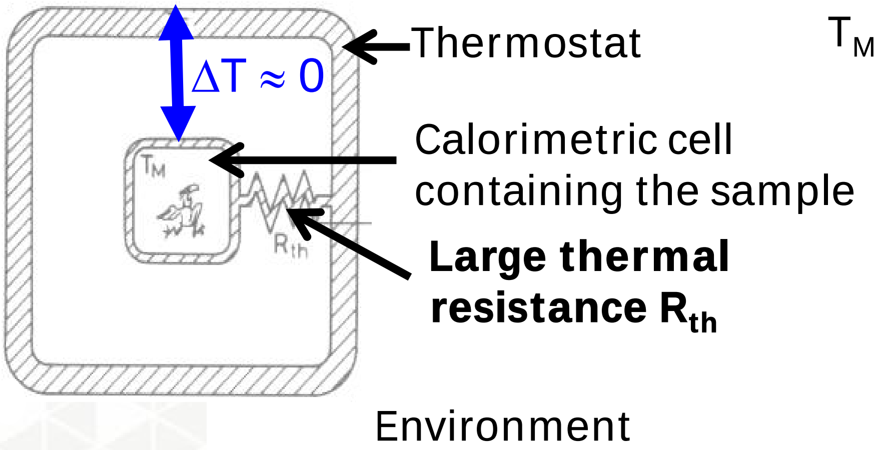
	Gibbs energy	$G=G(T,p,N_i)$		Generally, no direct measurement
1^{st} derivatives of G	entropy	$S=-\left(\frac{\partial G_{\mathrm{m}}}{\partial T}\right)_{p,N_i}$	>0	Integration of $C_p(T)/T$ from 0 to T
	enthalpy	$H=\left(\frac{\partial(G/T)}{\partial(1/T)}\right)_{p,n_i}$ $H=G+TS=G-T\left(\frac{\partial G}{\partial T}\right)_{p,N_i}$		Isothermal calorimetry
	volume	$V=\left(\frac{\partial G}{\partial p}\right)_{T,N_i}$	>0	XRD, dilatometry, pycnometry
	chemical potential of component i	$\mu_i=\left(\frac{\partial G}{\partial N_i}\right)_{T,N_{j\neq i}}$		Heterogeneous equilibria, EMF, p_{vap}...
2^{nd} derivatives of G	heat capacity	$C_p=-T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N_i}$	>0	Scanning calorimetry: DSC or adiabatic
	thermal expansion	$\alpha=\frac{1}{V}\left(\frac{\partial^2 G}{\partial p\,\partial T}\right)_{N_i}$		Derivative of V(T)
	isothermal compressibility	$\kappa=-\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N_i}$	>0	Derivative of V(P)
	bulk modulus	$B=1/\kappa$		

And the intensive variables of G: *T*, *p*, chemical composition

Calorimetric techniques for measuring the thermal functions

- Thermal functions are :
  - Heat capacity: $C_p(T)$
  - Heat increment: $H(T)-H(T_{ref})$
- **0 < T < 360 K**
  - Adiabatic calorimetry
- **300 < T < 800 K**
  - DSC
- **800 < T < 1800 K**
  - DSC or drop calorimetry
  - 1800 K = upper temperature limit of the use of Pt-Rh thermopiles
  - Main condition for accurate C_p measurement by DSC is the reproducibility of the baseline in consecutive runs: difficult to achieve at T > 1100 K
- **T > 1800 K**
  - Drop calorimetry is the only technique
  - T > 2600 K, levitated samples / laser heating / pyrometry

Adiabatic calorimetry - principle



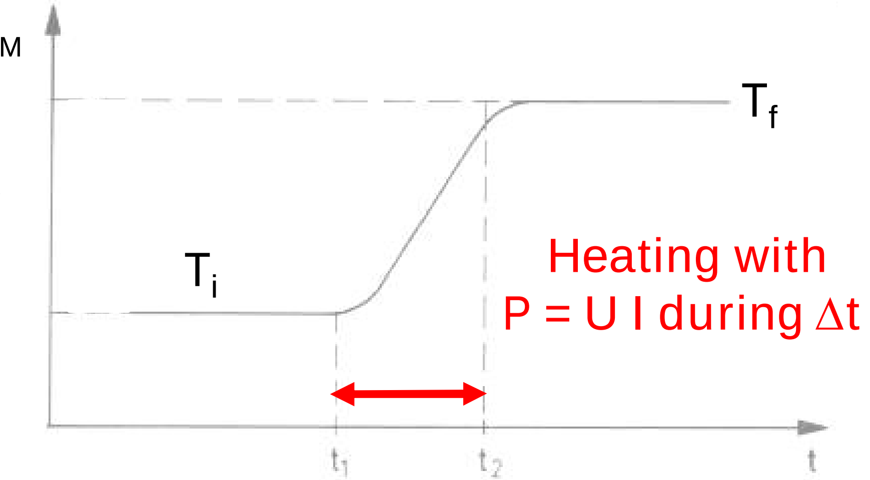
$\Delta T \approx 0$

Thermostat

Calorimetric cell containing the sample

Large thermal resistance R_{th}

Environment



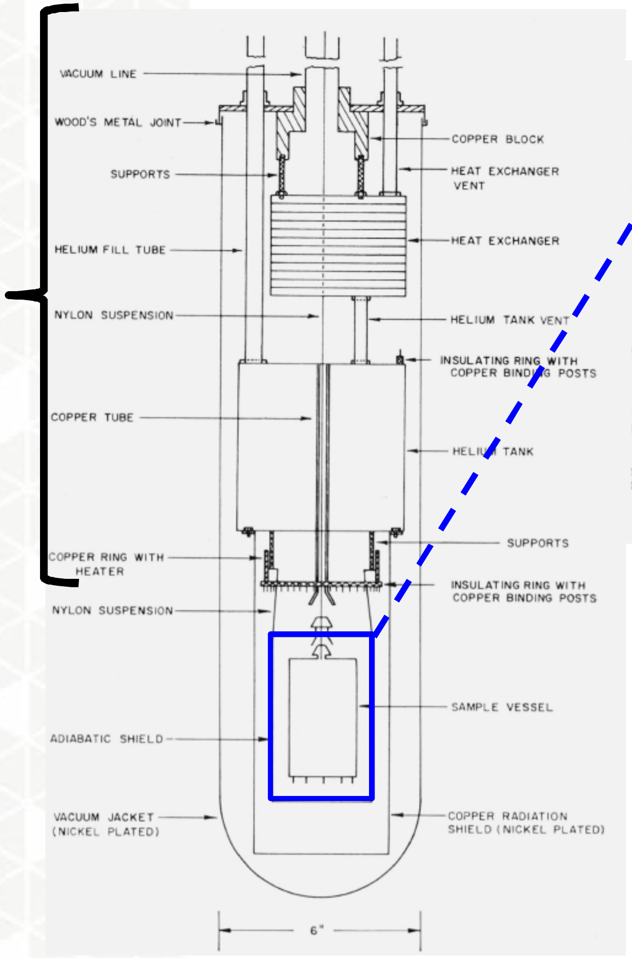
Heating with $P = U\,I$ during Δt

- To minimize the heat leak between the sample and the thermostat
  - **Large R_{th}** : suspended sample under vacuum to reduce heat transfer by conduction, convection + shields to limit heat transfer by radiation
  - **The temperature difference ΔT between the calorimetric cell and the thermostat is continuously monitored and cancelled by active control**
- The calorimetric cell is equipped with an electric heater and a temperature probe

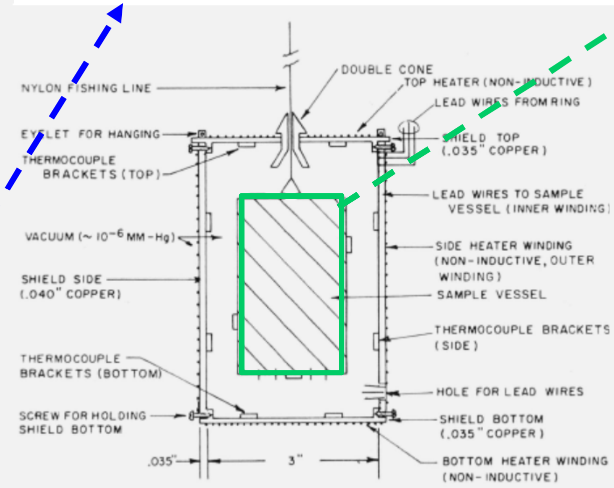
$$C_p(T)=C_p\left(\frac{T_i+T_f}{2}\right)=\frac{U\,I\,\Delta t}{m(T_f-T_i)}$$

Adiabatic calorimeter of the NBS (10 - 360 K)

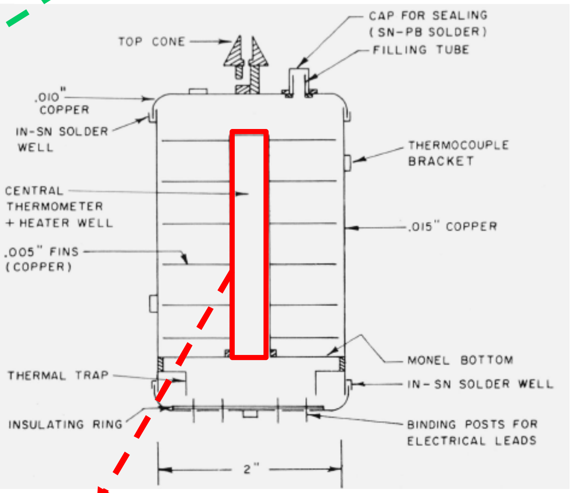
Cryostat, liquid or solid nitrogen or liquid helium



Detail of the adiabatic shield



Sample vessel



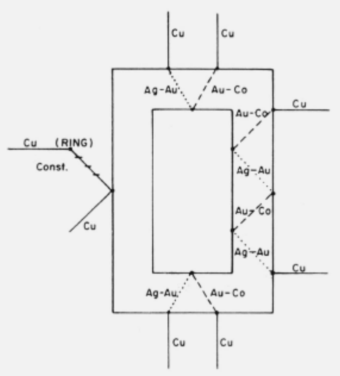
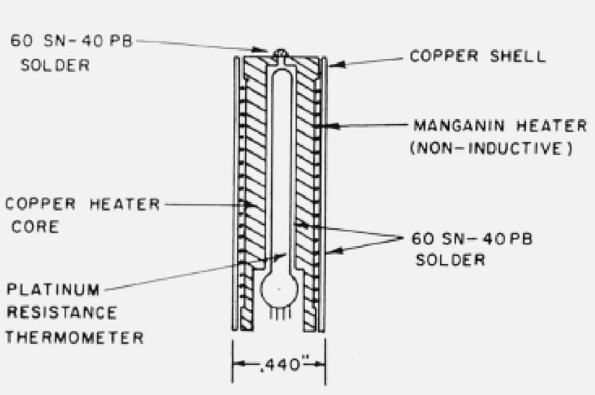


FIGURE 3. *Thermocouple schematic.*

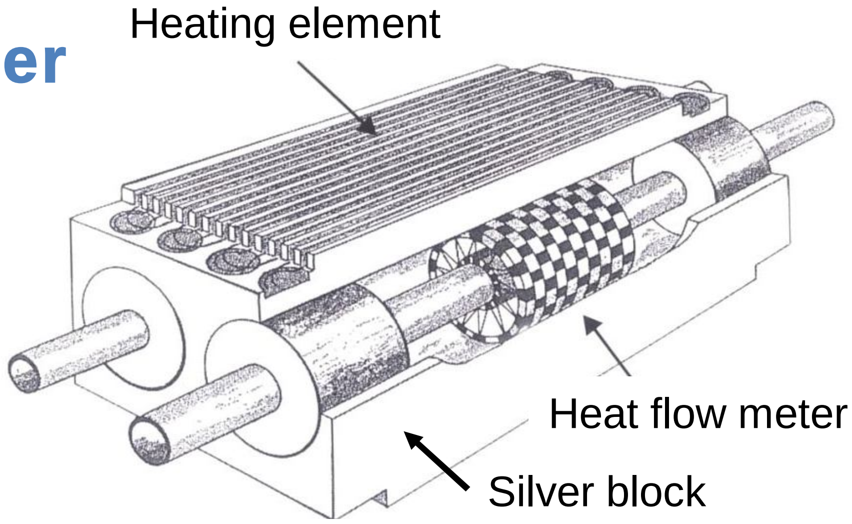
Thermometer and heater



Sterrett, K.F., D.H. Blackburn, A.B. Bestul, S.S. Chang, and J. Horman. 1965." Journal of Research of the National Bureau of Standards, Section C: Engineering and Instrumentation 69C (1): 19

Differential Scanning Calorimeter

- Setaram model DSC 111 / SENSYS
  - 2 cells : sample + reference
  - 3D sensors : 2 Tian-Calvet thermopiles (each having 120 thermocouples) connected in a differential setup
    - Spatial integration of the heat flow
  - 150 to 1100 K
  - 0.02 to 30 K/min scanning rate



