Thermal Analysis

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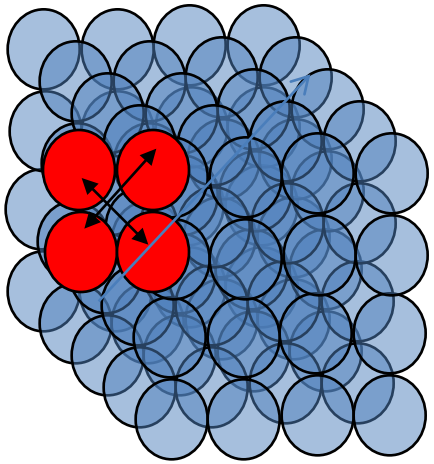
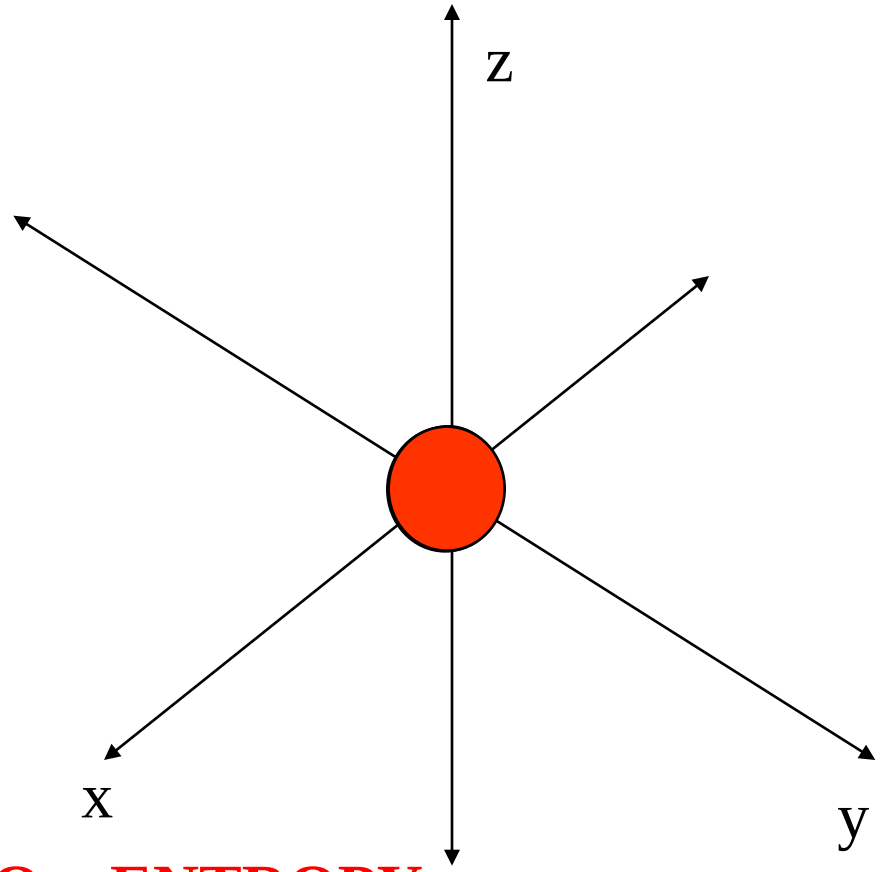
Short Courses POLYCHAR 25
Kuala Lumpur

Thermal Analysis

Definition ? → Temperature, Heat metrology

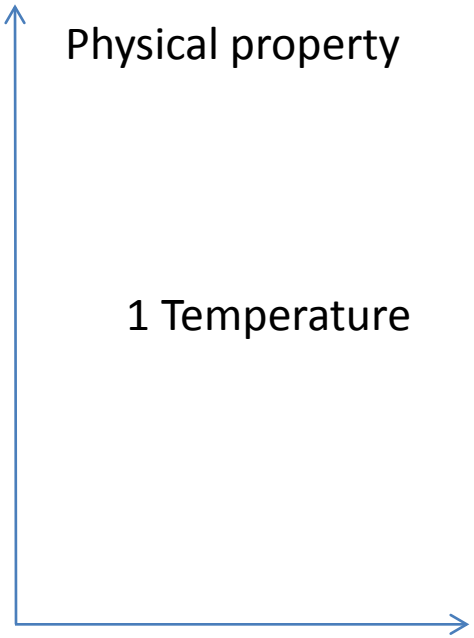


$T_2 > T_1$

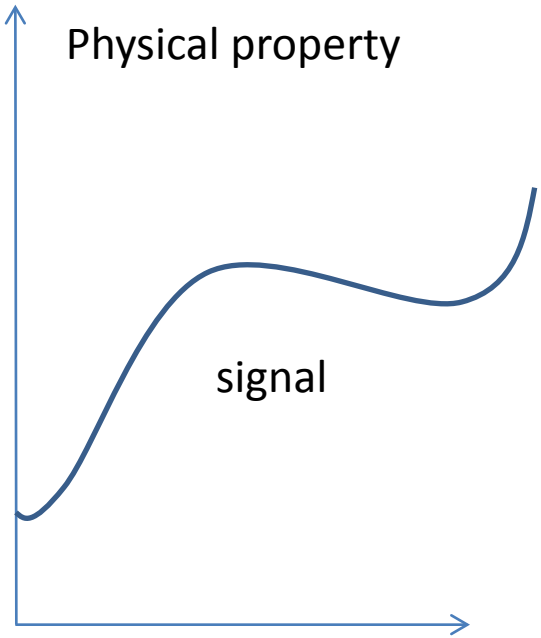


ALL IS LINKED TO : ENTROPY

Thermal Analysis



Isothermal method



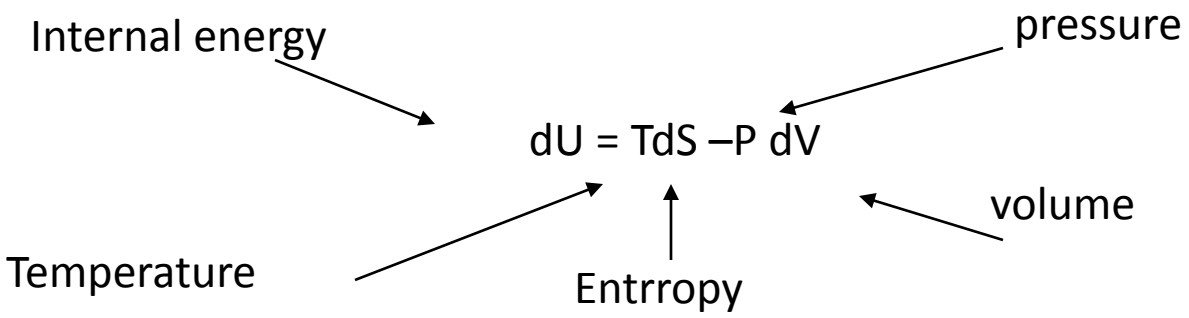
dynamic method

Physical properties

Temperature	Calorimetry adiabatic	T
Delta Temperature	ATD	ΔT
Power (Delta)	DSC	ΔP
Mass	Thermogravimetry	Δm
magnetic		
optical		
Position, distance	dilatation	Δl
Volume	expansion	ΔV
Current	Dielectric constant	
	CDTS	

Plus a fequency

Thermodynamic



Enthalpy → dH = TdS + VdP

Work → dU = d W = dQ if V = cst ← Heat

dH = d W = dQ if P = cst

From Thermodynamic

$$C_p = \left(\frac{\delta Q}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Isothermal compressibility

$$Cp - Cv = \alpha^2 T/\rho\beta_T$$

density

Coef of thermal expansion

Calorimetry

Very important

Heat transfert

Heat capacity

$\Delta Q = mC_p\Delta T$

This is a function of T and phase change

heat

mass

Temperature

This is what i want to know

This is the measurement

Must be a constant

If not we are blind

Before any Calorimetric, measurement, we have to be sure at 100% that no mass loss will occur during the experimental duration.

We never do a DSC measurement to see

We do a DSC measurement to get an answer to one question

Question ?

What the litterature said ?

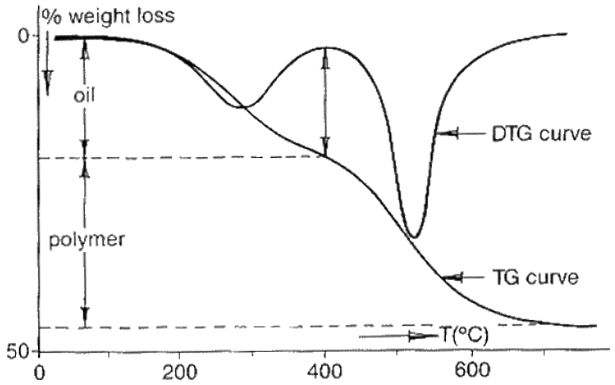
Mass stability
Chemical stability

Sample shape
Sample mass
Temperature domain scanned
Heating rate
Cooling rate
Atmosphere
Kind of calorimeter
Kind of pans