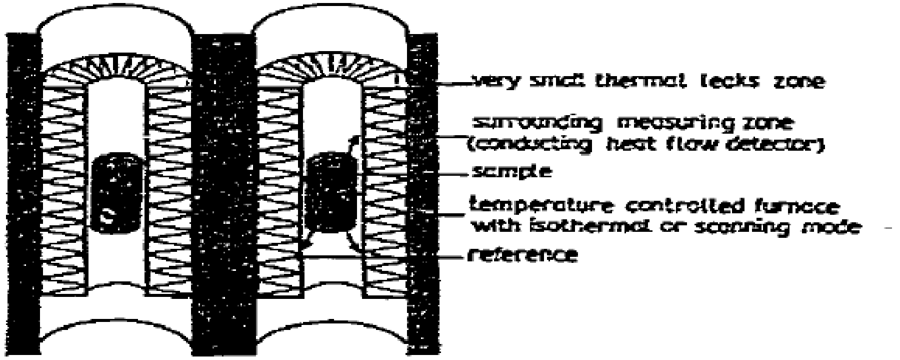
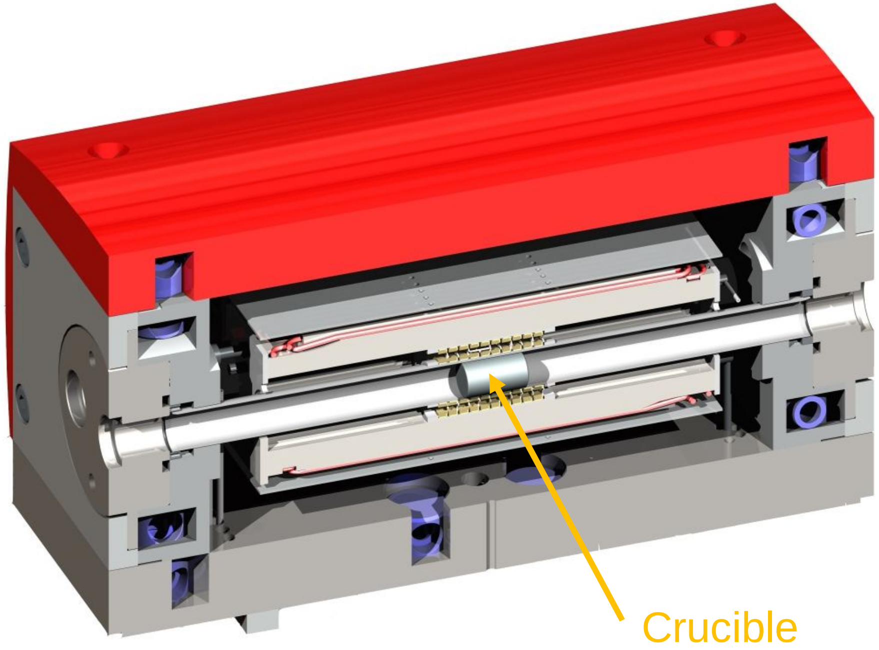


Fig. 2. Schematic of the heat-flow detector.



(from Setaram documentation and Marano, Ross T. 1978. "New Setaram Calvet Differential Scanning Calorimeter." Thermochimica Acta 26: 27–37)

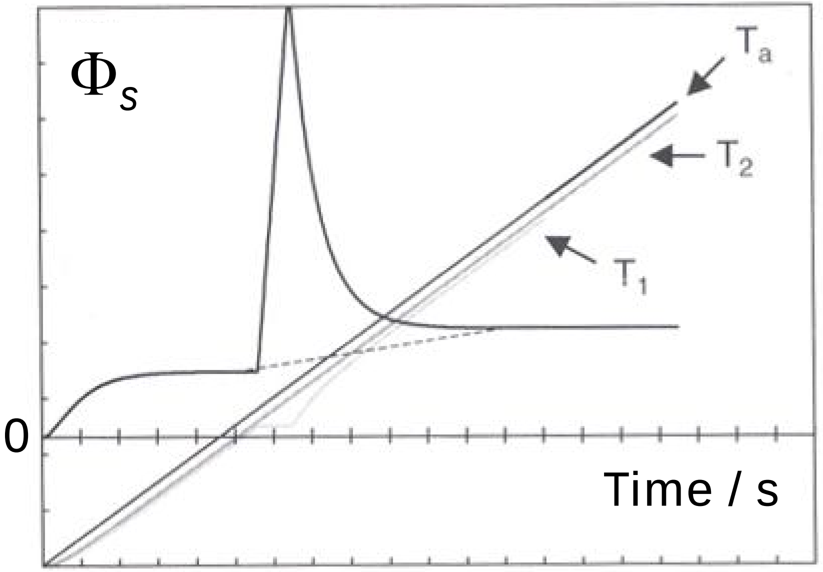
C_p measurement at continuous rate of temperature change

$Q =$ heat quantity $/J$
$m =$ sample mass $/g$
$T =$ temperature $/K$
$t =$ time $/s$

$\beta =$ heating/cooling rate $/ K\,s^{-1}$
$\Phi =$ true heat flow exchanged by the sample $/W$
$\Phi_S =$ differential heat flow measured during the sample run $/W$
$\Phi_0 =$ differential heat flow measured during the zeroline run $/W$

$$C_p\left(J.g^{-1}.K^{-1}\right)=\frac{dQ}{m.dT}=\frac{\frac{dQ}{dt}}{m.\frac{dT}{dt}}=\frac{\Phi}{m.\beta}\propto\frac{\Phi_S-\Phi_0}{m.\beta}$$

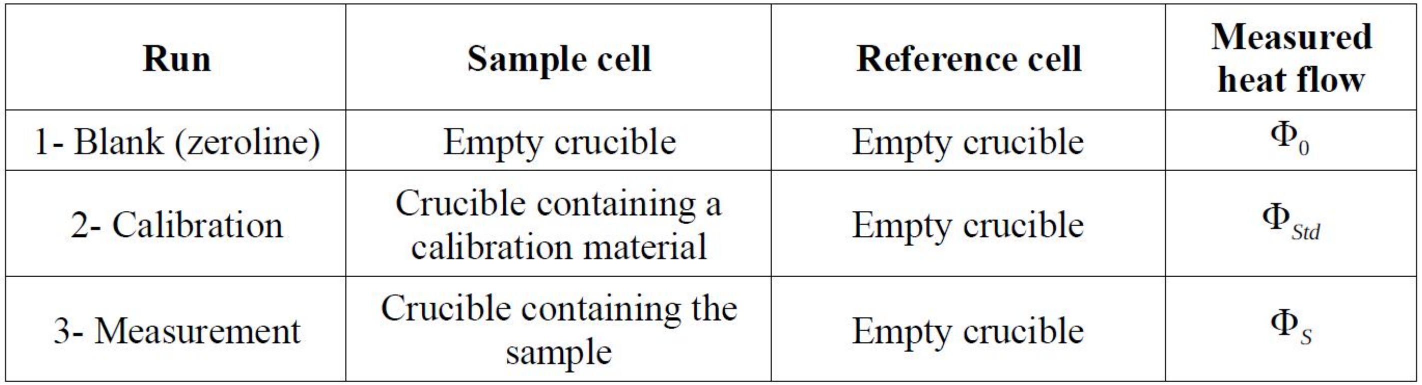
Differential signal recorded with a DSC during a 1st order transition with C_p change



(*from* Claudy, Pierre. 2005. *Analyse Calorimétrique Différentielle - Théorie et Applications de La DSC*. Lavoisier)

C_p measurement by DSC – 3 step method

- A DSC is never perfectly symmetrical
  - A blank experiment (zeroline) is required to quantify the dissymmetry of the instrument
- The differential heat flow sensor of the DSC delivers a voltage and only detects a fraction of the heat flux released or absorbed by the sample
  - A calibration is necessary to convert the calorimetric signal measured in mV (or µV) to a thermal power in W
- Hence, 3 consecutive runs under identical thermal conditions are required

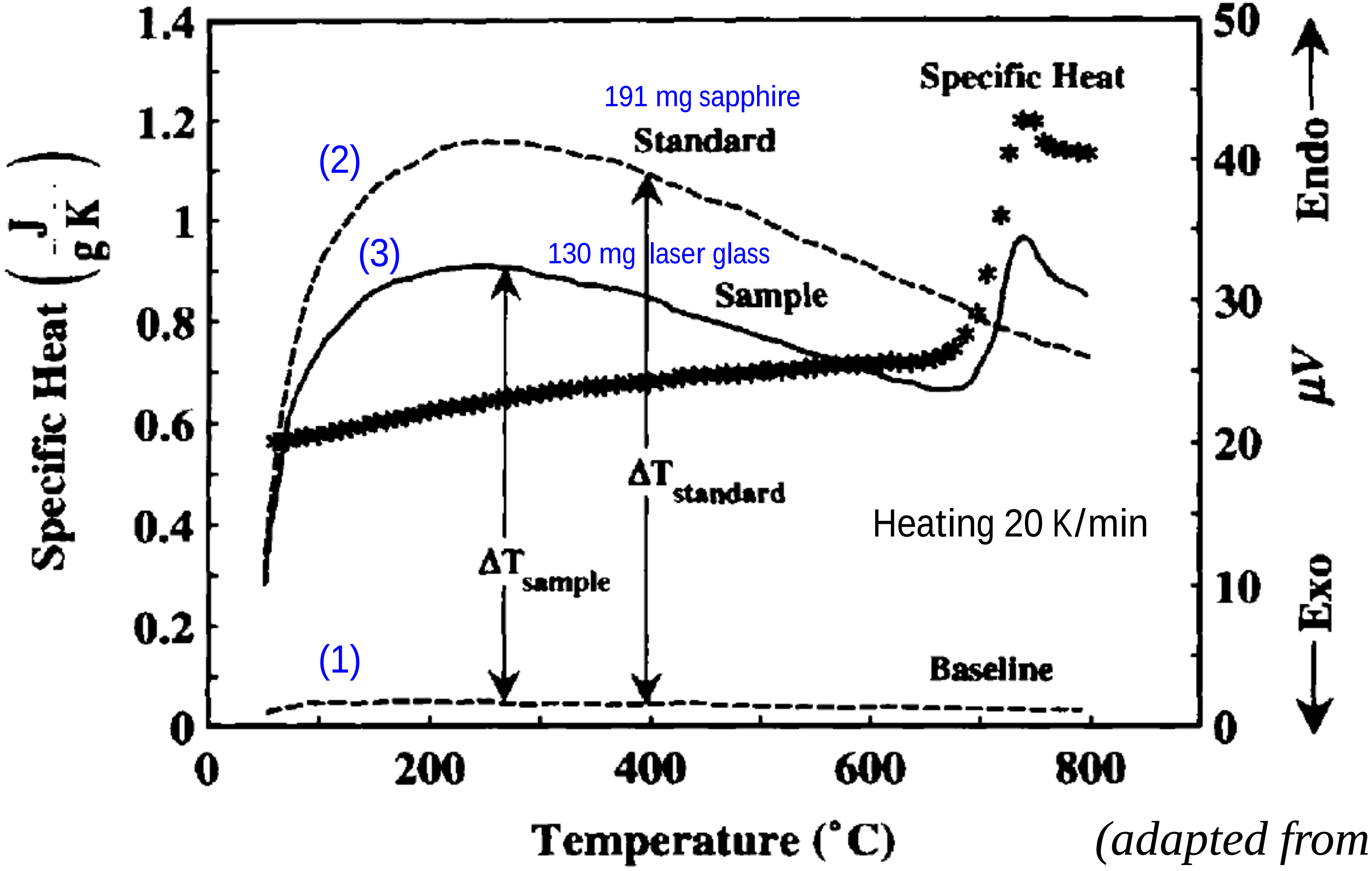


Run	**Sample cell**	**Reference cell**	**Measured heat flow**
1- Blank (zeroline)	Empty crucible	Empty crucible	Φ_0
2- Calibration	Crucible containing a calibration material	Empty crucible	Φ_{Std}
3- Measurement	Crucible containing the sample	Empty crucible	Φ_S

  - The crucibles used must all be identical
    - Same material, same mass, same geometry

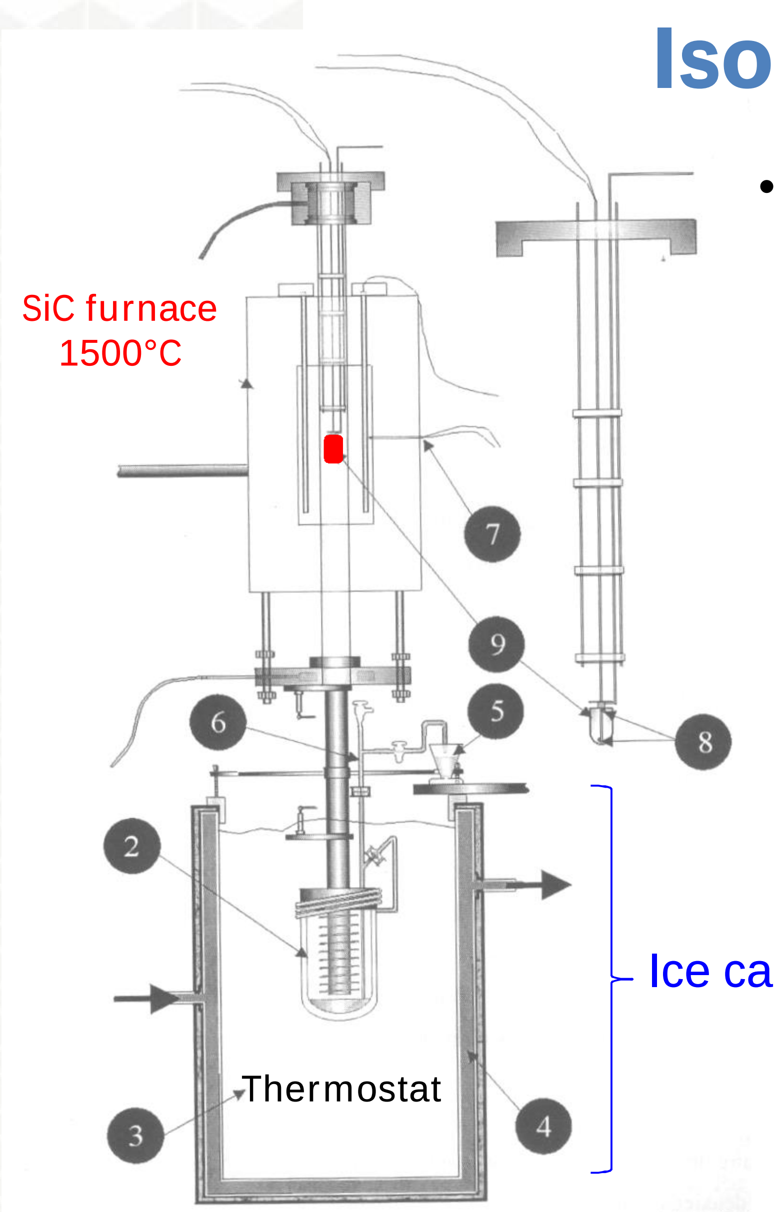
Example of C_p measurement by continuous heating

$$C_{p,s}(T)=\frac{m_{std}}{m_s}\frac{\Phi_S(T)-\Phi_0(T)}{\Phi_{Std}(T)-\Phi_0(T)}C_{p,std}(T)$$



(adapted from Speyer 1993)

Isothermal drop calorimetry



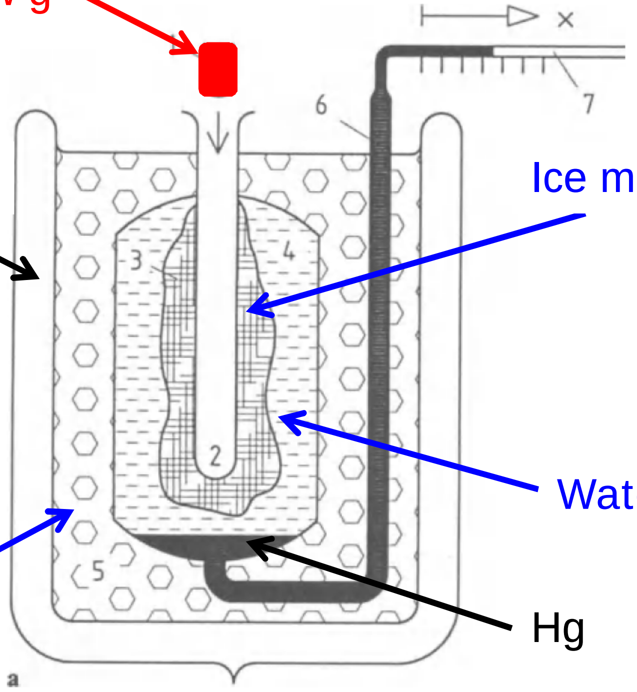
SiC furnace
1500°C

Thermostat

Ice calorimeter

Adapted from P. Richet (1982) and Y. Linard (2000) theses

- *IPG Paris ice calorimeter*
  - **Measurement of H_T -H_{273}**
  - Relative uncertainty 0.2%
  - 5-6 exp./day



Crucible Pt-Rh15
m_{Sample} = few g

Thermostat

Ice mantle

Water

Water + ice
mixture at 0°C

Hg

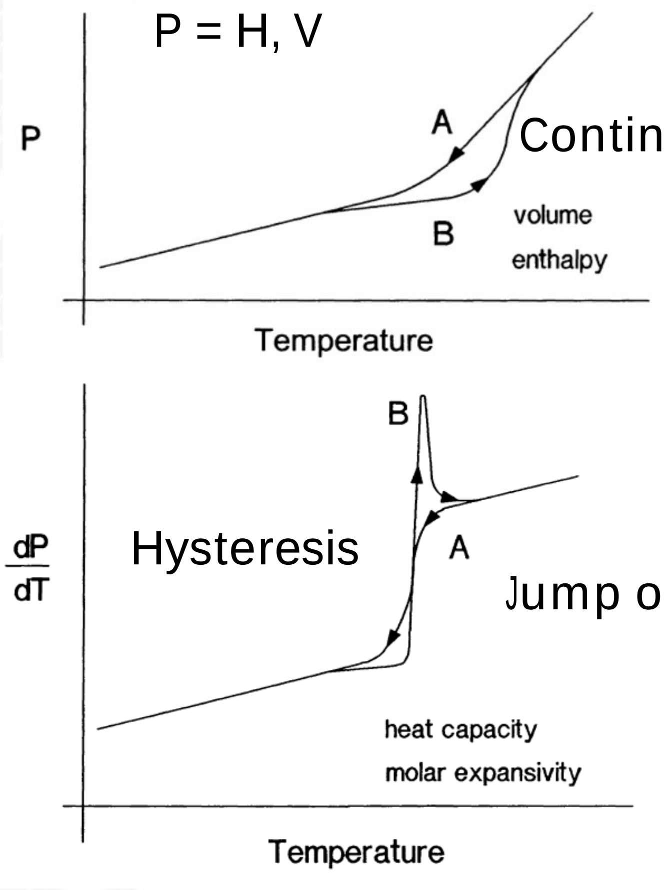
from Höhne et al. (2003)

Thermodynamics of the glass transition

Schematic evolution of the thermodynamic functions at the glass transition

Webb, S. L., R. Knoche, and D. B. Dingwell. 1992. European Journal of Mineralogy 4 (1): 95–104

Moynihan, C. T., A. J. Easteal, J. Wilder, and J. Tucker. 1974. The Journal of Physical Chemistry 78 (26): 2673–77

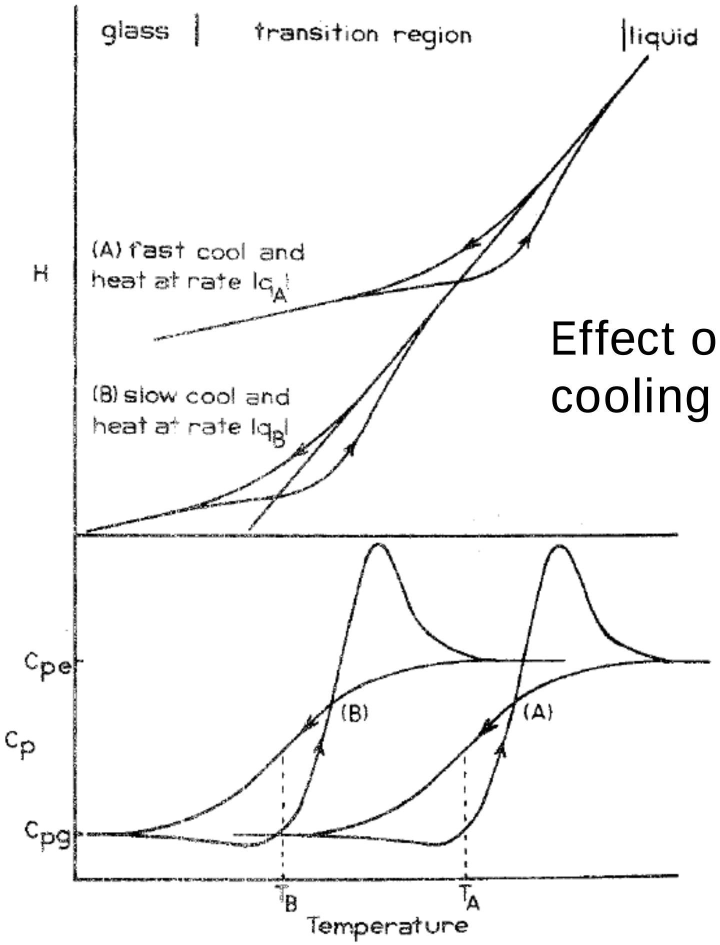


P = H, V

Continuity on P

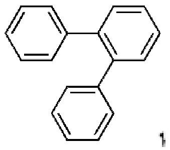
Hysteresis

Jump on dP/dT



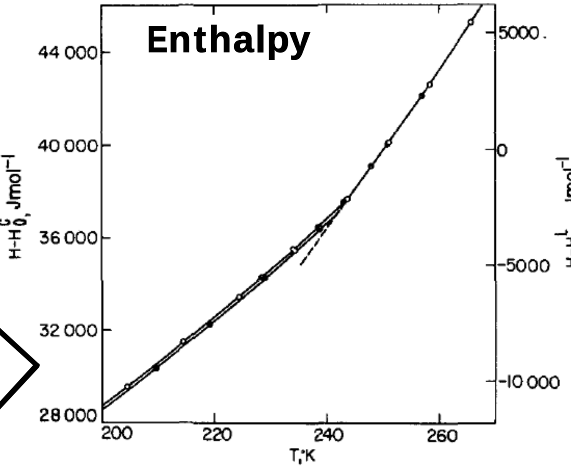
Effect of the cooling rate

Example of ortho-terphenyl

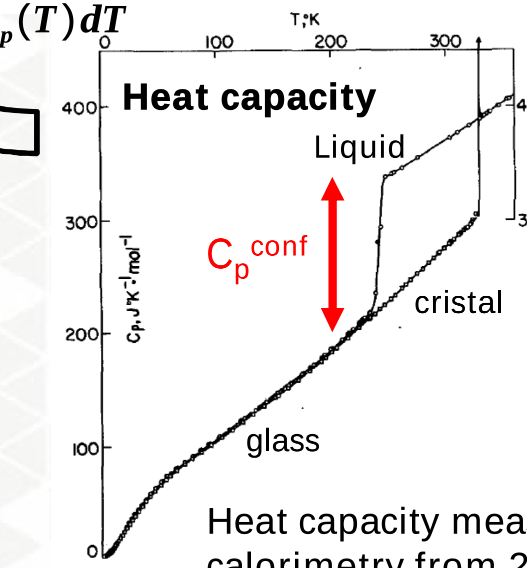


Chang, S. S., and A. B. Bestul. 1972. The Journal of Chemical Physics 56 (1): 503–16

Naoki, M., and S. Koeda. 1989. The Journal of Physical Chemistry 93 (2): 948–55

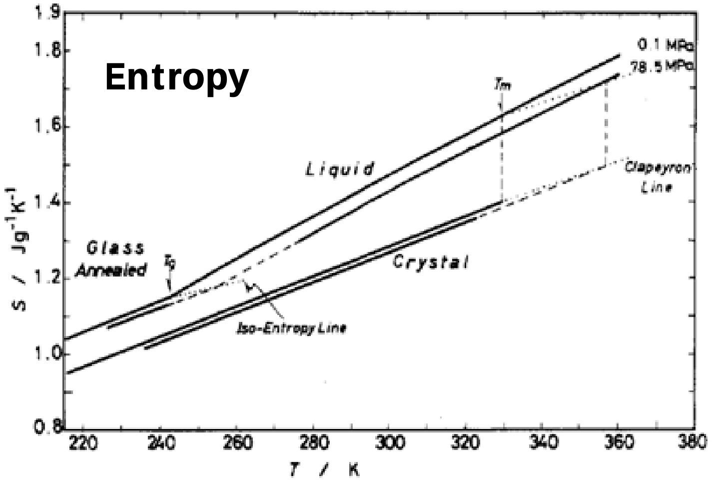

Enthalpy

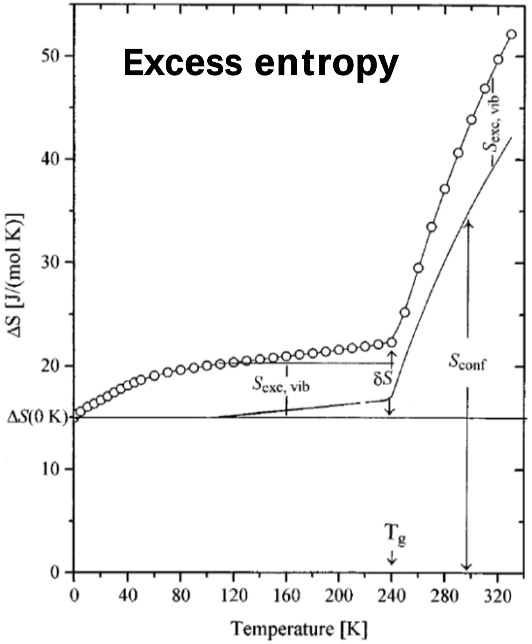
$$\int_0^T C_p(T)\,dT$$


Heat capacity

Heat capacity measured by adiabatic calorimetry from 2 to 360 K

$$\int_0^T C_p(T)/T\,dT$$

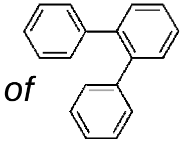

Entropy


Excess entropy

Johari, G. P. 2000. The Journal of Chemical Physics 112 (20)

Example of ortho-terphenyl

Naoki, M., and S. Koeda. 1989. *The Journal of Physical Chemistry* 93 (2): 948–55