protocole

Thermogravimetry

measurements



Cheking mass constant

Data analysis

Needs

Measurement with a pre calibrated probe

Control of the probe

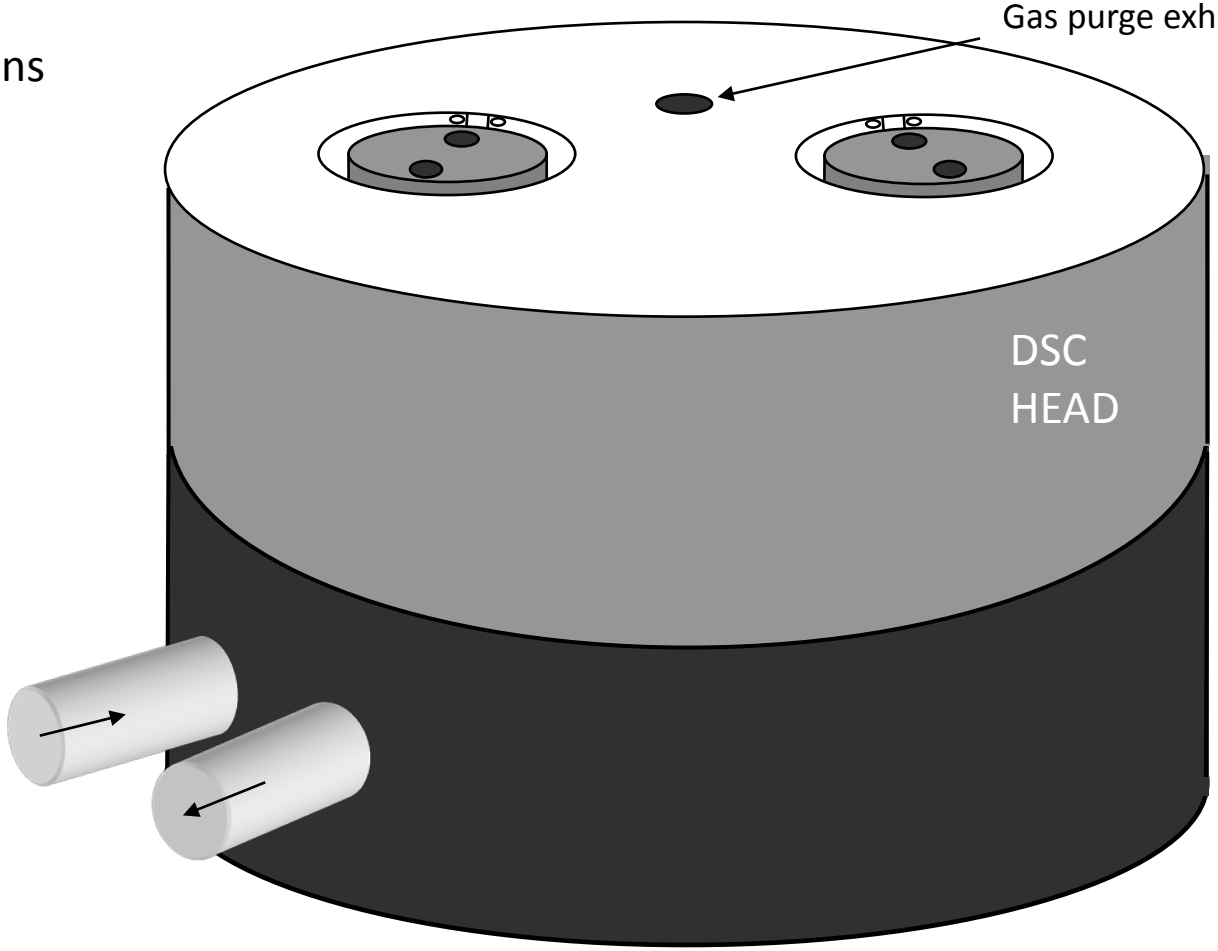
Measurement by a comparison to zero

Control the zero

=

base line

Two owens

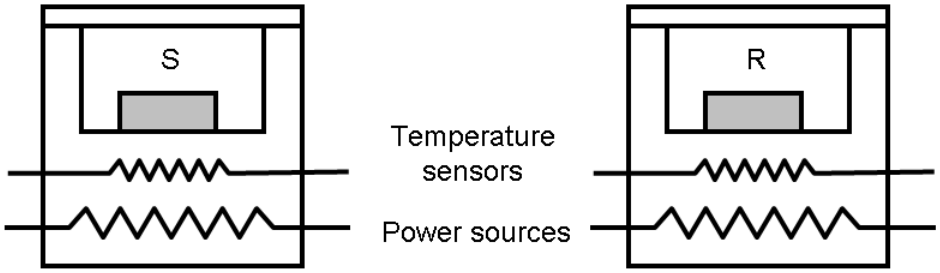


Low inertia

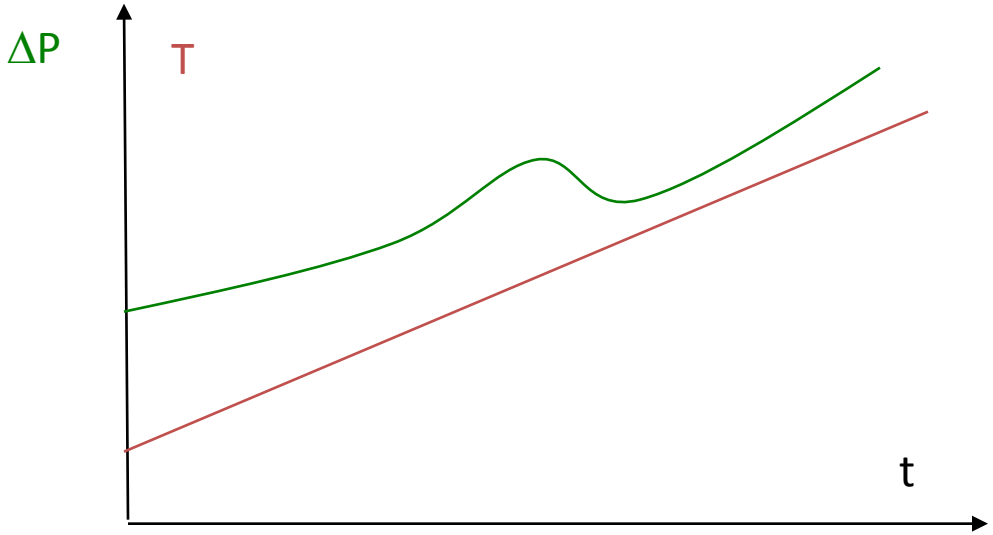
Compensation method

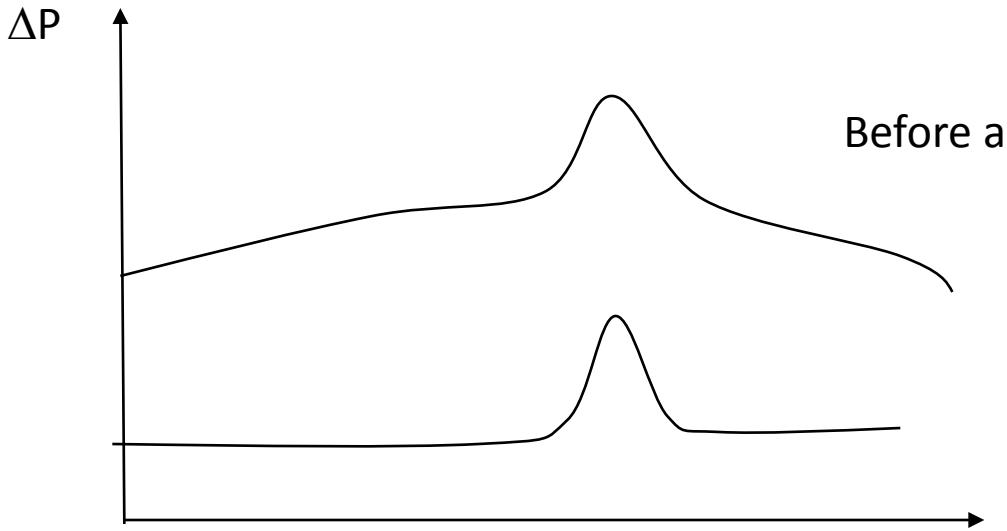
Electronic calibration

$P=UI = RI^2$



Power compensated DSC





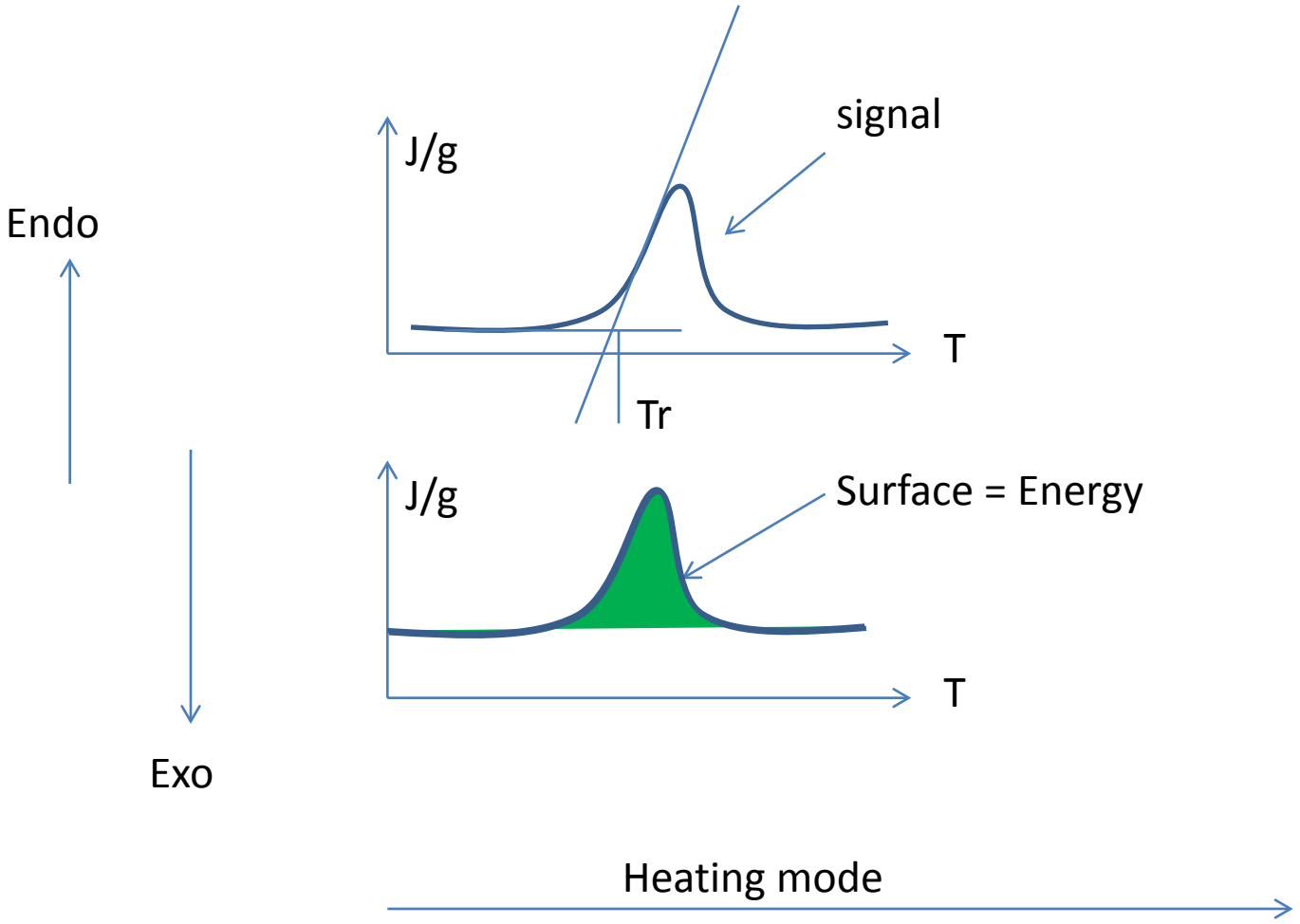
The signal is proportional to

the sample mass

the heating rate

Good balance

How to do to get a good signal by means of DSC measurement



How to do

Best signal

Small sample mass

Small heating Rate

Sample mass increases

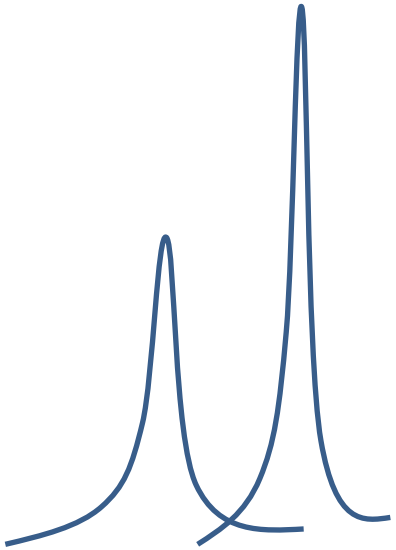
heating Rate increases

What a good calibration is ?