Mercury pressure dilatometer
V(T) at constant p
V(P) at constant T

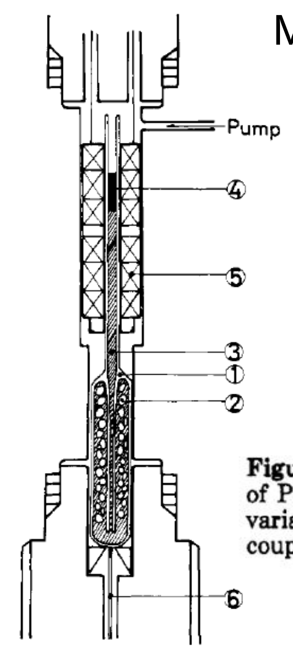
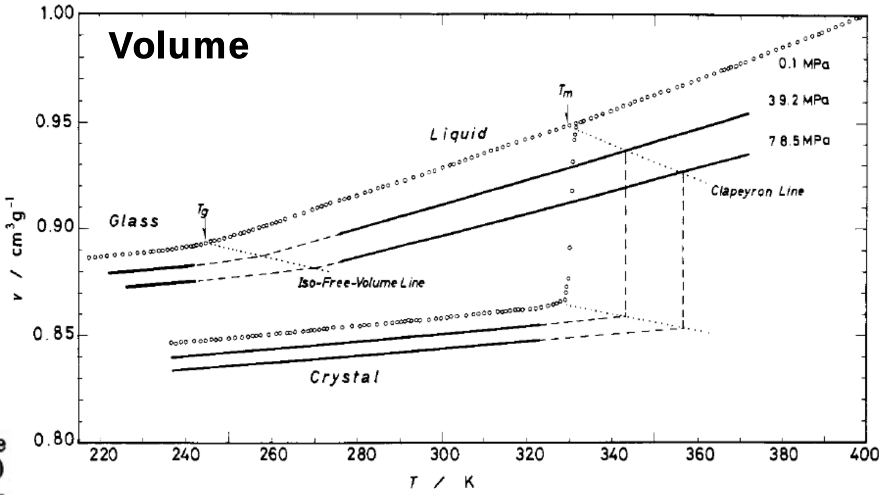
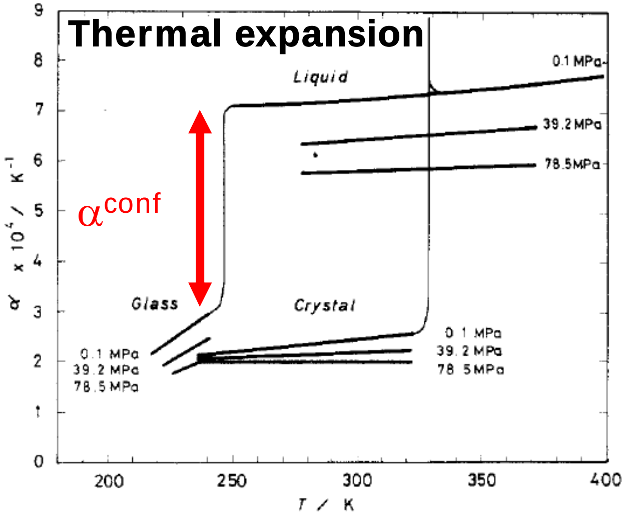


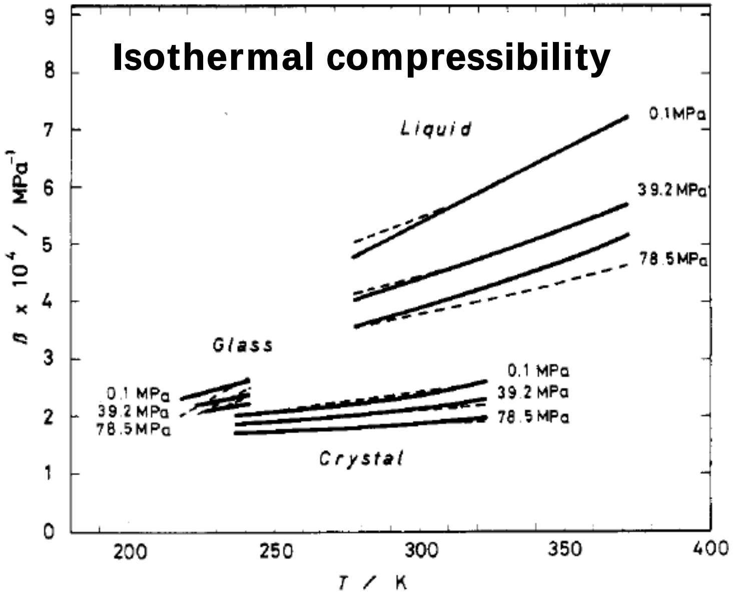
Figure 2. Diagram of pressure dilatometer: (1) dilatometer made of Pyrex glass; (2) sample; (3) mercury; (4) Permalloy; (5) variable differential transformer; (6) alumel–chromel thermocouple.



Volume



Thermal expansion



Isothermal compressibility

Glass description using the thermodynamic theory of irreversible processes

- For a given composition, and contrarily to what is observed for equilibrium phases like crystals or liquids
  - The state of a glass does not only depend on T and p
  - **At least one (or possibly more than one) additional thermodynamic variable(s) is (are) necessary to represent the internal state of the glass**
  - **Such variables are called structural (or internal) order parameters ξ_i**
  - Physically they might represent the number of holes or vacancies in the liquid, the number of broken or flexed bonds of various types, the number of sites with a particular coordination geometry… (Moynihan, Gupta 1976)
- Assuming that only one order parameter is required to describe the state of the glass/liquid (simplest hypothesis)
  - Using a lattice-hole model (Möller, Gutzow & Schmelzer 2006),
    - ξ = fraction of free volume
    - $0 \le \xi \le 1$
    - $\xi = 0$ for the perfectly ordered crystal
    - $\xi = 1$ for the complete disordered state (gas)
  - **The value of this parameter is frozen at the glass transition**

Glass description using the thermodynamic theory of irreversible processes

- In a closed system, any thermodynamic function (G, H, S...) is then a function of the 3 variables T, p and ξ :
- For the Gibbs energy:

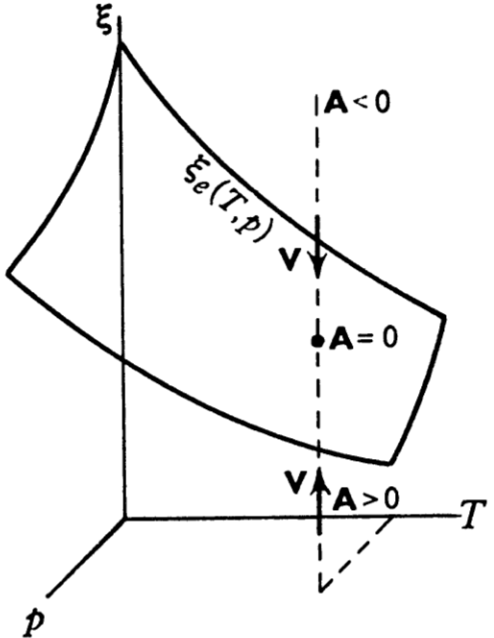
$$G=G(T,p,\xi)$$

$$dG=\left(\frac{\partial G}{\partial T}\right)_{p,\xi} dT+\left(\frac{\partial G}{\partial p}\right)_{T,\xi} dp+\left(\frac{\partial G}{\partial \xi}\right)_{T,p} d\xi$$

- By introducing the affinity : $A=-\left(\frac{\partial G}{\partial \xi}\right)_{T,p}$

$$dG=-S\,dT+V\,dp-A\,d\xi$$

- At equilibrium A = 0 and $\xi=\xi_e(T,p)$



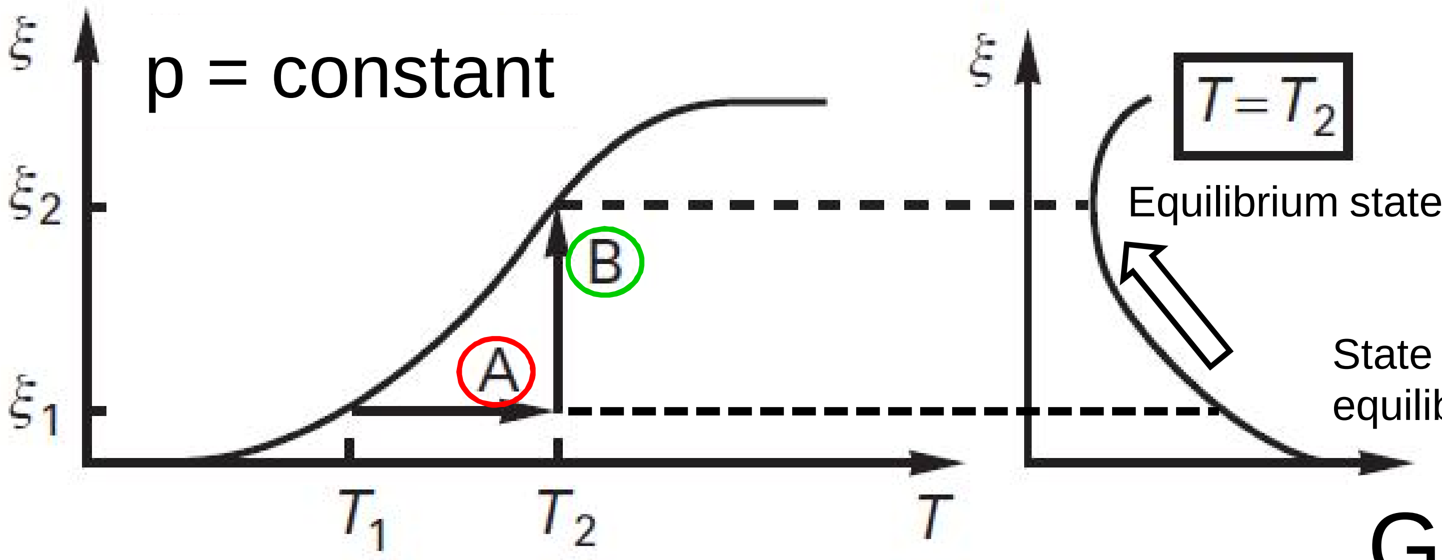
(From Prigogine and Defay 1954)

- **The experimentalist can arbitrarily control T(t) and p(t) ...**
- **... but not $v=\frac{d\xi(t)}{dt}$ which depends on the state of the system**

Order parameter evolution during a quick temperature change

Equilibrium value of the order parameter

Evolution of ξ to minimize G



p = constant

Equilibrium state at T_2

State out of equilibrium at T_2

G

A = quick temperature change from T_1 to T_2

B = gradual approach of the equilibrium state at T_2

(Adapted from Hillert 2007)

Jumps in the thermodynamic coefficients – configurational functions

- The thermodynamic quantities
  - at constant A = 0 correspond to the stable or metastable equilibrium liquid
  - at constant ξ (frozen structure) correspond to the glass
- It can be shown that:

$$C_{p,A=0}=C_{p,\xi}+\left(\frac{\partial H}{\partial \xi}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_{p,A=0}=C_{p,\xi}+\overbrace{\underbrace{\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{p,T}}_{>0\ \text{stability condition}}\underbrace{\left(\frac{\partial \xi}{\partial T}\right)^2_{p,A=0}}_{>0}}^{>0}$$

$$\underset{\text{Liquid}}{C_{p,A=0}}=\underset{\text{Glass}}{C_{p,\xi}}+\underset{\text{Jump}}{C_p^{conf}}\ \text{and}\ \boxed{C_p^{conf}>0}$$

- Similarly

$$\kappa_{T,A=0}=\kappa_{T,\xi}-\frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{T,p}\left(\frac{\partial \xi}{\partial p}\right)_{T,A=0}=\kappa_{T,\xi}+\frac{1}{V}\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}\left(\frac{\partial \xi}{\partial p}\right)^2_{T,A=0}$$

$$\kappa_{T,A=0}=\kappa_{T,\xi}+\kappa_T^{conf}\ \text{and}\ \boxed{\kappa_T^{conf}>0}$$

$$\alpha_{A=0}=\alpha_\xi+\frac{1}{V}\left(\frac{\partial V}{\partial \xi}\right)_{T,p}\left(\frac{\partial \xi}{\partial T}\right)_{p,A=0}=\alpha_\xi-\frac{1}{V}\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,p}\left(\frac{\partial \xi}{\partial p}\right)_{T,A=0}\left(\frac{\partial \xi}{\partial T}\right)_{p,A=0}$$

$$\alpha_{A=0}=\alpha_\xi+\alpha^{conf}\ \text{and}\ \boxed{\alpha^{conf}>0\ \text{or}<0}$$

(From Prigogine and Defay 1954)

To summarize

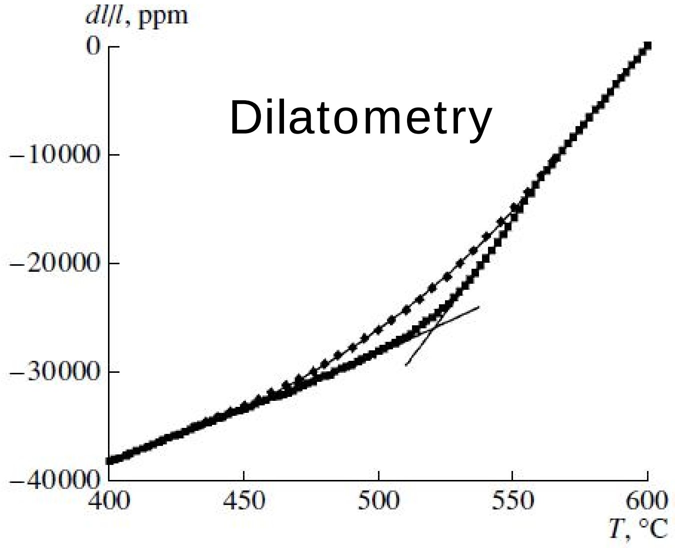
- If we restrict the scope of the presentation to the (T, S) couple of thermodynamic conjugate variables
- Knowing the thermodynamic properties of the crystal and the equilibrium liquid
- The relevant thermodynamic quantities which can be experimentally determined to define the thermodynamic state of the glass are
  - The glass transition temperature
  - The heat capacity of the glass and the magnitude of the heat capacity jump at the glass transition
  - The frozen-in value of the enthalpy
  - The frozen-in value of the entropy