The position of the signal depends upon the heating rate

If q+ increases the T signal increases

This is a effect of the oven geometry and heat transfert inertia

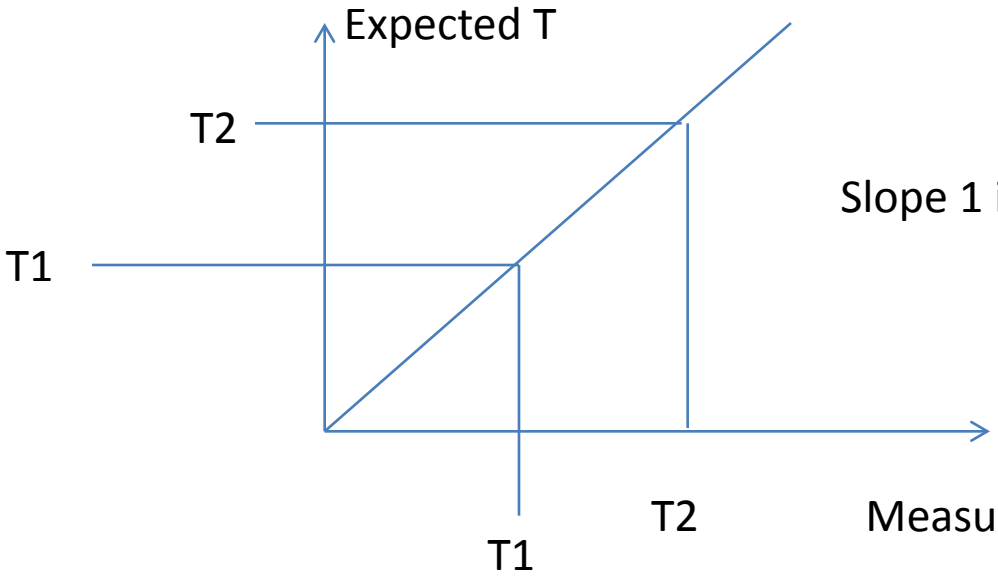


q1 < q2

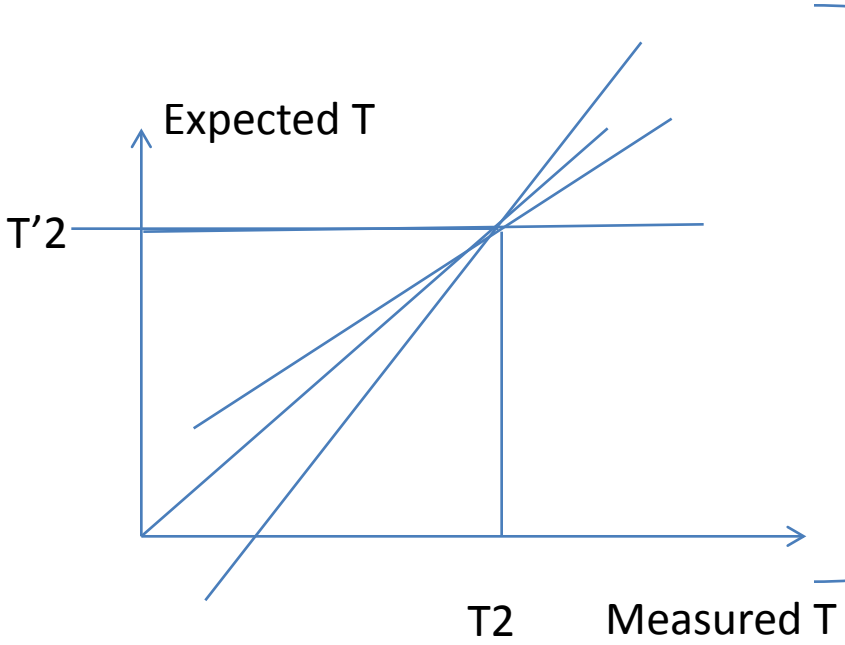
but: the melting temperature of a pure element is an invariant

So we may calibrate the Temperature scale according the values given in the data handbooks

This is true for the surface.

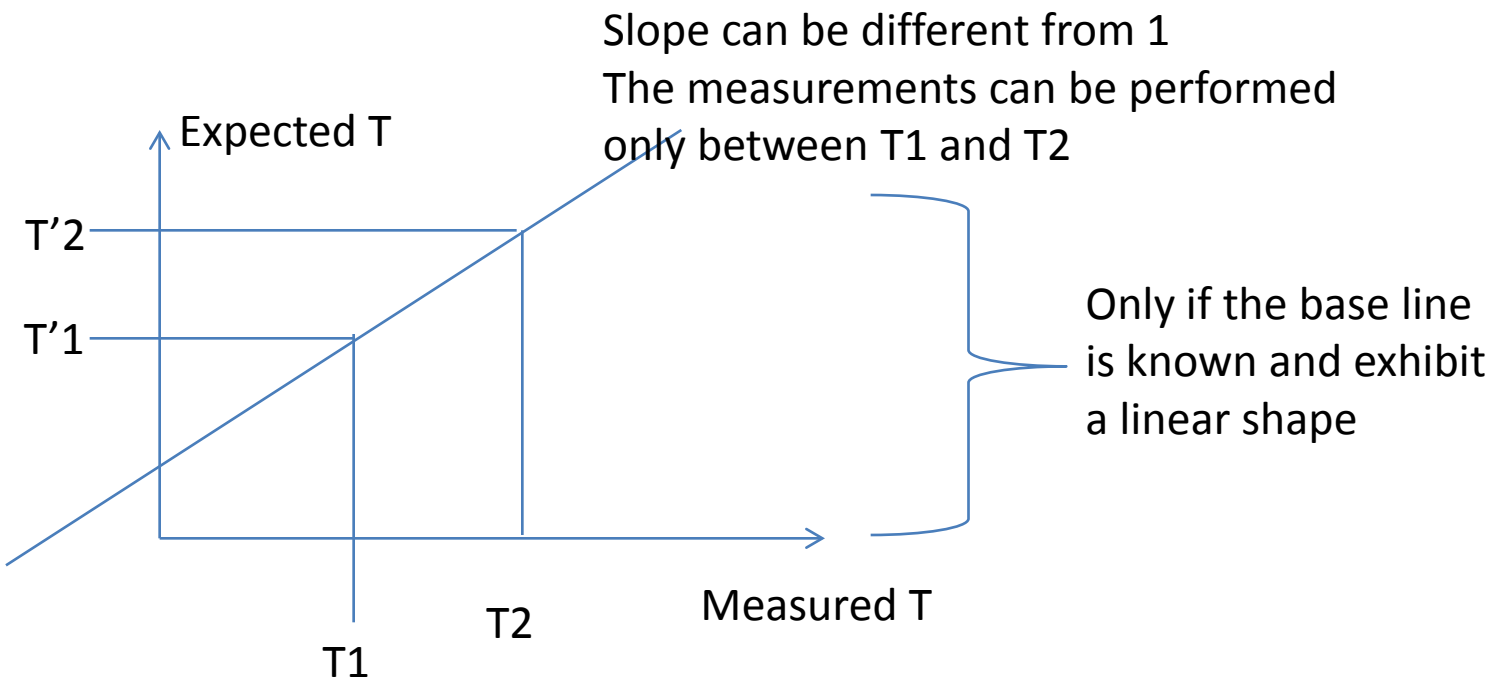


Slope 1 is the best



If only one element is used, i can find an infinity of line passing by this point
So the calibration is good for T2 and absolutly not good for all the other temperatures

To be able to calibrate the Temperature scale, we need at least to know the melting temperature of 2 pure elements



What is true for T is true for the enthalpy

OPEN THE BIG QUESTION OF THE BASE LINE QUALITY

If the base line quality is bad
The data obtained will be bad too

If the base line quality is bad

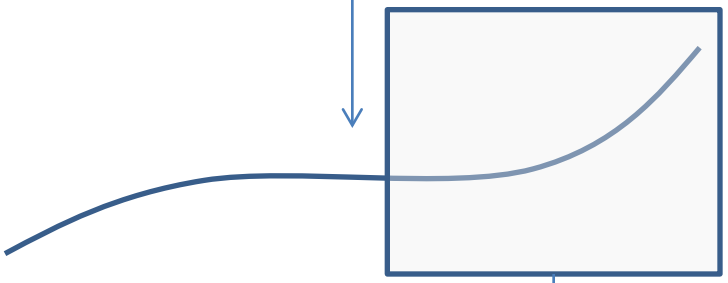
different options

30 k$ to 60k$

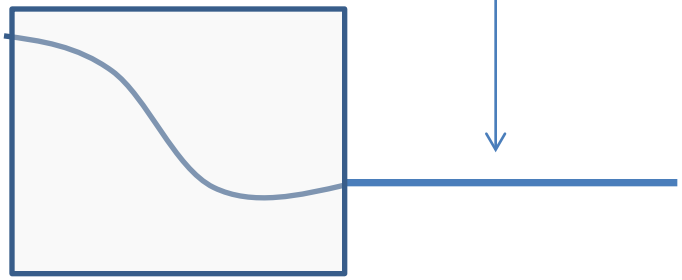
That is not possible for all the different kind of equipments available on the market

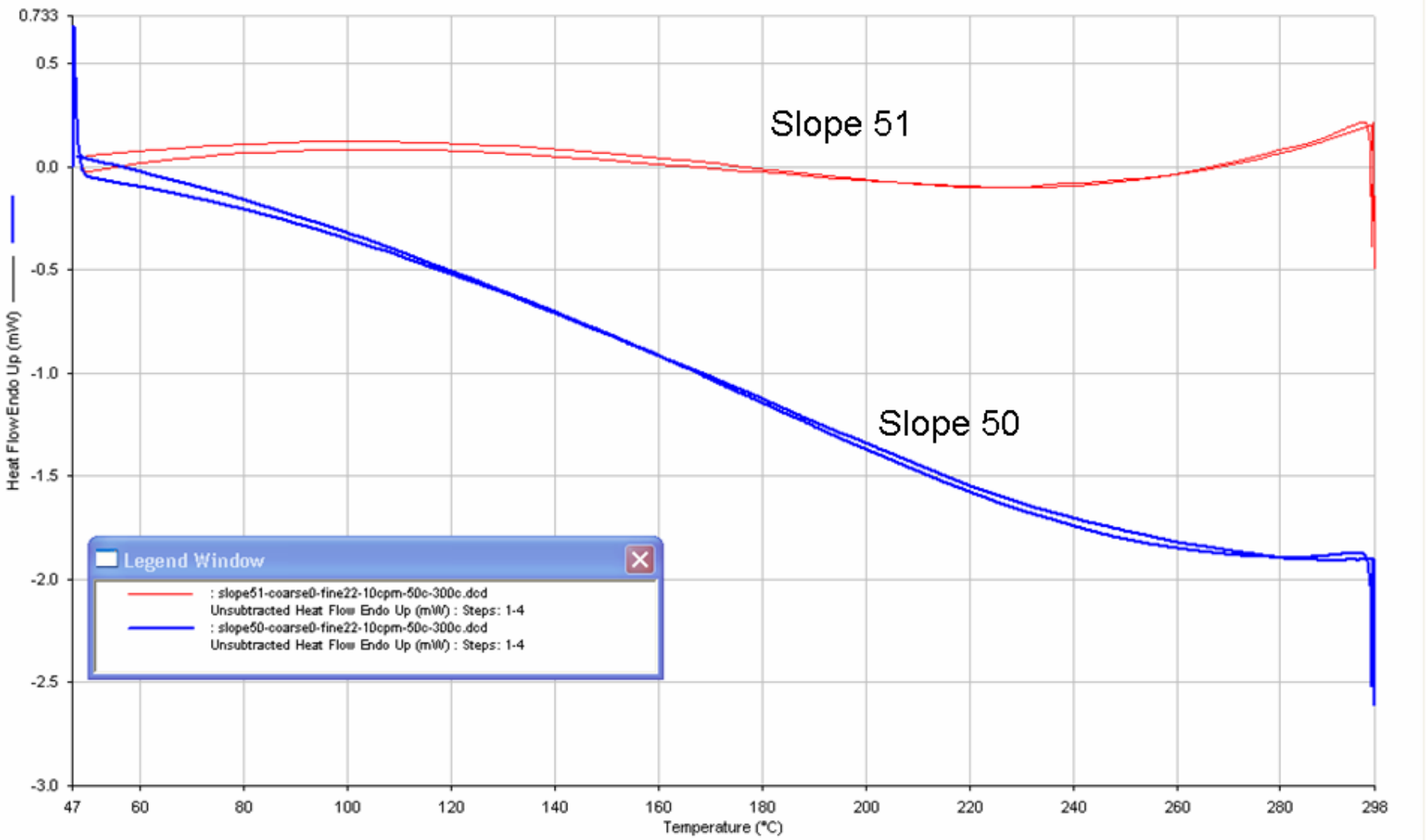
Cleaning procedure

Work to optimize the base line

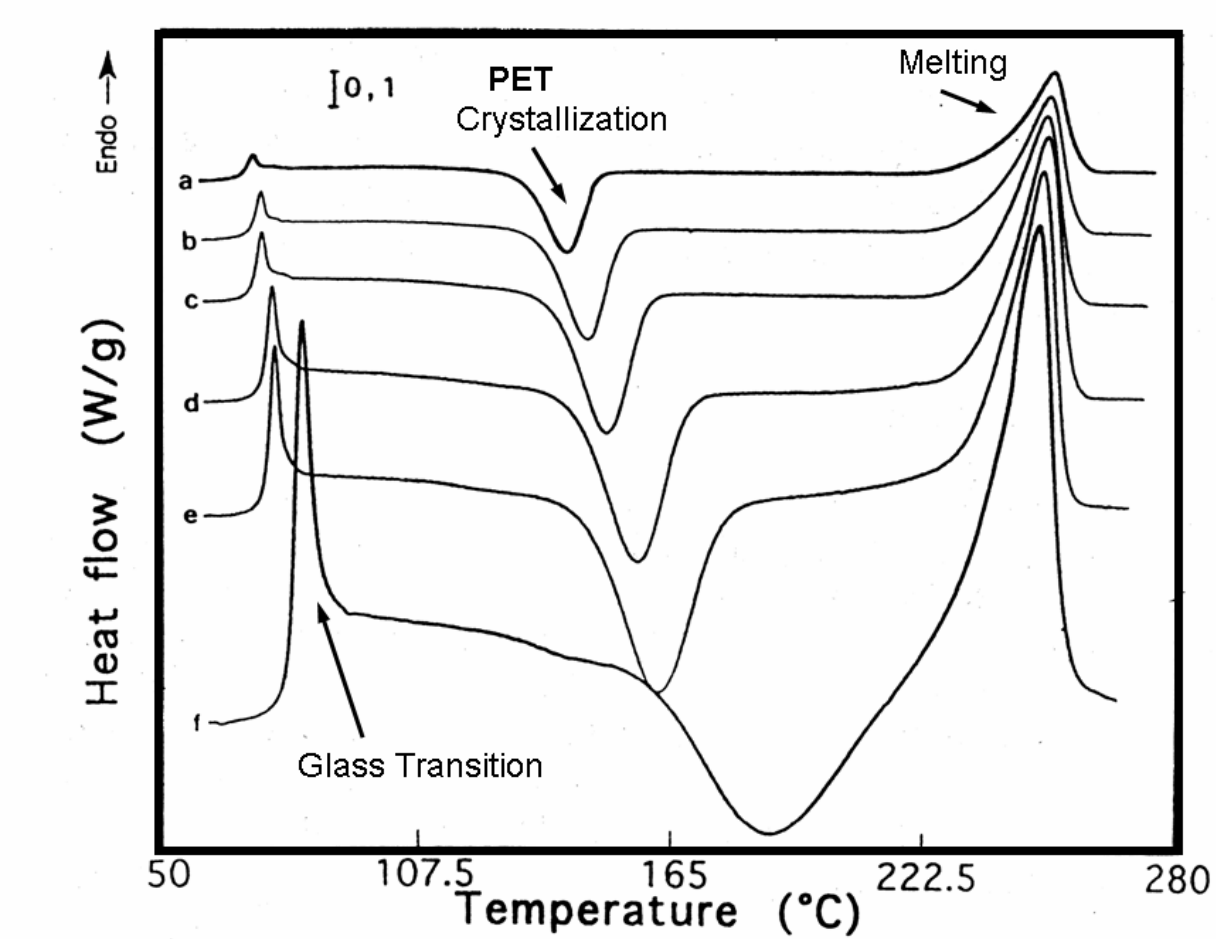


We have to linearise only in the temperature domain needs for the study



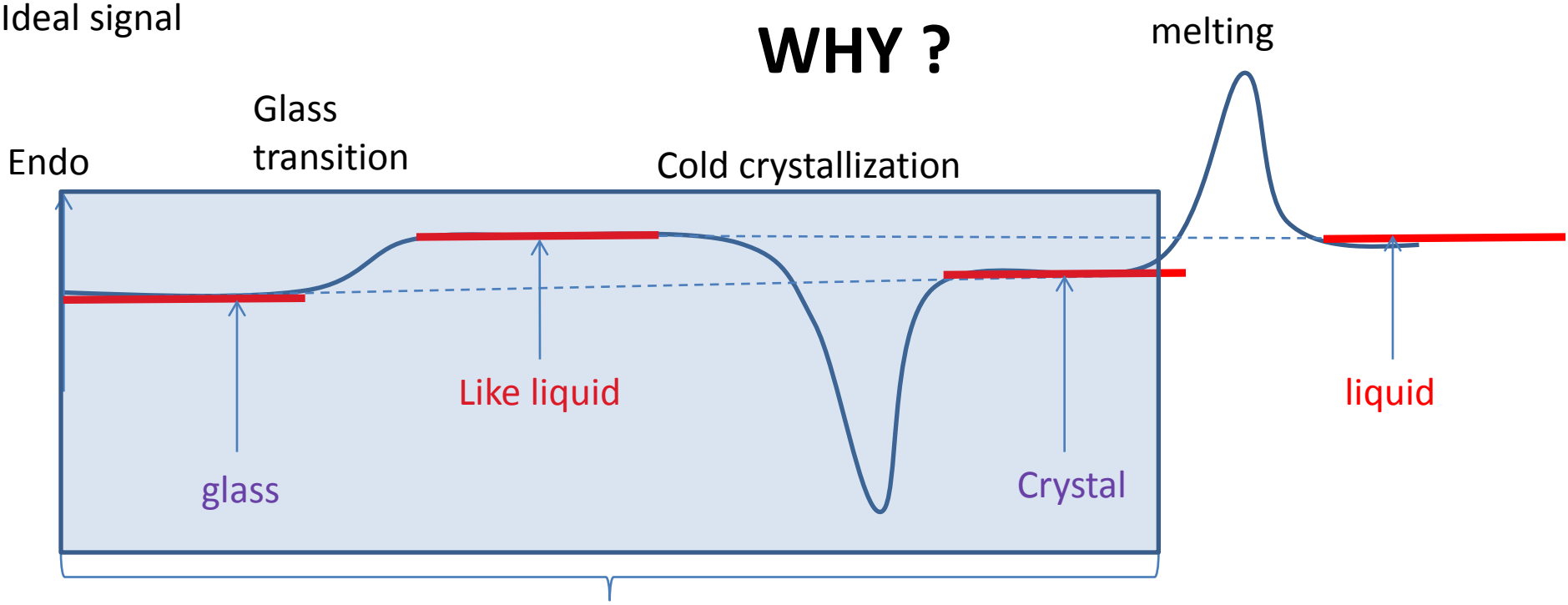


How to do to extract the good temperature and good the enthalpy from a DSC curves