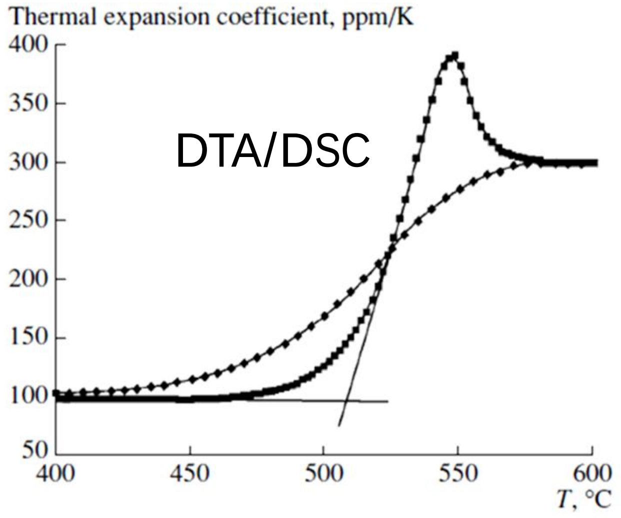
Measurement of the glass transition temperature T_g

Graphical T_g determinations

- According to Mazurin
  - T_g is determined by dilatometry or DTA/DSC in 99 % of the published papers
- For determining the T_g, he recommends that
  - The rate of cooling from above the glass transition interval should be equal to the rate of subsequent heating
  - This rate should be 10 K/min in DTA/DSC and 5 K/min in dilatometry
  - To adopt the linear extrapolation constructions hereto

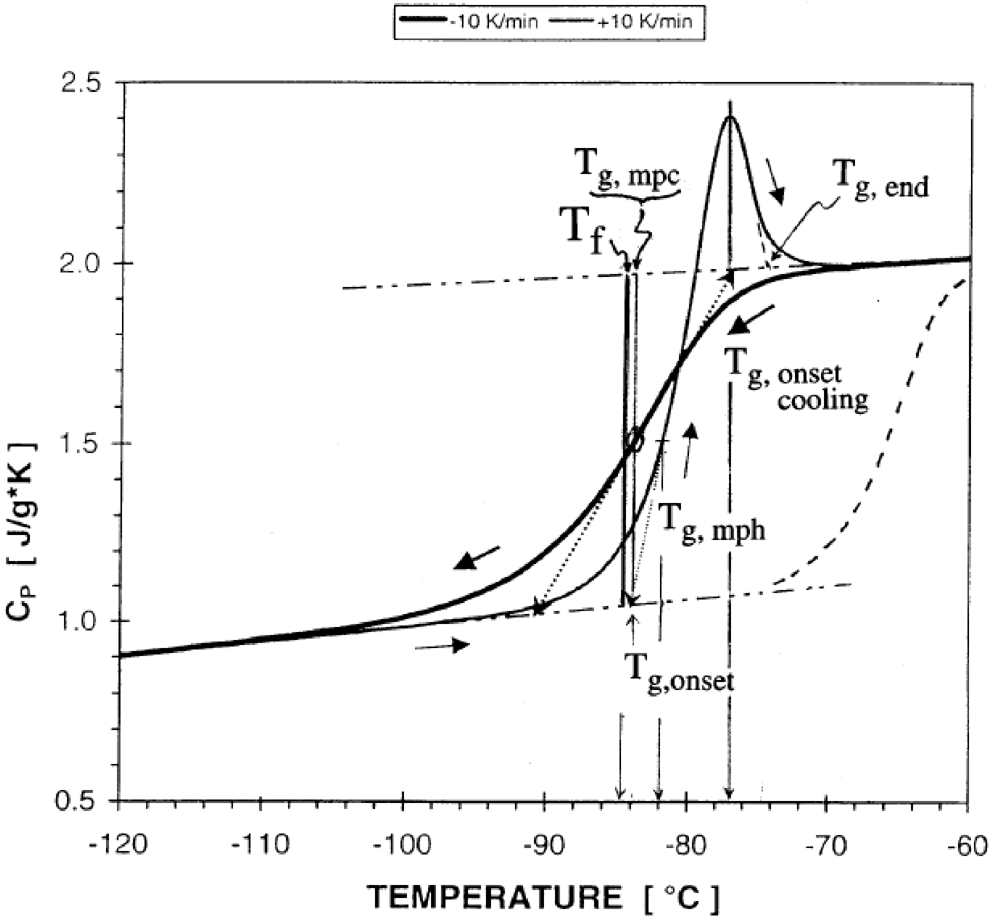
Mazurin, O. V. 2007. "Problems of Compatibility of the Values of Glass Transition Temperatures Published in the World Literature." Glass Physics and Chemistry 33 (1): 22–36





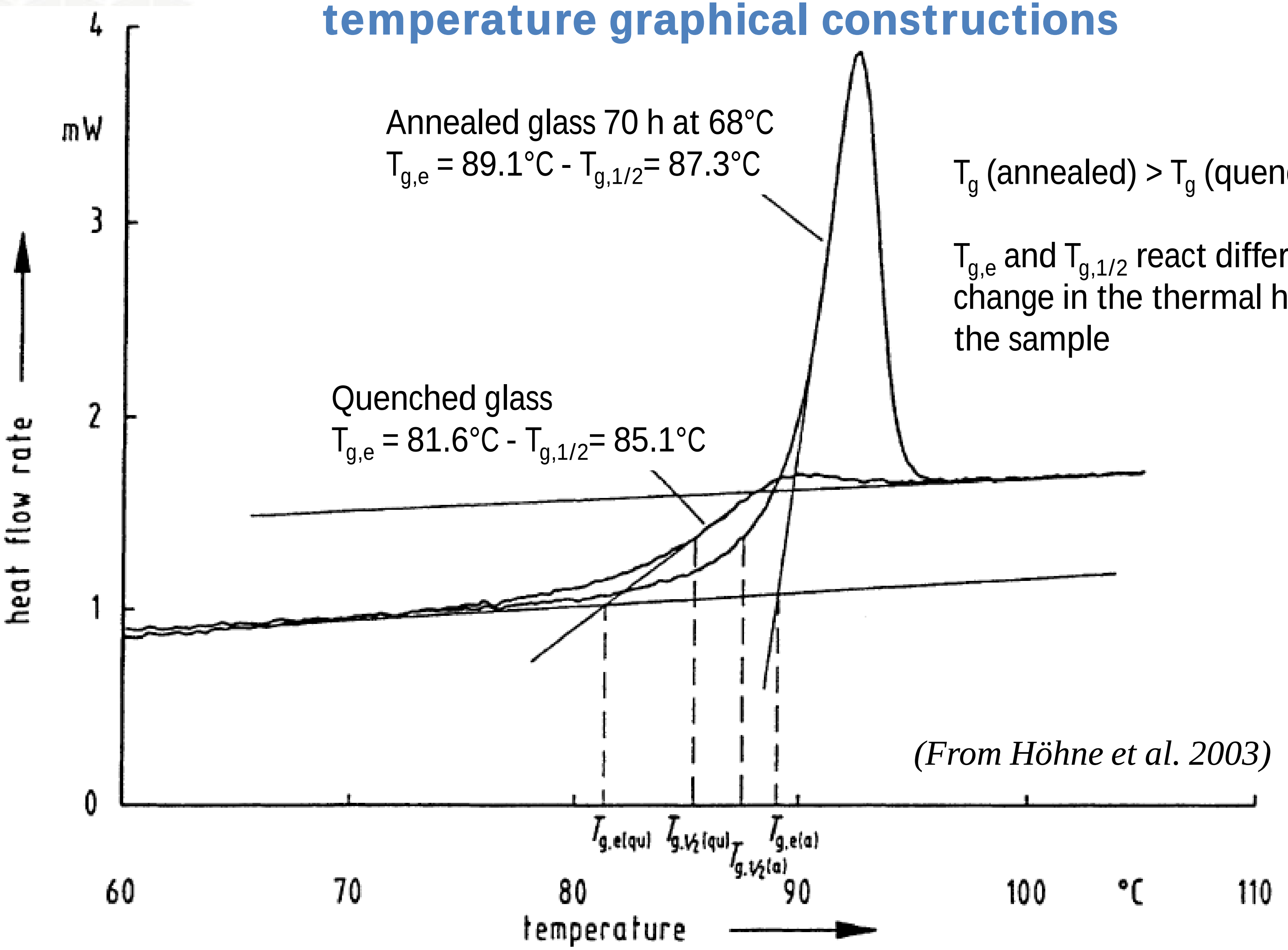
Graphical T_g determinations

- Various characteristic temperatures are used in literature
- They are obtained by graphical constructions from the cooling or the heating DSC curves
  - Extrapolated onset
  - Mid point also called half-step
  - Inflexion point
  - …
- These graphical methods are easy to apply
- But can give paradoxical results in some cases



Angell, C.A. 2002. “Liquid Fragility and the Glass Transition in Water and Aqueous Solutions.” Chemical Reviews 102: 2627–50

Drawbacks of the extrapolated onset or mid-point/half-step temperature graphical constructions



Annealed glass 70 h at 68°C
$T_{g,e}$ = 89.1°C - $T_{g,1/2}$= 87.3°C

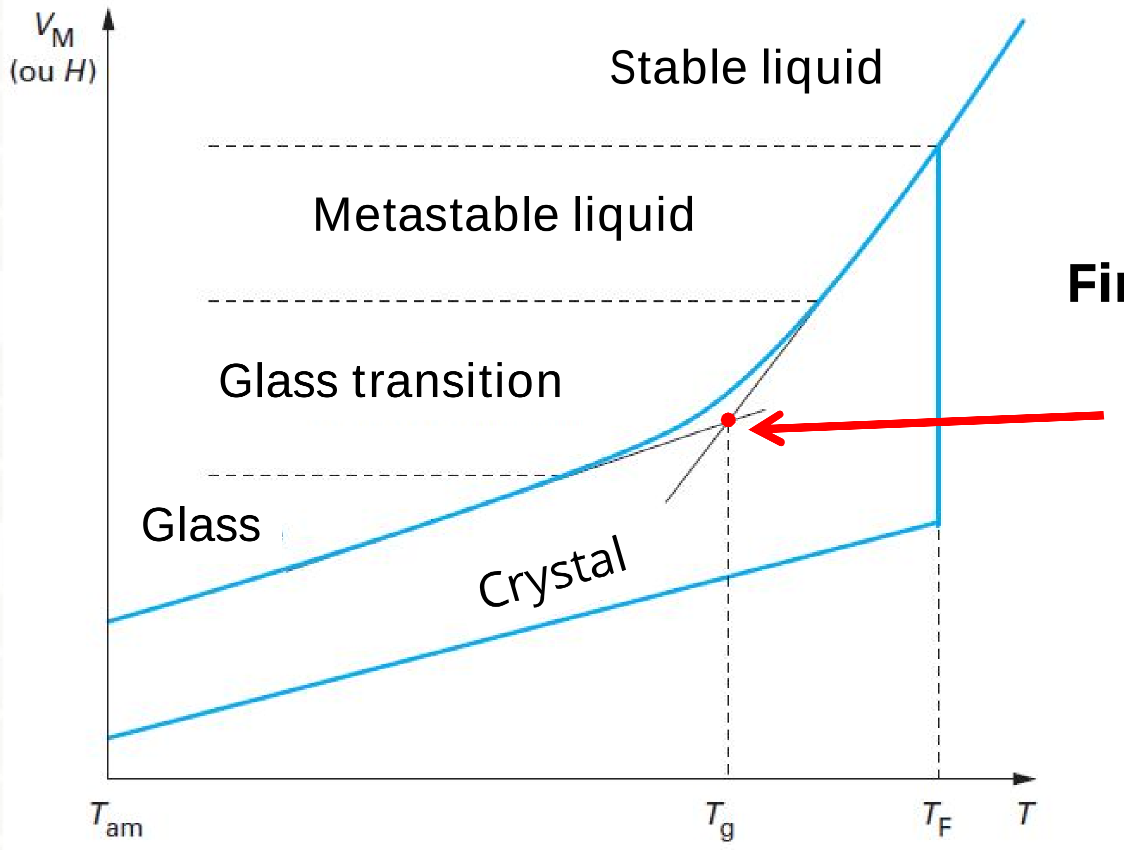
Quenched glass
$T_{g,e}$ = 81.6°C - $T_{g,1/2}$= 85.1°C

T_g (annealed) > T_g (quenched) ???