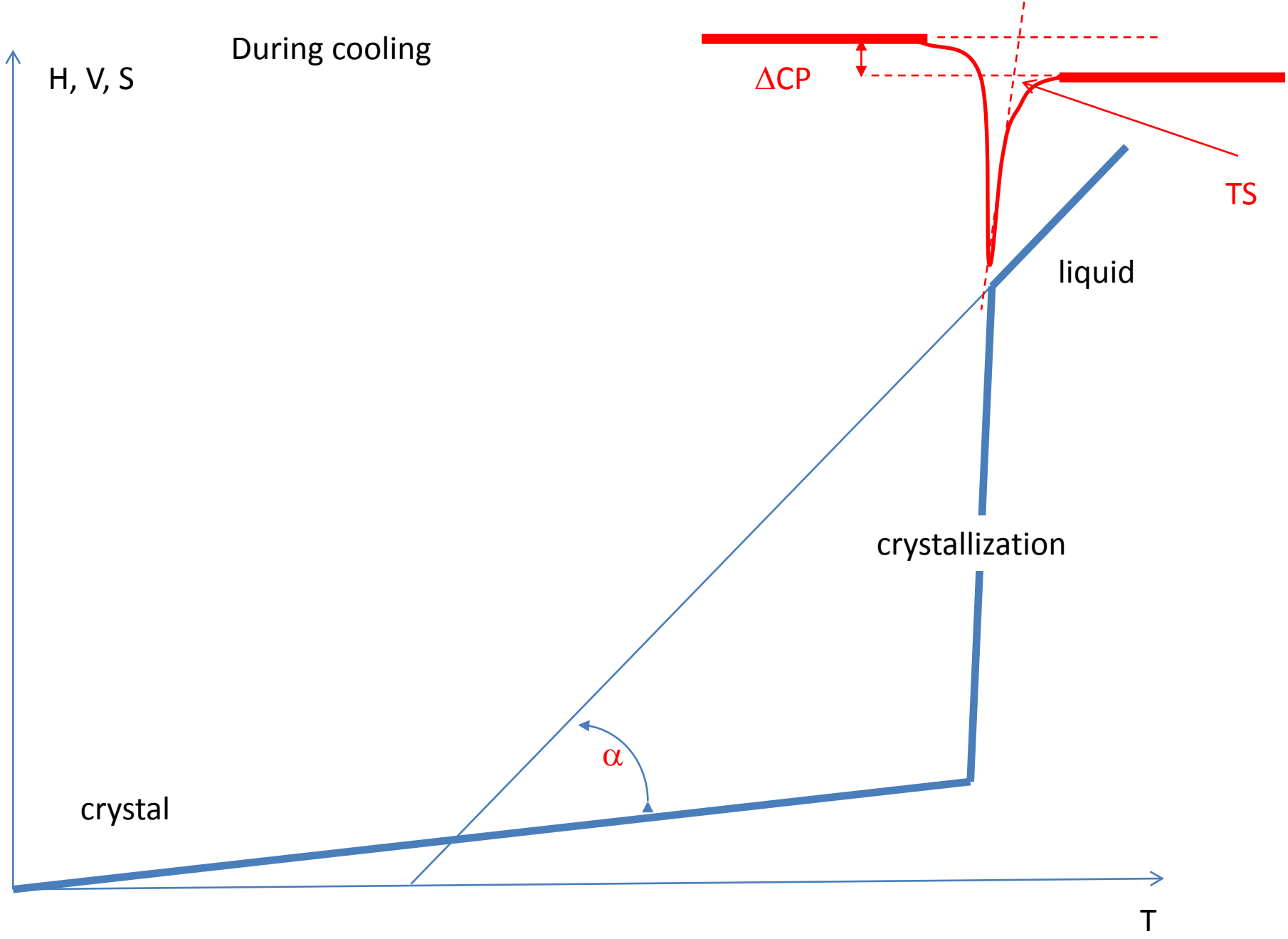


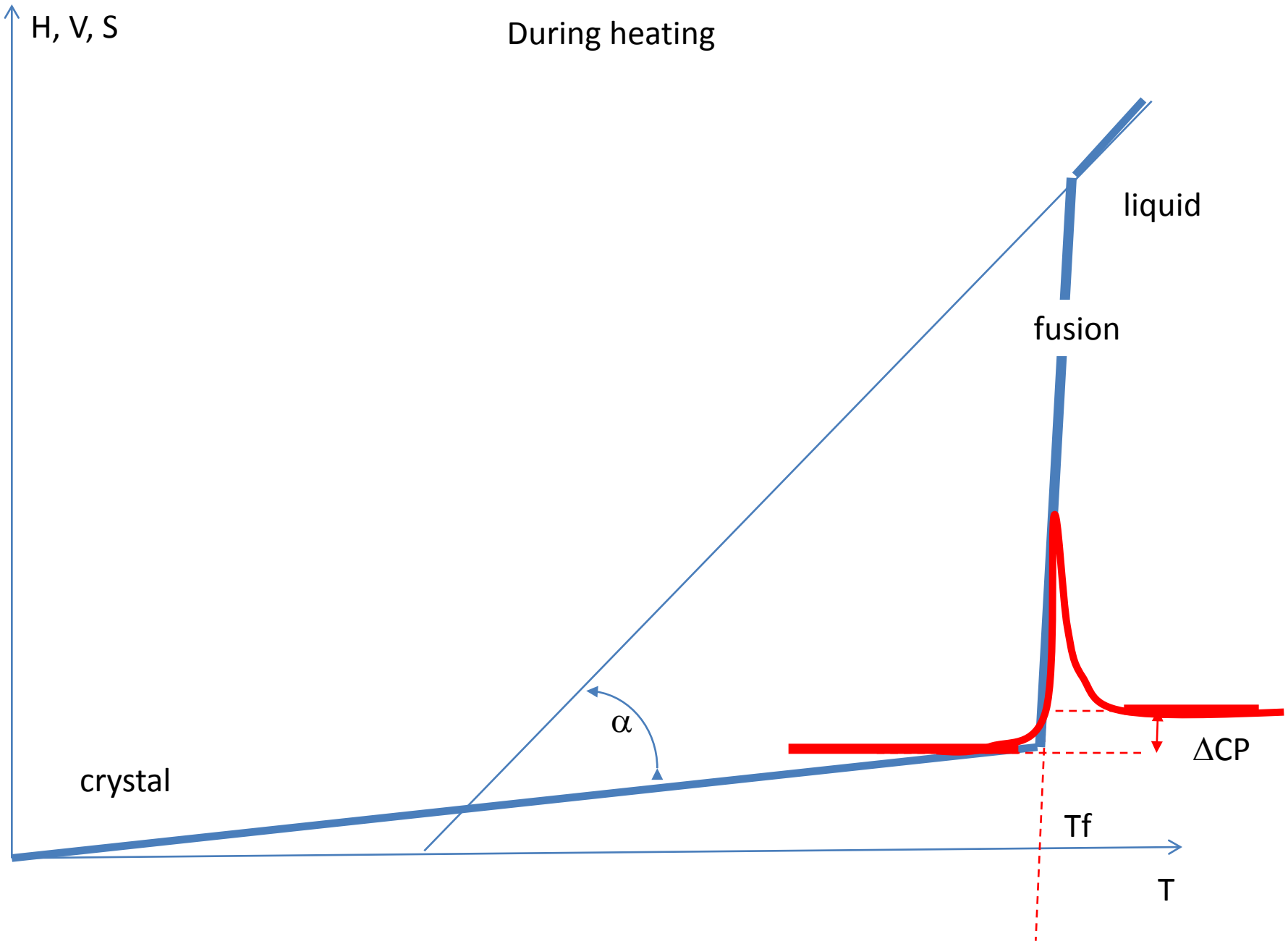
Ideal signal

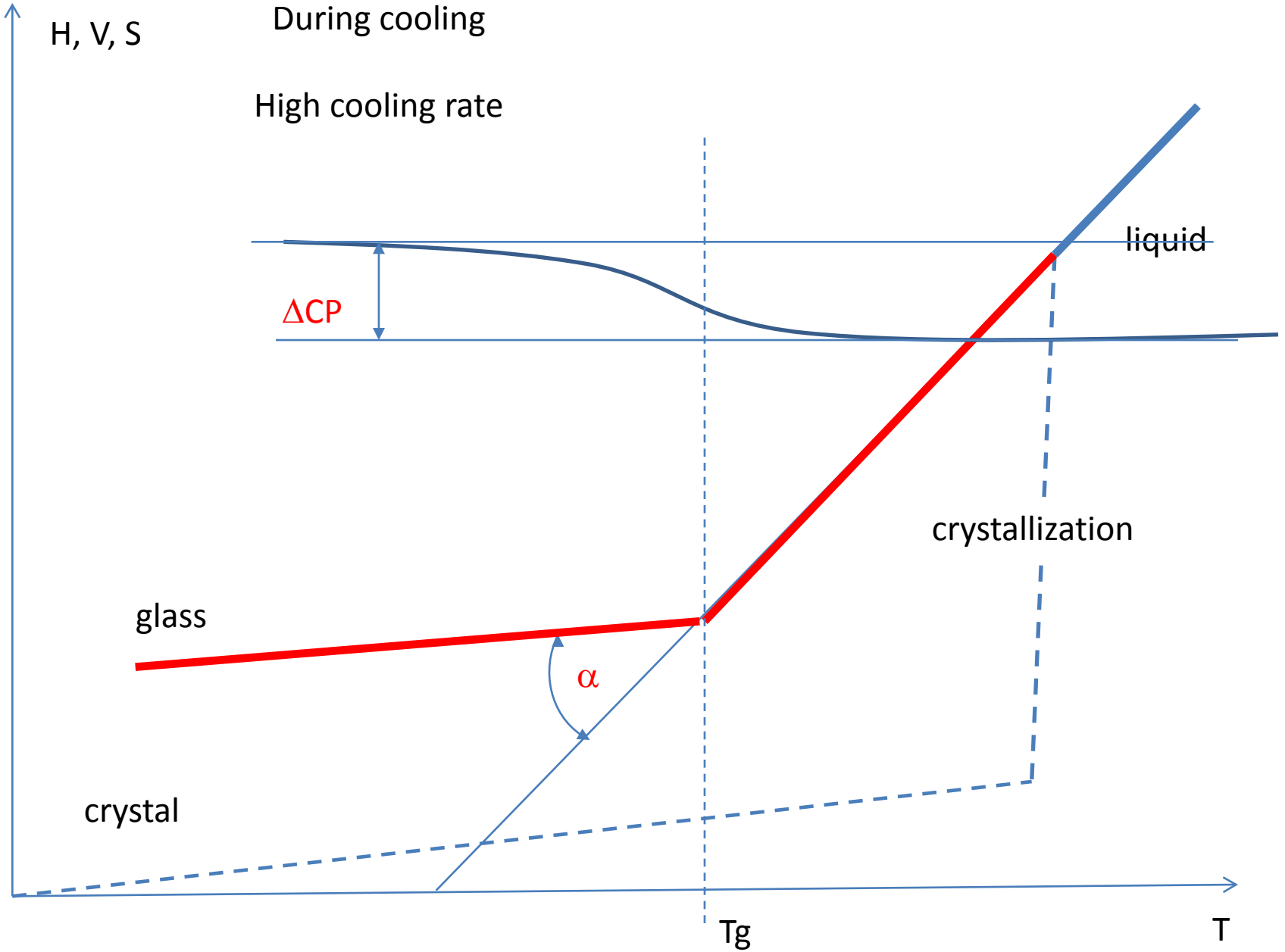
WHY ?



Are not material constants
q+ and q- play a game

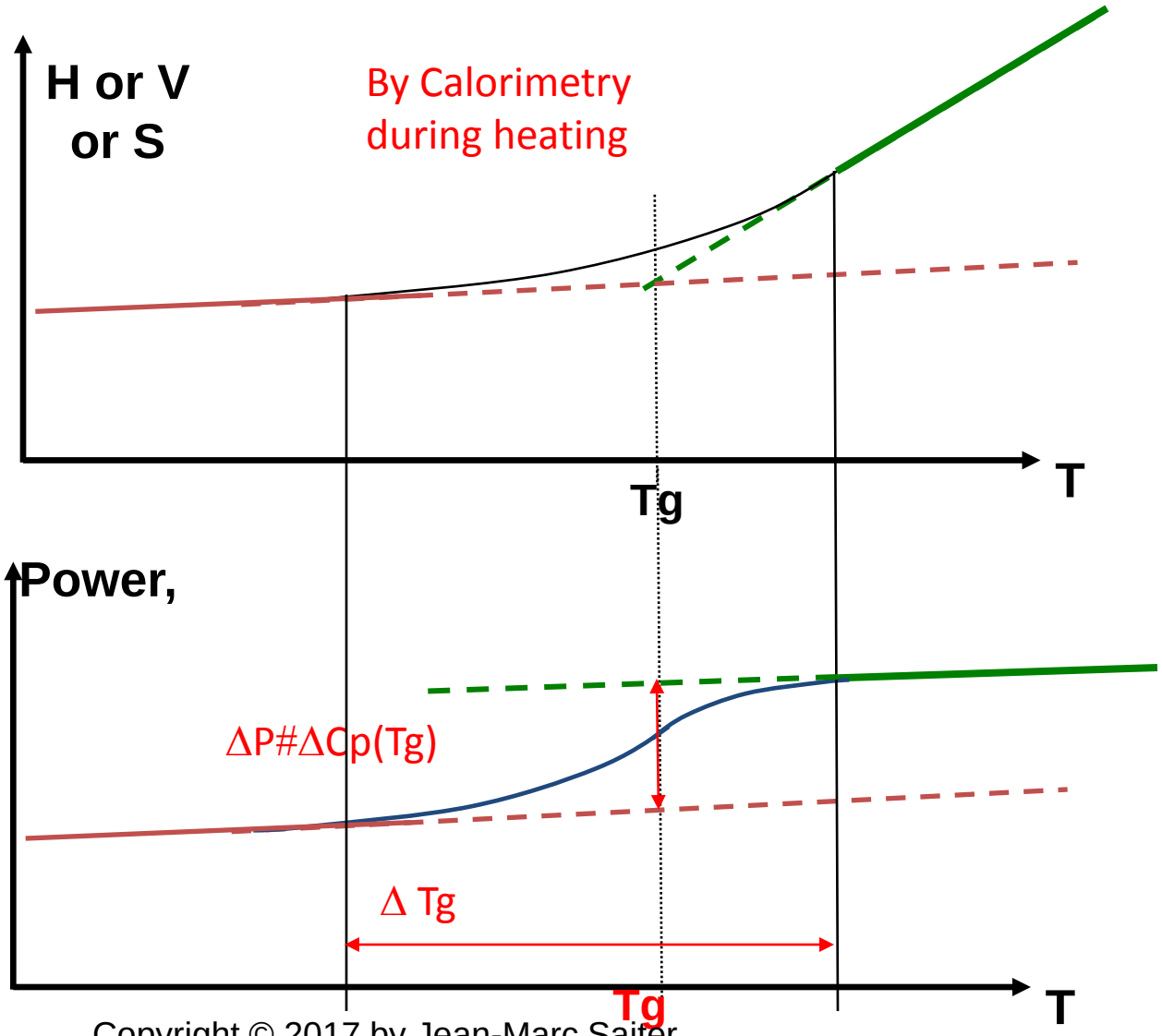




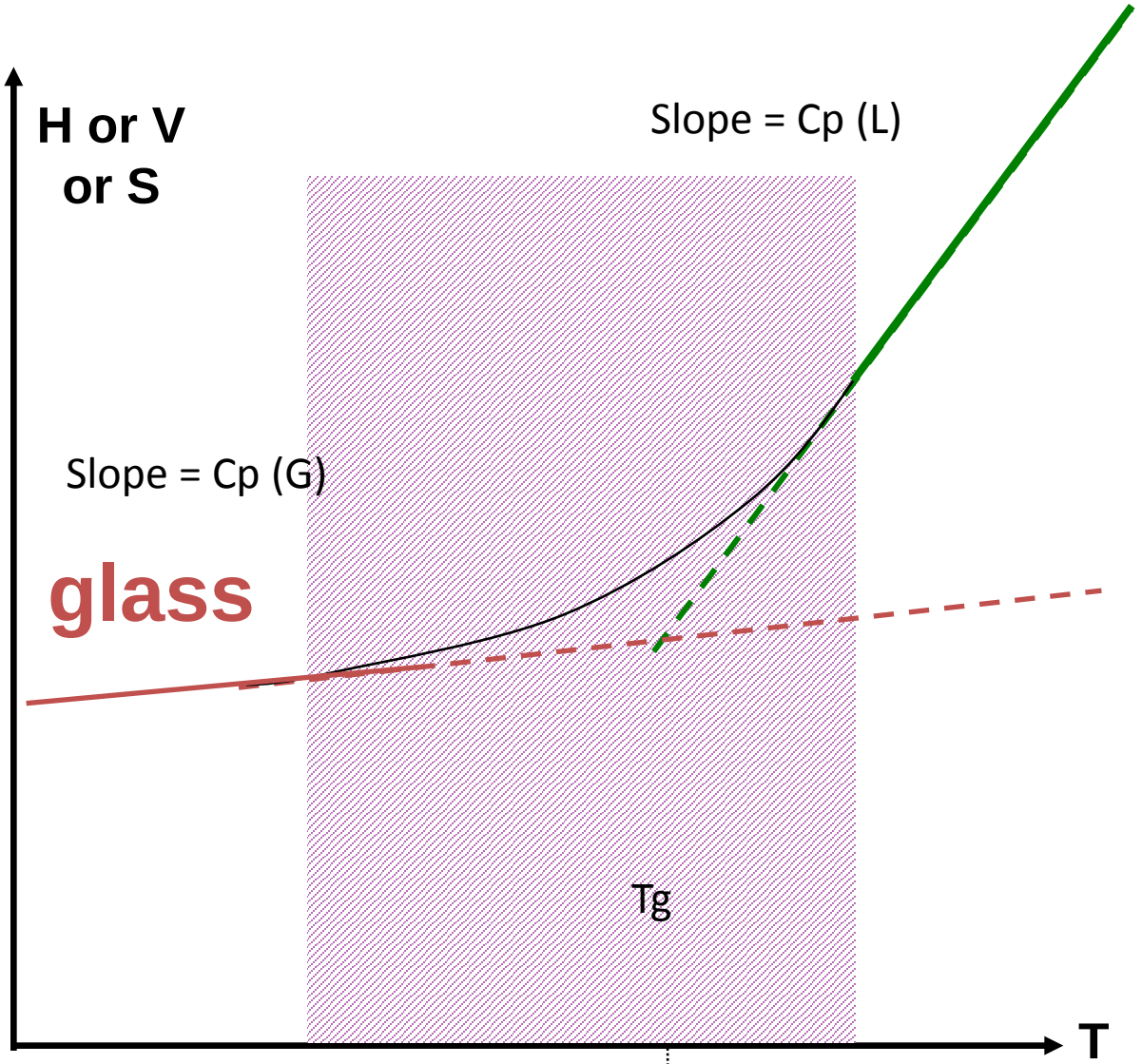


Glass transition Tg
During heating

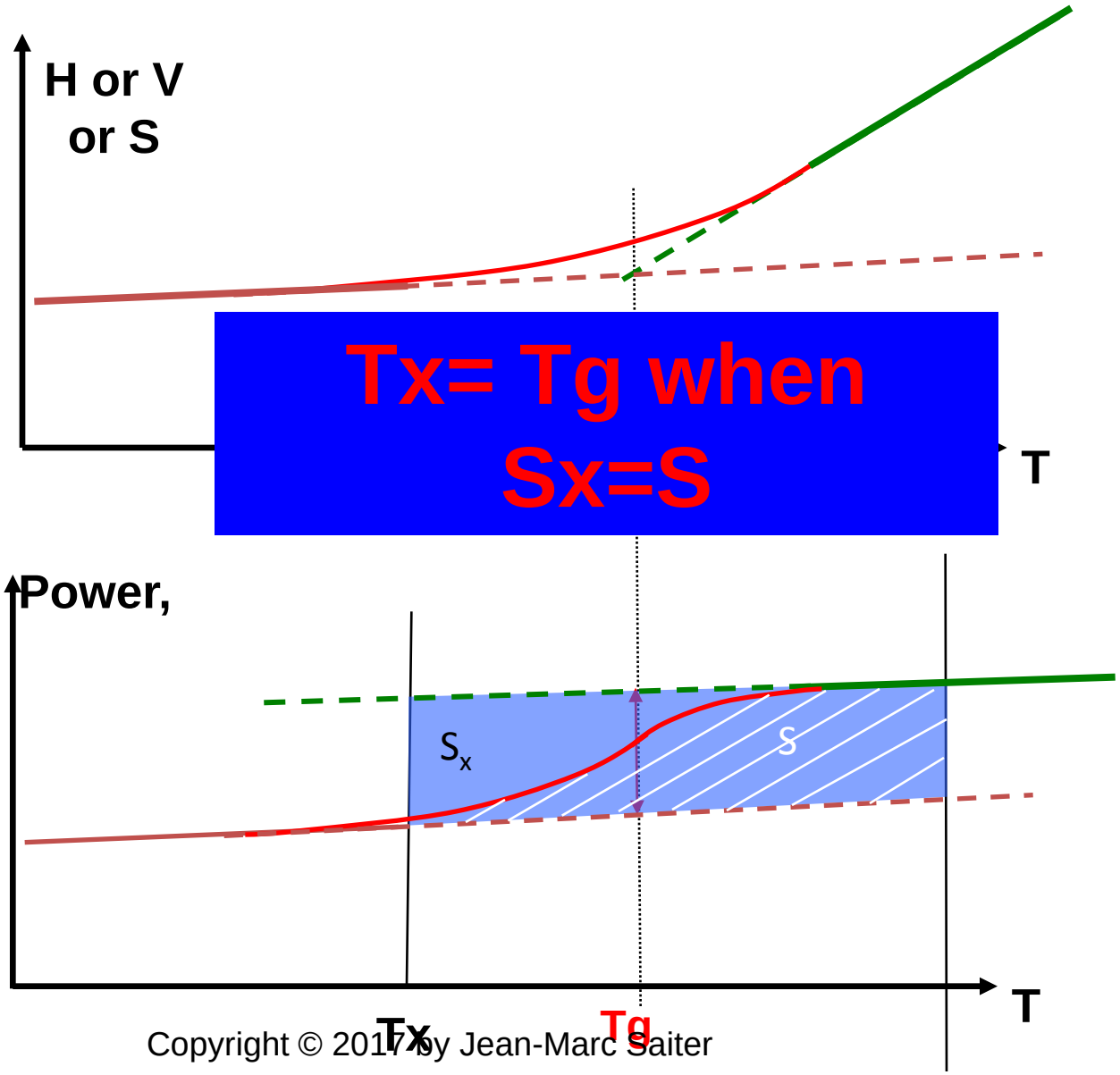
TRUE : ONLY if q+ = q- and no ageing