$T_{g,e}$ and $T_{g,1/2}$ react differently to a change in the thermal history of the sample

(From Höhne et al. 2003)

Thermodynamic definition of the fictive temperature

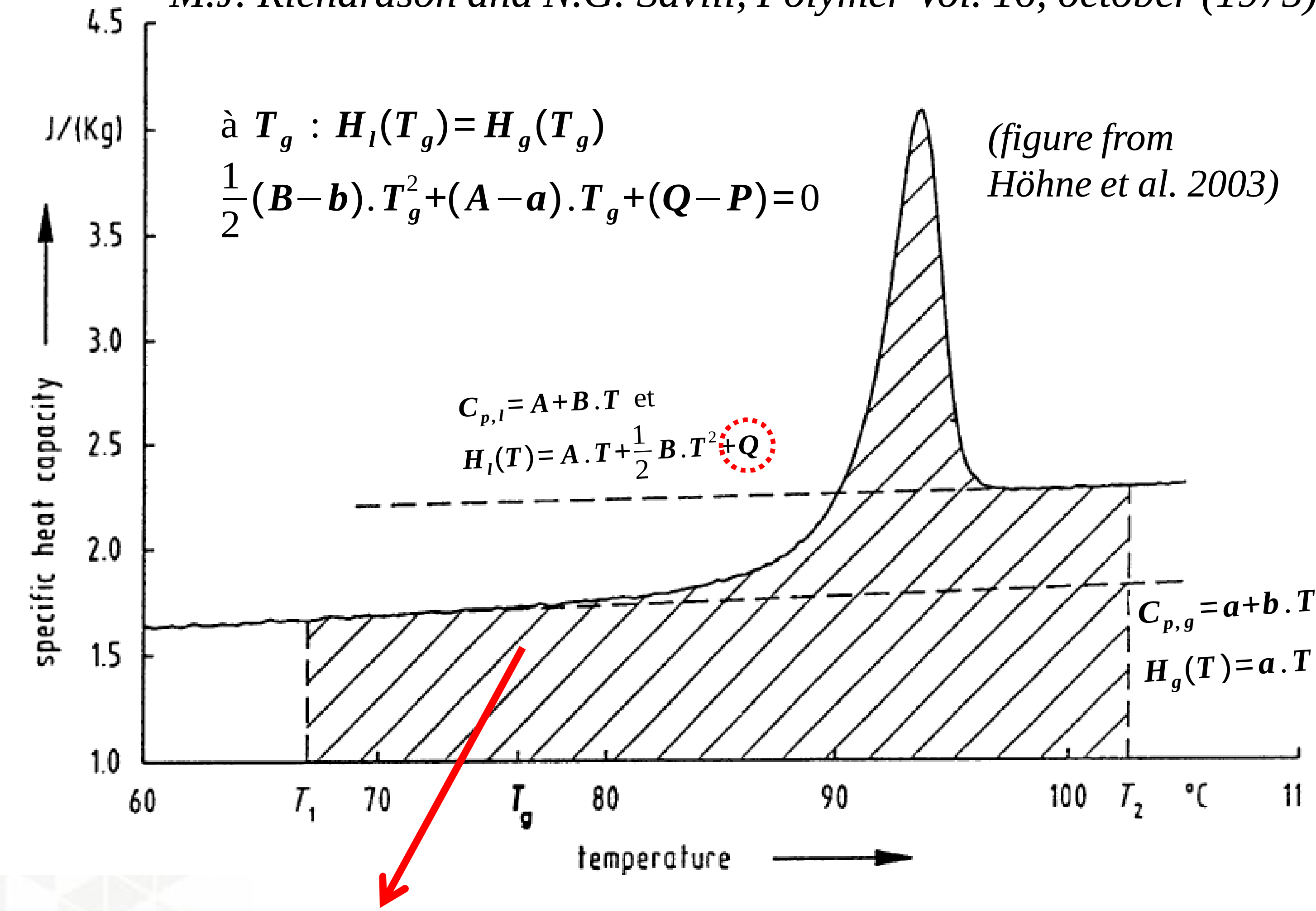


Find the T_g for which:

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

Richardson and Savill method

M.J. Richardson and N.G. Savill, Polymer Vol. 16, october (1975) pp. 753-57



(figure from Höhne et al. 2003)

à T_g : $H_l(T_g)=H_g(T_g)$

$$\frac{1}{2}(B-b).T_g^2+(A-a).T_g+(Q-P)=0$$

$C_{p,l}=A+B.T$ et

$H_l(T)=A.T+\frac{1}{2}B.T^2\boxed{+Q}$

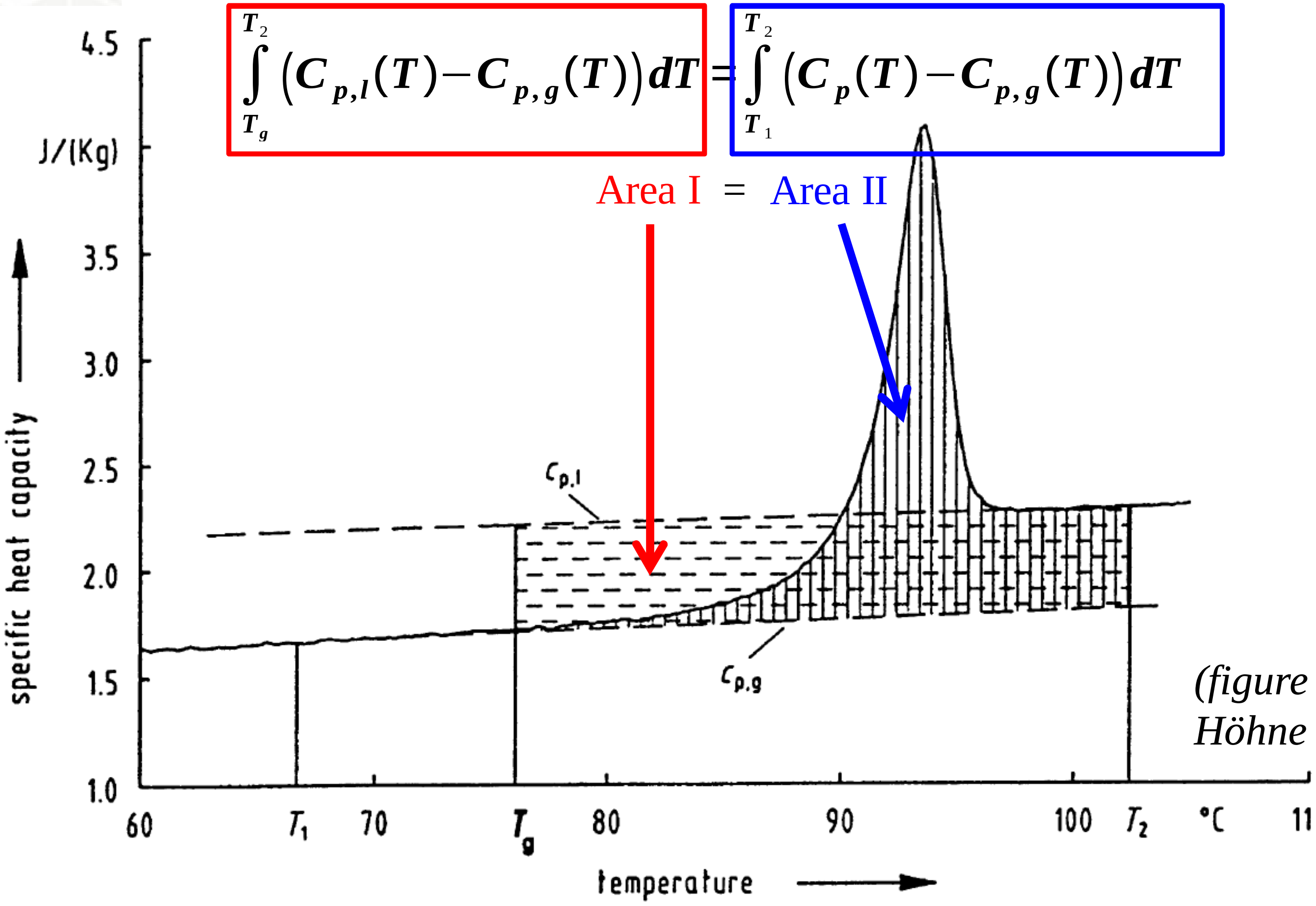
$C_{p,g}=a+b.T$ et

$H_g(T)=a.T+\frac{1}{2}b.T^2\boxed{+P}$

Hatched area = $H_l(T_2)-H_g(T_1)=A.T_2-a.T_1+\frac{1}{2}B.T_2^2-\frac{1}{2}b.T_1^2\boxed{+(Q-P)}$

Moynihan et al. method (1)

C. T. Moynihan, A. J. Easteal, M. A. De Bolt, Journal of the American Ceramic Society, Vol. 59, No. 1- 2 (1976) pp.12-16



$$\int_{T_g}^{T_2} \left(C_{p,l}(T) - C_{p,g}(T)\right) dT = \int_{T_1}^{T_2} \left(C_p(T) - C_{p,g}(T)\right) dT$$

Area I = Area II

(figure from Höhne et al. 2003)

Moynihan et al. method (2)

- Proof of the graphical construction

$$\int_{T_g}^{T_2} \left(C_{p,l}(T) - C_{p,g}(T)\right) dT = \int_{T_1}^{T_2} \left(C_p(T) - C_{p,g}(T)\right) dT$$

$$\int_{T_g}^{T_2} C_{p,l}(T)\,dT - \int_{T_g}^{T_2} C_{p,g}(T)\,dT = \int_{T_1}^{T_2} C_p(T)\,dT - \int_{T_1}^{T_2} C_{p,g}(T)\,dT$$

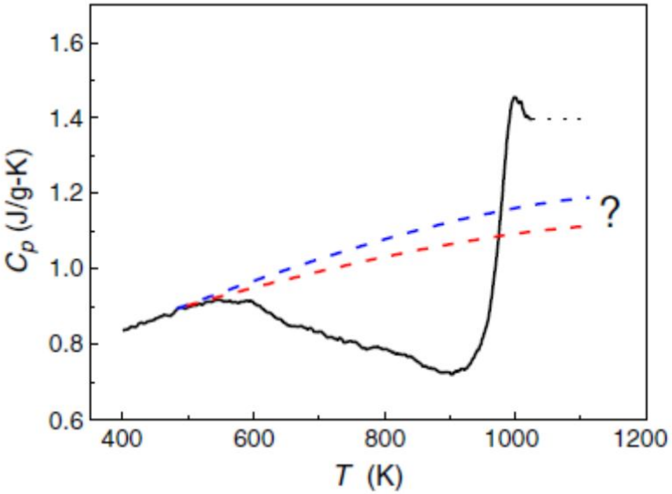
$$\cancel{H_l(T_2)} - H_l(T_g) - \left(\cancel{H_g(T_2)} - H_g(T_g)\right) = \cancel{H_l(T_2)} - \cancel{H_g(T_1)} - \left(\cancel{H_g(T_2)} - \cancel{H_g(T_1)}\right)$$

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

Guo et al. method (1)

X. Guo, M. Potuzak, J.C. Mauro, D.C. Allan, T.J. Kiczenski, Y. Yue, Unified approach for determining the enthalpic fictive temperature of glasses with arbitrary thermal history, J. Non. Cryst. Solids. 357 (2011) 3230–3236.

- The Richardson and Savill or Moynihan et al. methods require the DSC heating rate (R) to be comparable to the cooling rate (q) used to obtain the glass sample
  - Not appropriate for hyper-quenched glasses for which
    - $q \approx 10^6$ K/s >> $R \approx 10$ - 20 K/min classical DSC scan rates
  - Difficulty to extrapolate the C_p of the glass in the liquid domain



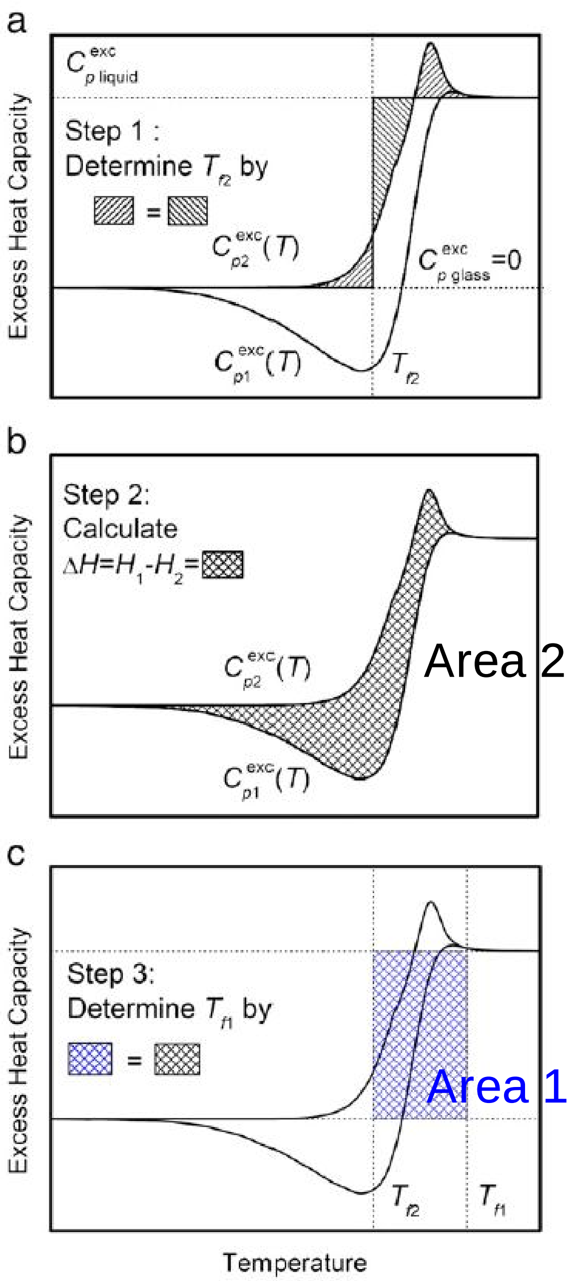
DSC heating scan at 20K / min on an hyper-quenched glass

Guo et al. method (2)

- General method appropriate for all glasses obtained under isobar conditions
  - The result is independent of the kinetic effects occurring on heating in the DSC
  - It is not necessary to know the thermal history of the glass prior to the measurement
- Principle
  - Comparison of the $C_{p1}(T)$ and $C_{p2}(T)$ curves obtained during two consecutive upscans at the same rate
  - A downscan is interposed between the two upscans
  - No constraint on the heating rate

$$\underbrace{\int_{T_{f2}}^{T_{f1}} \left(C_{p\,\mathrm{liquid}} - C_{p\,\mathrm{glass}}\right) dT}_{\text{Area 1}} = \underbrace{\int_{0}^{\infty} \left(C_{p2} - C_{p1}\right) dT.}_{\text{Area 2}}$$