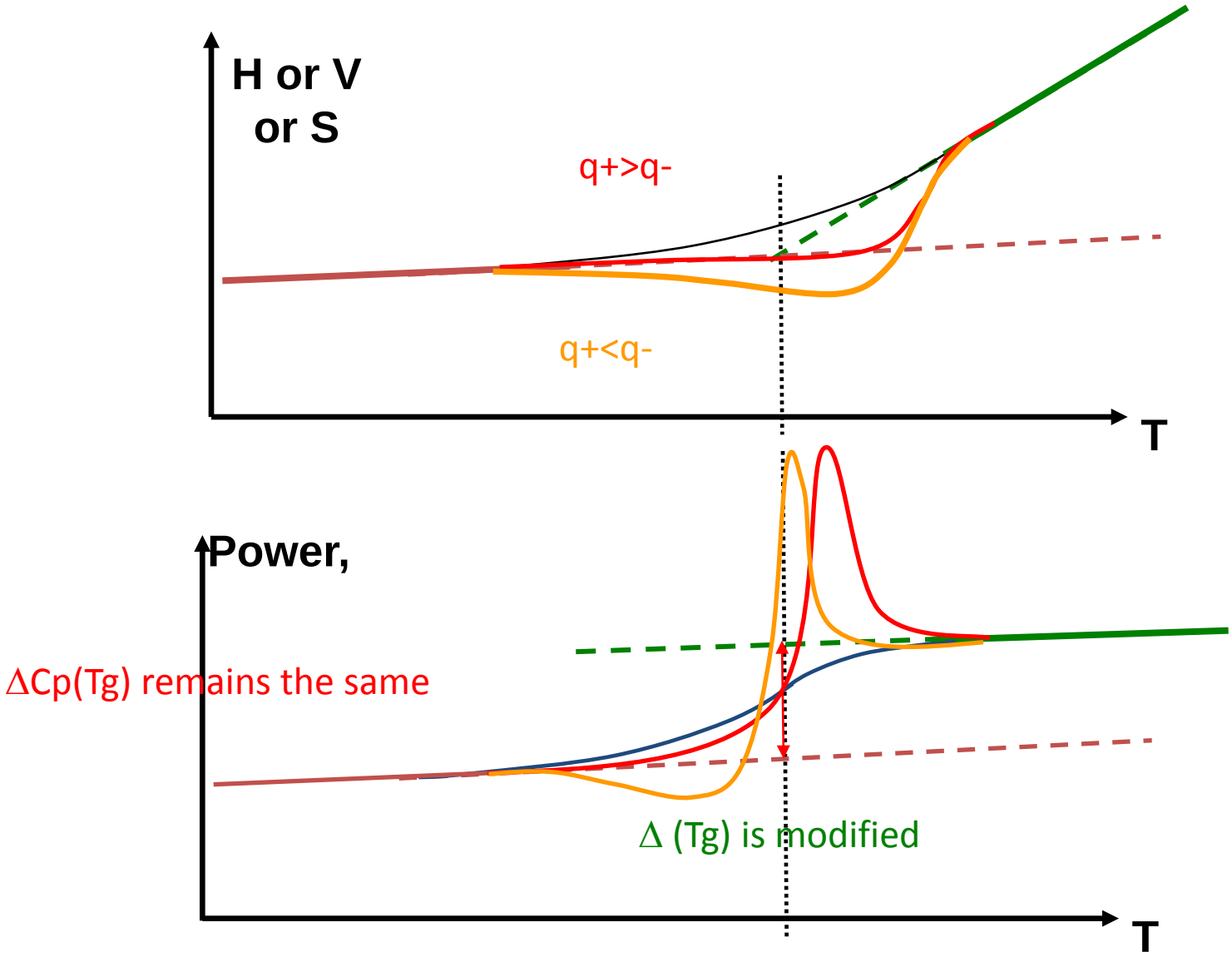
Tg mesurement



Tg mesurement



If q+ ≠ q- but the same q-



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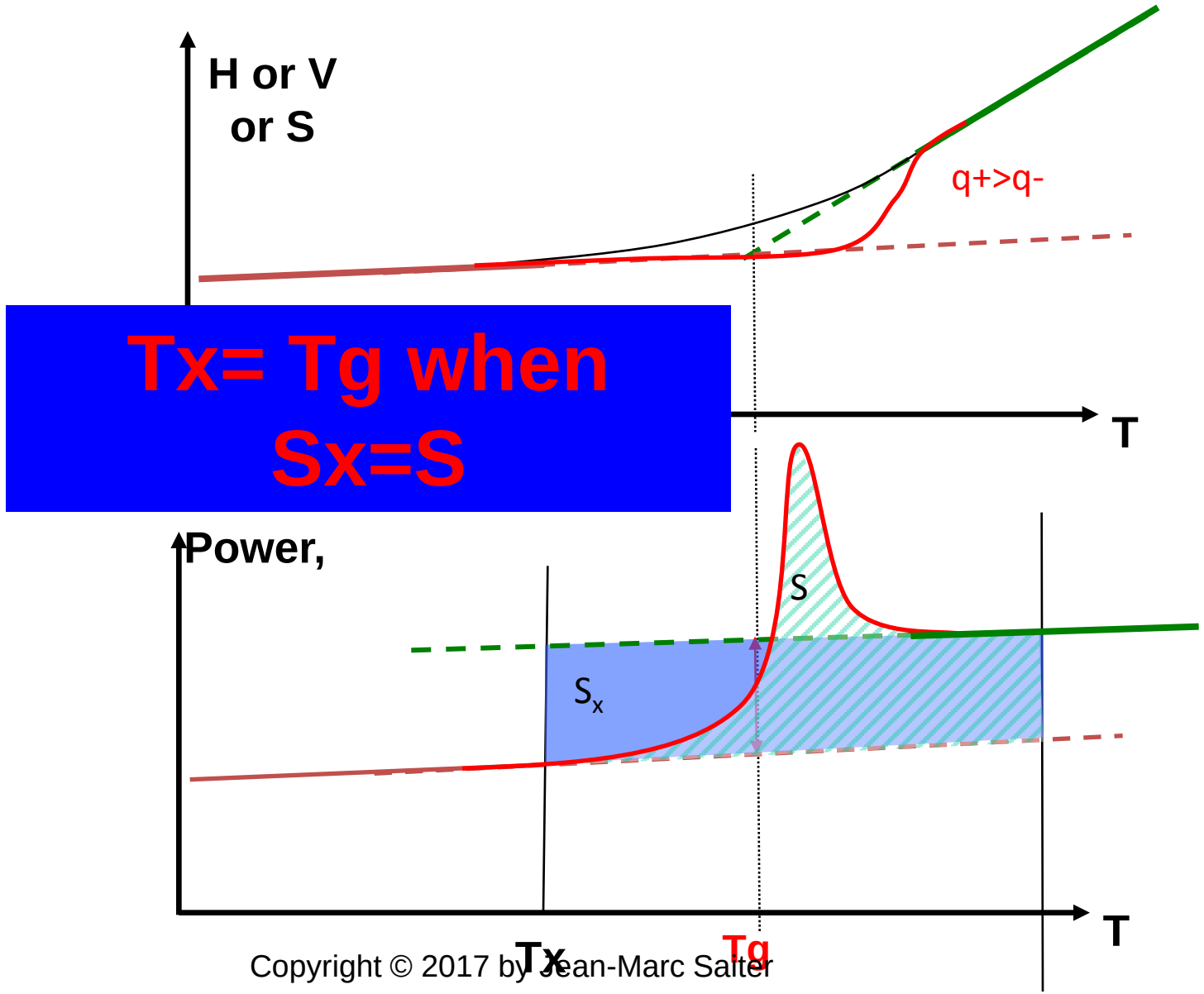
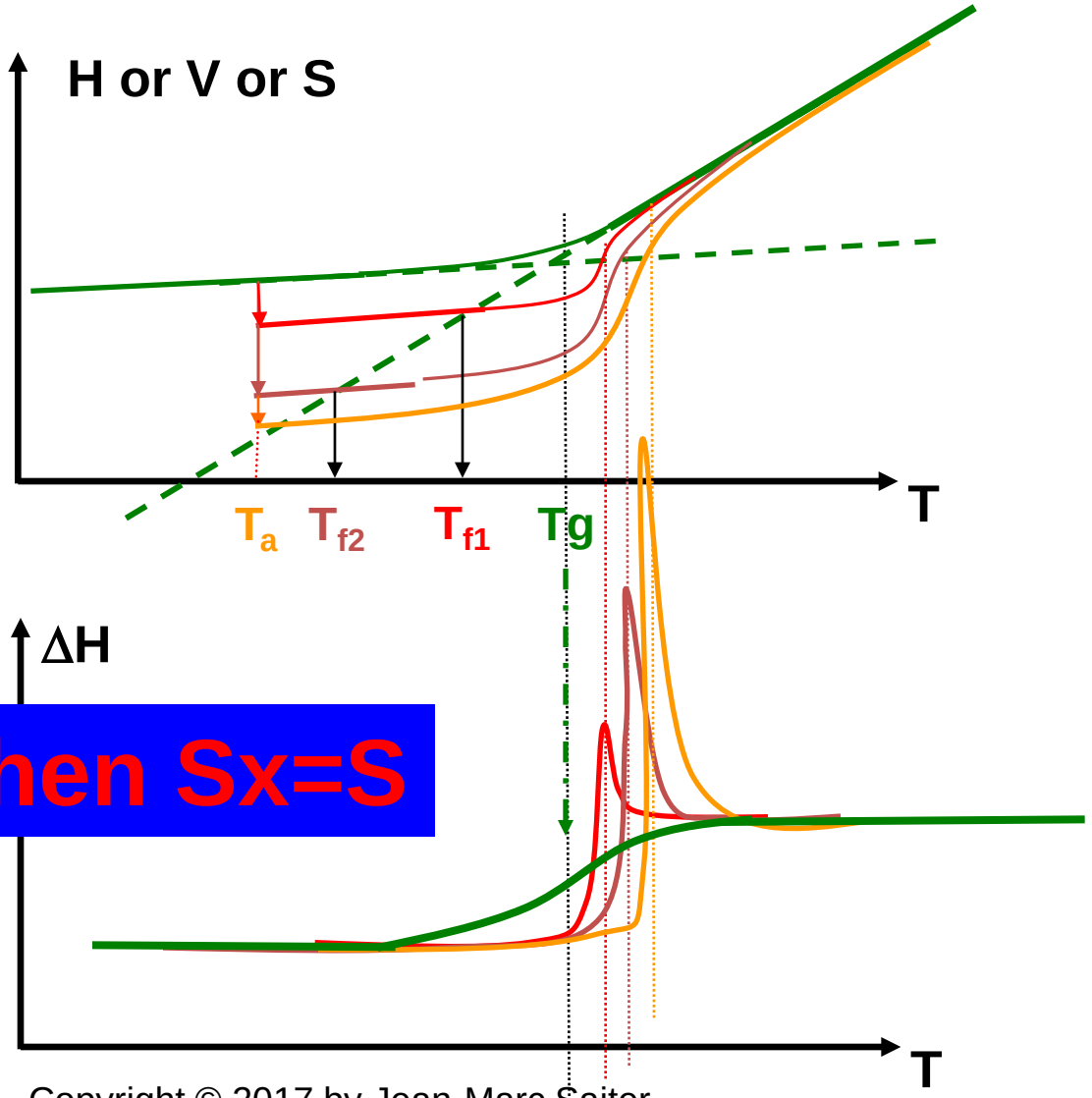