Guo, X., M. Potuzak, J. C. Mauro, D. C. Allan, T. J. Kiczenski, and Y. Yue. 2011. "Unified Approach for Determining the Enthalpic Fictive Temperature of Glasses with Arbitrary Thermal History." Journal of Non-Crystalline Solids 357 (16–17). Elsevier B.V.: 3230–36



Determination of T_{f2}, the fictive T of the rejuvenated glass by Moynihan et al. method

Calculation of the enthalpy difference between the quenched glass and the rejuvenated one

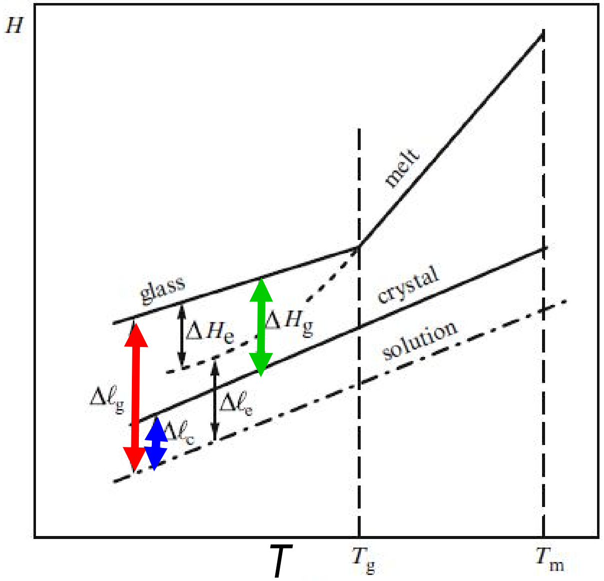
Determination of T_{f1}, the fictive T of the quenched glass by area matching

Measurement of the frozen-in enthalpy

Frozen-in enthalpy ΔH_g determination by isothermal solution calorimetry

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

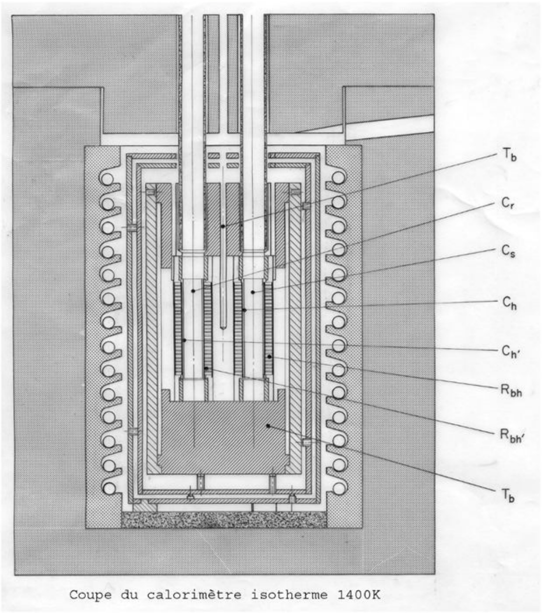
(1)–(2) Glass → Crystal (ΔH_g)
$\Delta H_g = \Delta l_g - \Delta l_c$



- Calorimetric experiments can be performed
  - At room T, in aqueous acid solutions (HF-HNO_3)
  - At high T (700-800°C), in oxide melt (2PbO-B_2O_3)

- For a ternary borosilicate 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)

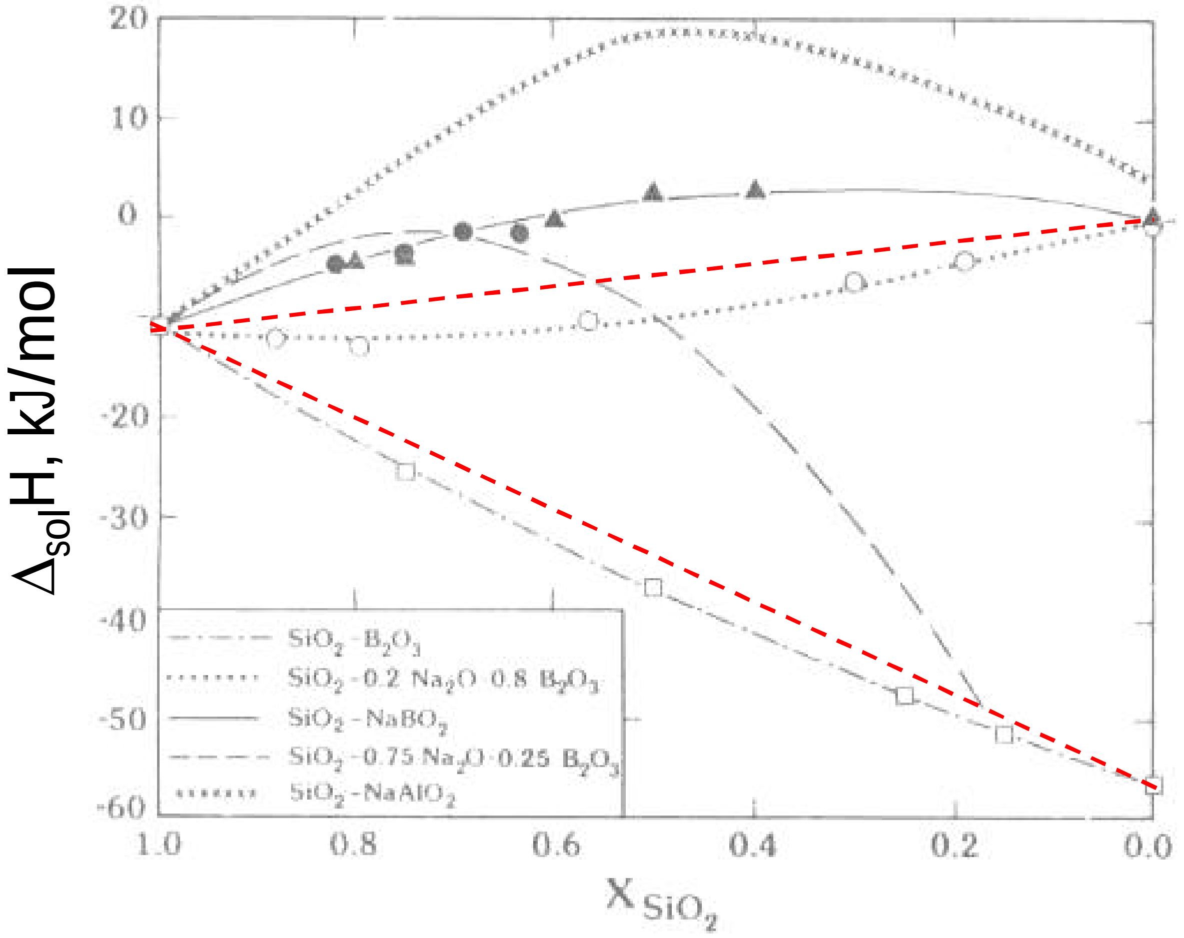
- The glass formation reaction is written as:
  - $x <SiO_2> + y <B_2O_3> + z <Na_2O> \rightarrow$ Glass
  - $\Delta_f H(\text{Glass}) = \Delta_{sol}H^\infty(b) + \Delta_{sol}H^\infty(c) + \Delta_{sol}H^\infty(d) - \Delta_{sol}H^\infty(a)$



Tian-Calvet calorimeter for high T < 1300K solution or drop-solution experiments

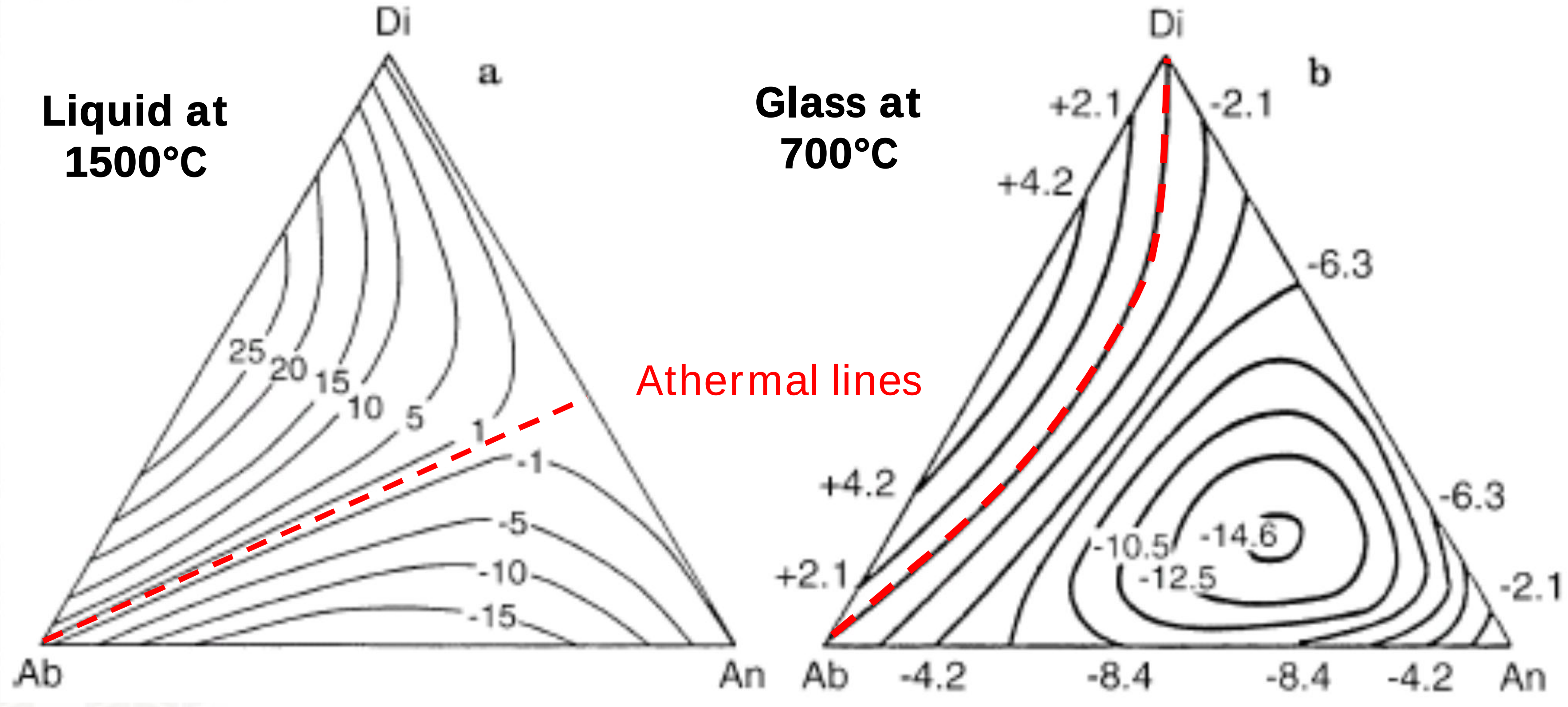
Mixing enthalpies in SiO_2 – B_2O_3 – Na_2O glasses

- Measured by solution calorimetry in $2PbO$-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 ternary liquid and glass

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



Liquid at 1500°C

Glass at 700°C

Athermal lines

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

Conclusions

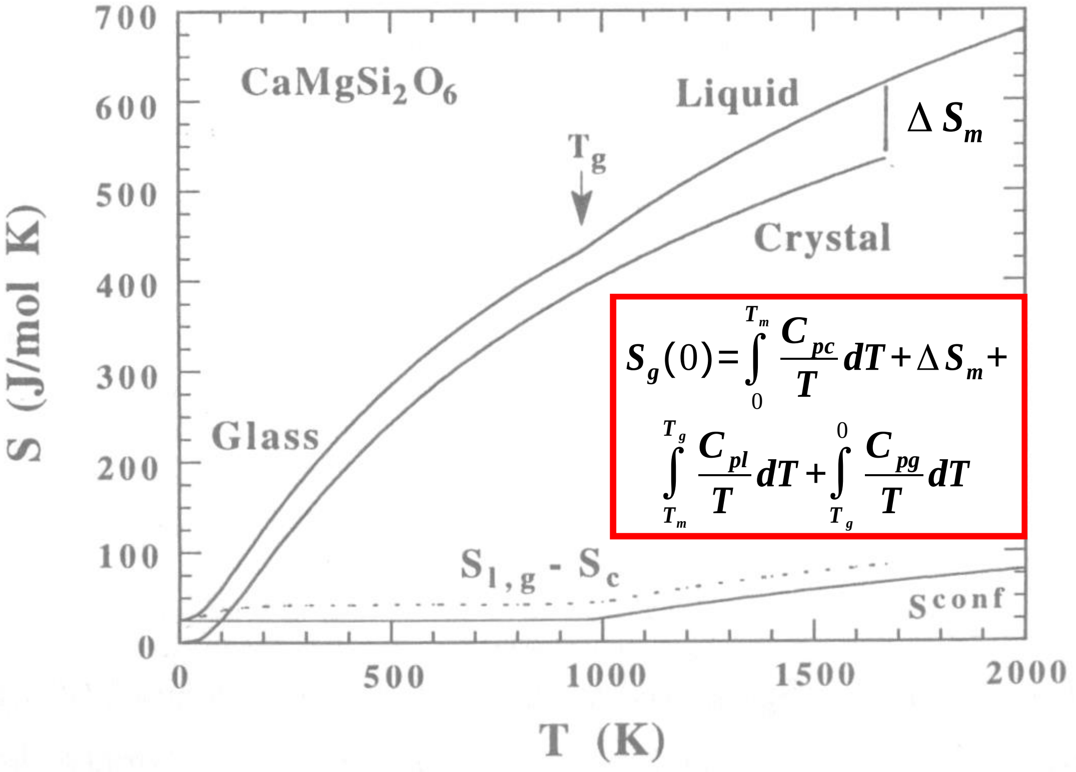
- At T_g a liquid in metastable equilibrium is kinetically frozen into a non thermodynamic equilibrium state: the glass
- The glass transition temperature T_g and the jumps of the thermodynamic coefficients at the transition can be measured
    - $T_{fictive}$ methods should be preferred to graphical constructions
- At $T << T_g$
    - Its frozen-in thermodynamic properties (ΔH_g, ΔS_g) do not evolve and can be measured
- The mixing enthalpies in ternary oxide liquids and glasses
    - Are weak (≈ few kJ/mol)
    - Sometimes endothermic (> 0), the liquid solution and the glass are then only stabilized by the entropy of mixing
    - These solutions can unmix when temperature is lowered

Thank you for your attention

Measurement of the frozen-in entropy

Frozen in entropy ΔS_g determination by calorimetric cycle

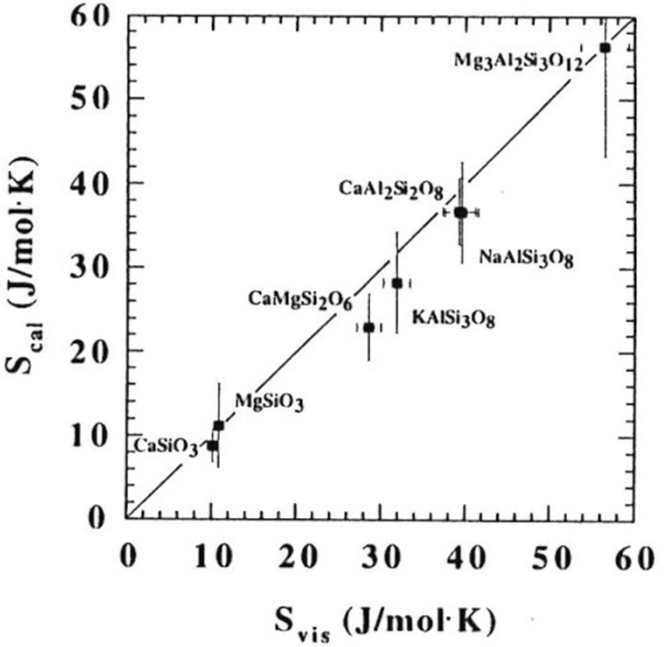
- Combining low temperature adiabatic calorimetry + DSC + drop calorimetry between 0 K and T_m to determine the S(T) curve for the crystal, the liquid and the glass phases
  - Requires that the crystal, the liquid and the glass have the same composition



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

P. Richet and Y. Bottinga, in Struct. Dyn. Prop. Silic. Melts - Rev. Mir 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.

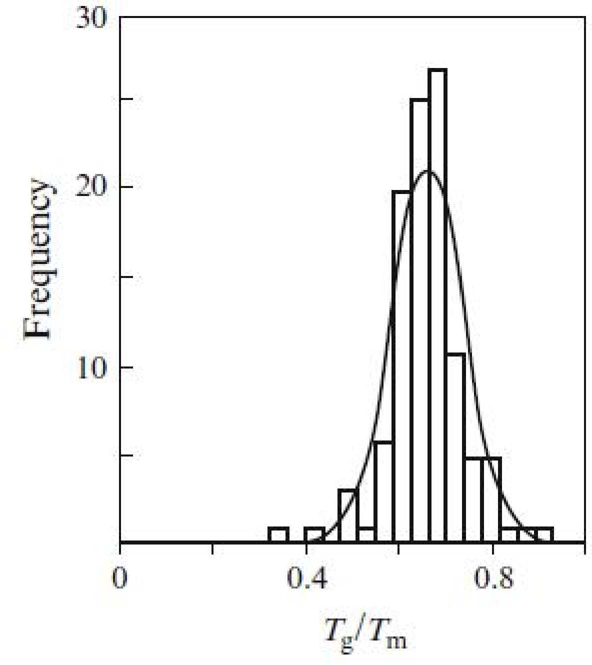
- Entropy can also be derived from viscosity curves on the basis of the Adam-Gibbs theory



Some orders of magnitude

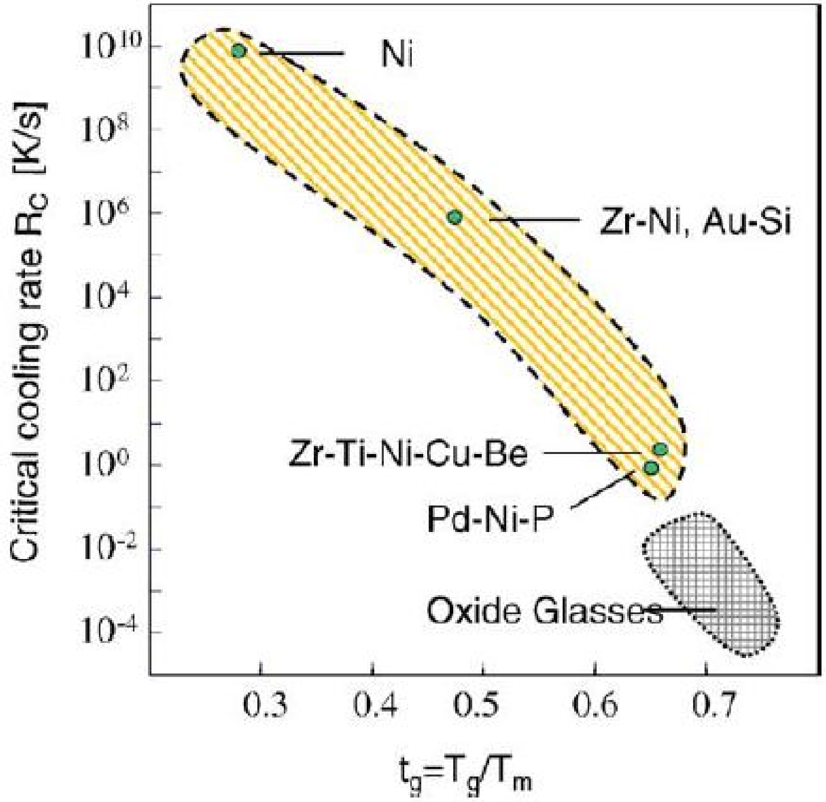
Glass transition temperature T_g

- Dimensionless glass transition temperature
  - Statistics for 108 unary substances which can be vitrified at classical cooling rates



$$\frac{T_g}{T_m} \approx \frac{2}{3}$$ Beaman-Kauzmann rule

From Schmelzer et Gutzow (2011, 2013)

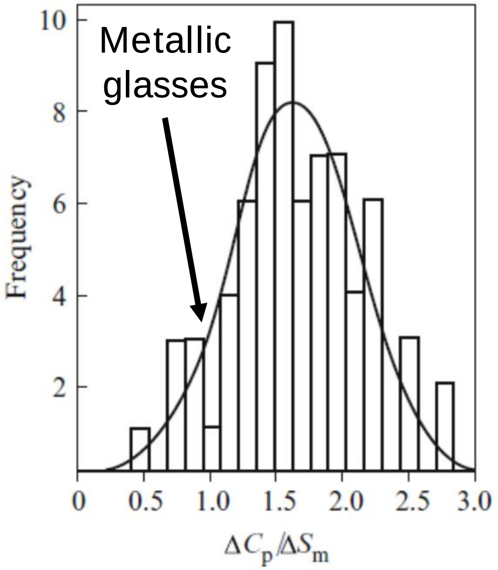


From Fecht & Johnson (2004)

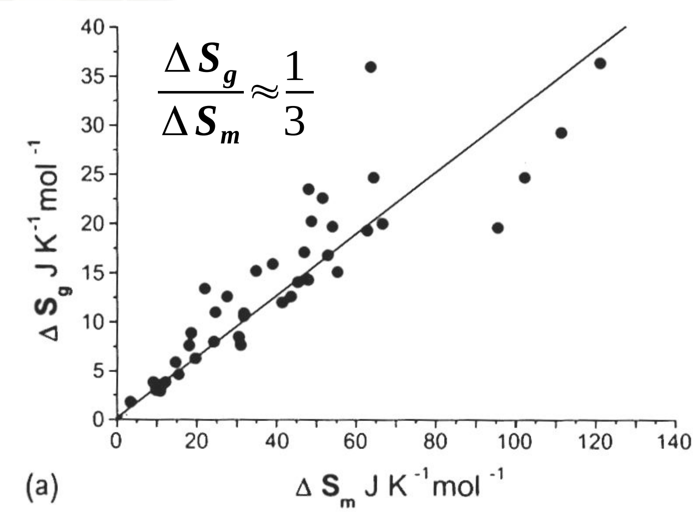
Dimensionless thermodynamic quantities

- Dimensionless C_p jump
  - Statistics from 80 substances

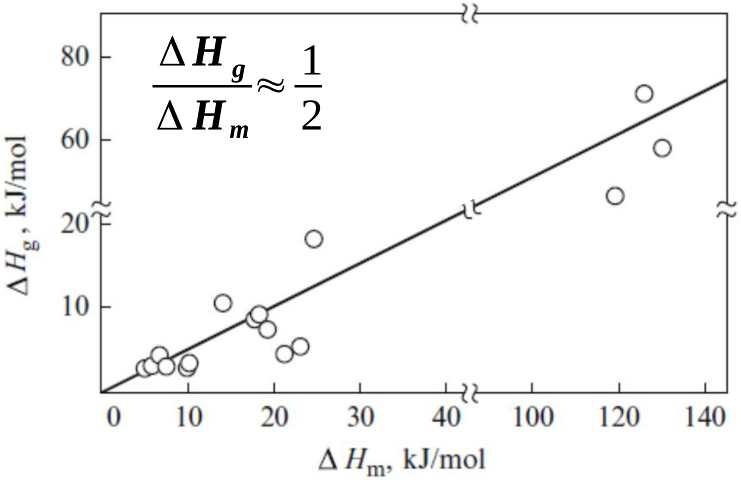
$$\frac{\Delta C_p(T_g)}{\Delta S_m} \approx \frac{3}{2}$$



- Frozen-in dimensionless entropy and enthalpy



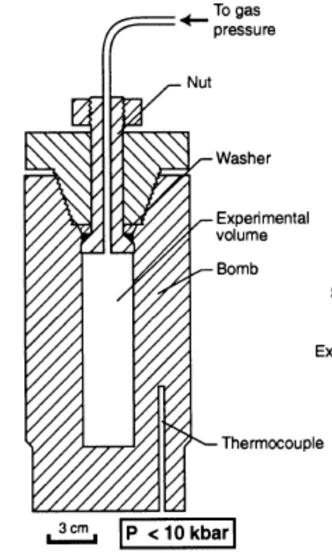
$$\frac{\Delta S_g}{\Delta S_m} \approx \frac{1}{3}$$



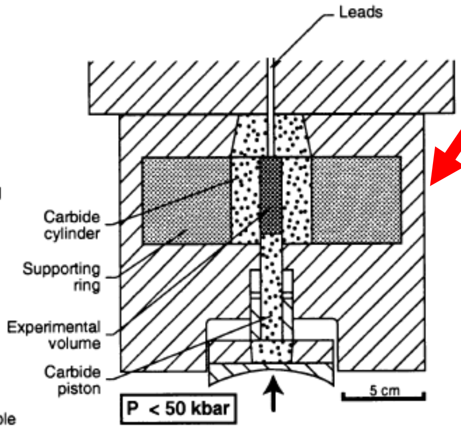
$$\frac{\Delta H_g}{\Delta H_m} \approx \frac{1}{2}$$

From Schmelzer et Gutzow (2011, 2013)

High pressure apparatuses

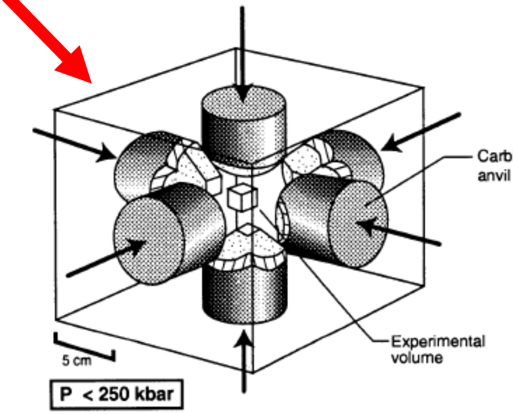


GAS-PRESSURE APPARATUS



PISTON-CYLIND ER APPARATUS

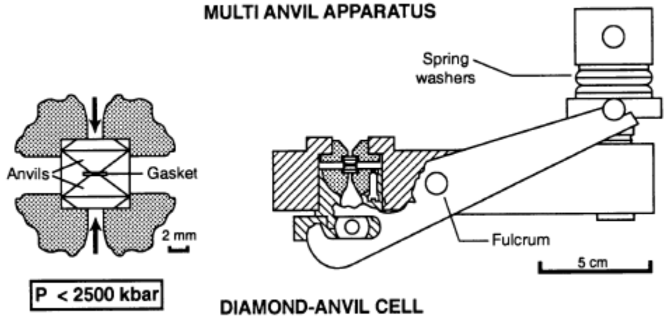
T_{max} = 2000 K if the sample is inserted in a small graphite furnace



MULTI ANVIL APPARATUS

- T_{max} = 1200 K if the autoclave is put in furnace
- T_{max} = 1800 K if a furnace is put in a cooled autoclave

- T_{max} = 1000 K if a small furnace is wired around the diamonds
- T_{max} = several kK if the sample is laser heated



DIAMOND-ANVIL CELL

Shockwaves for Mbar pressures

From Richet, P. 2001. The Physical Basis of Thermodynamics With Applications to Chemistry. Springer