Tx= Tg when Sx=S

Tg mesurement

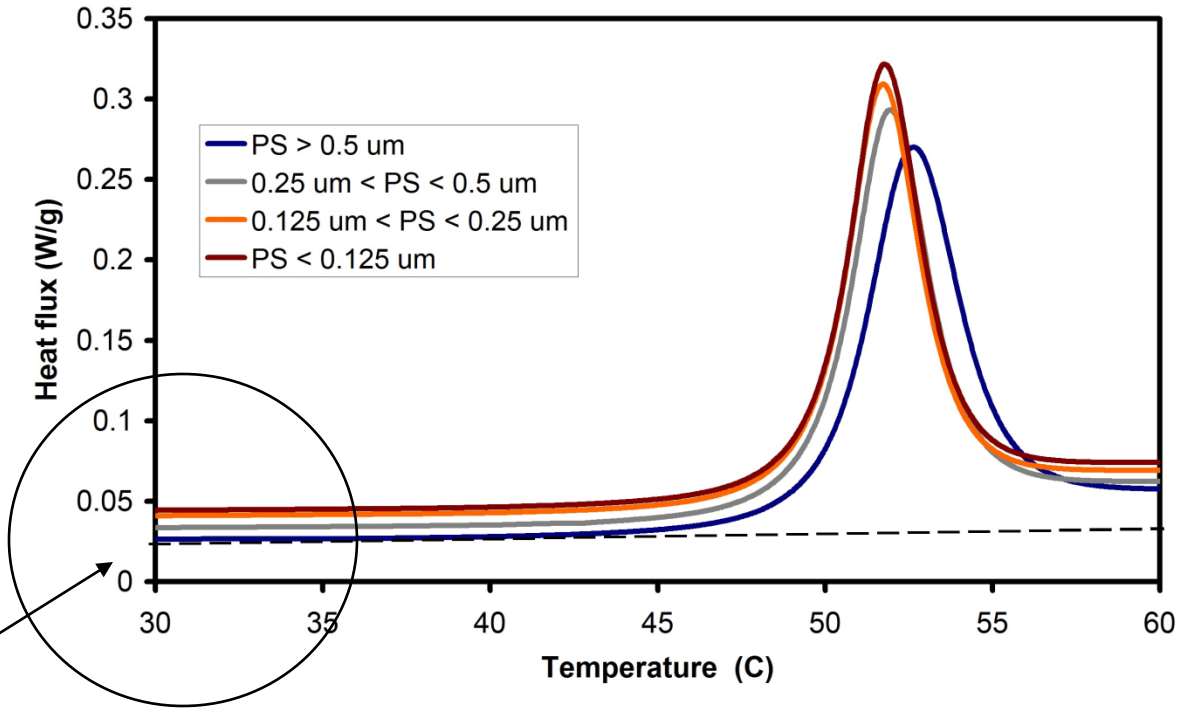
Ageing effects



Tx= Tf when Sx=S

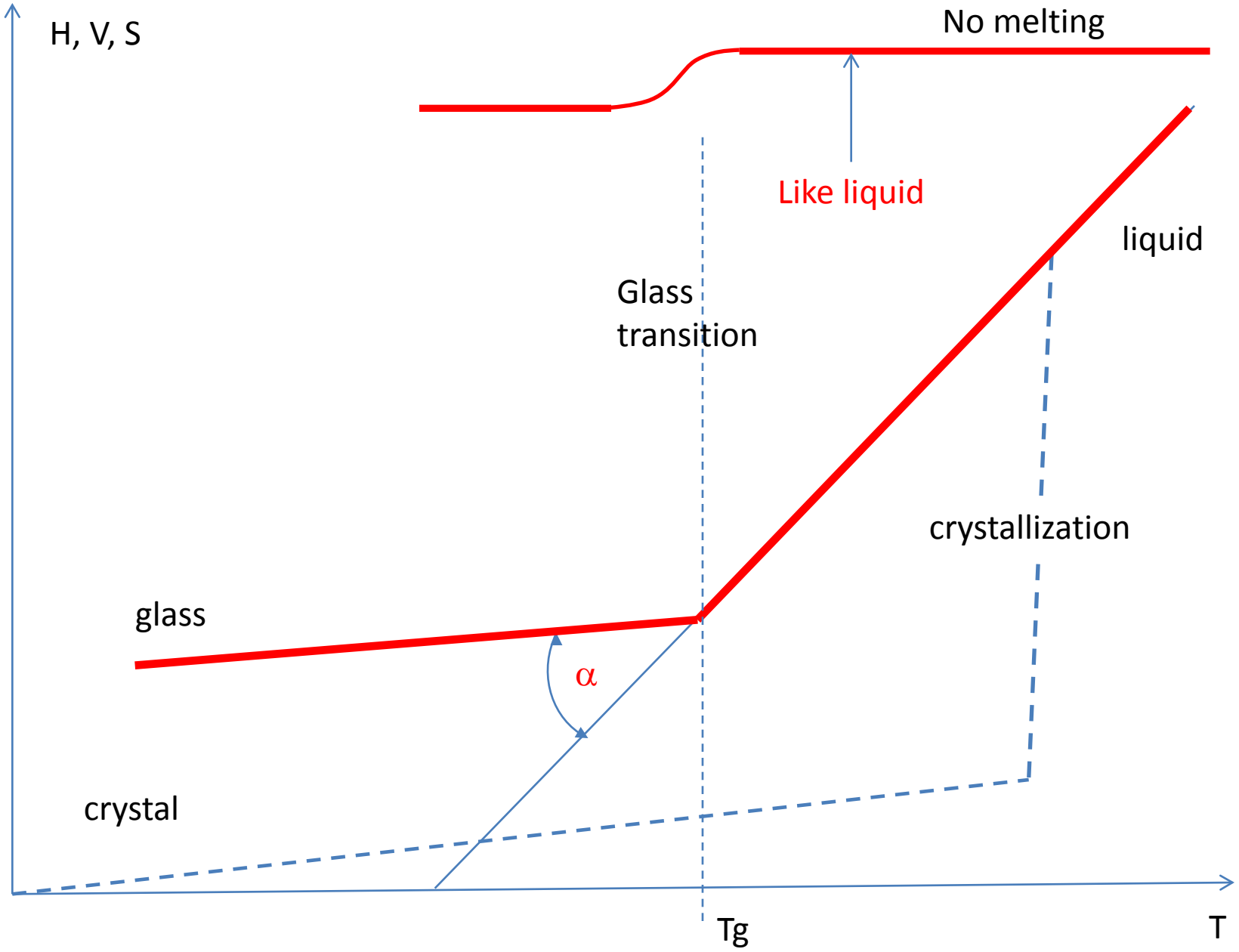
Tg mesurement

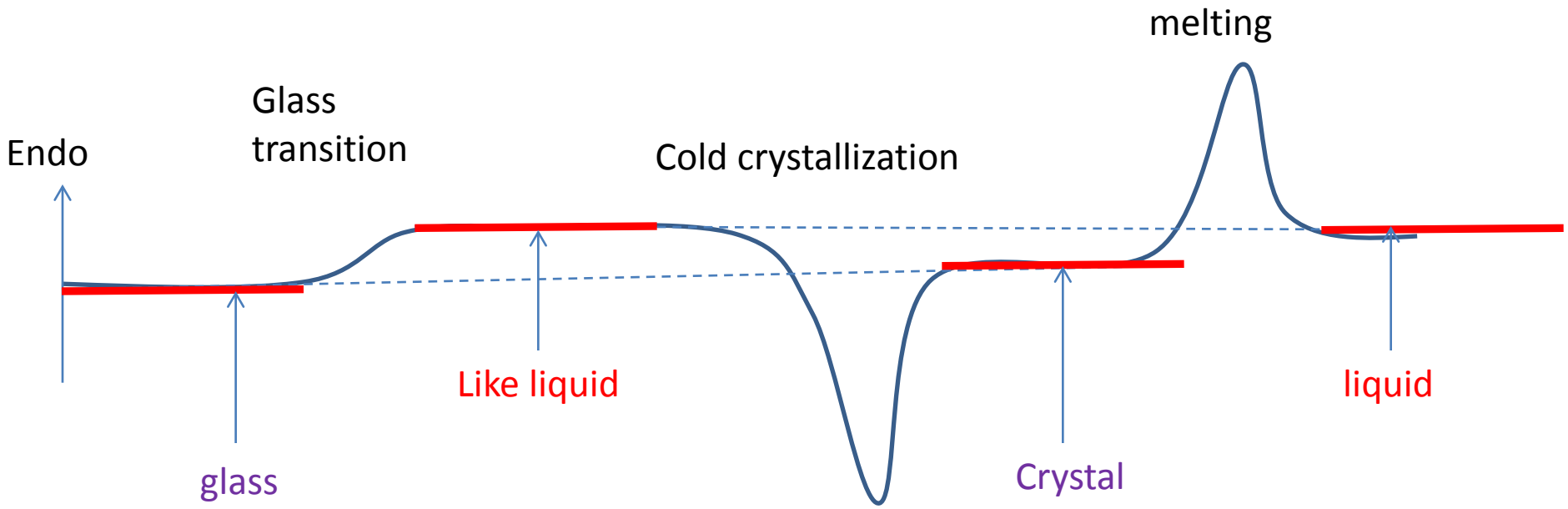
Ageing effects and particles sizes

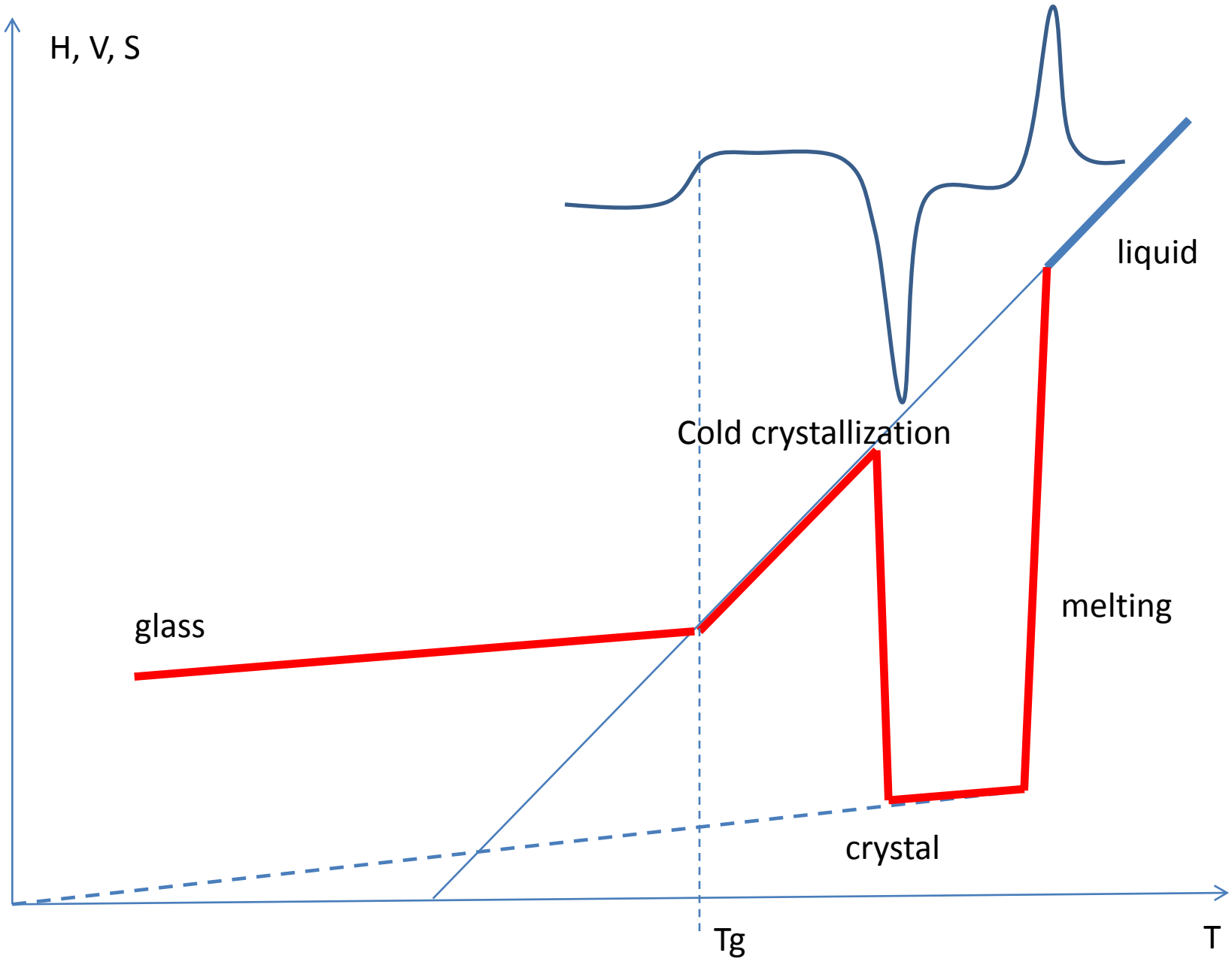


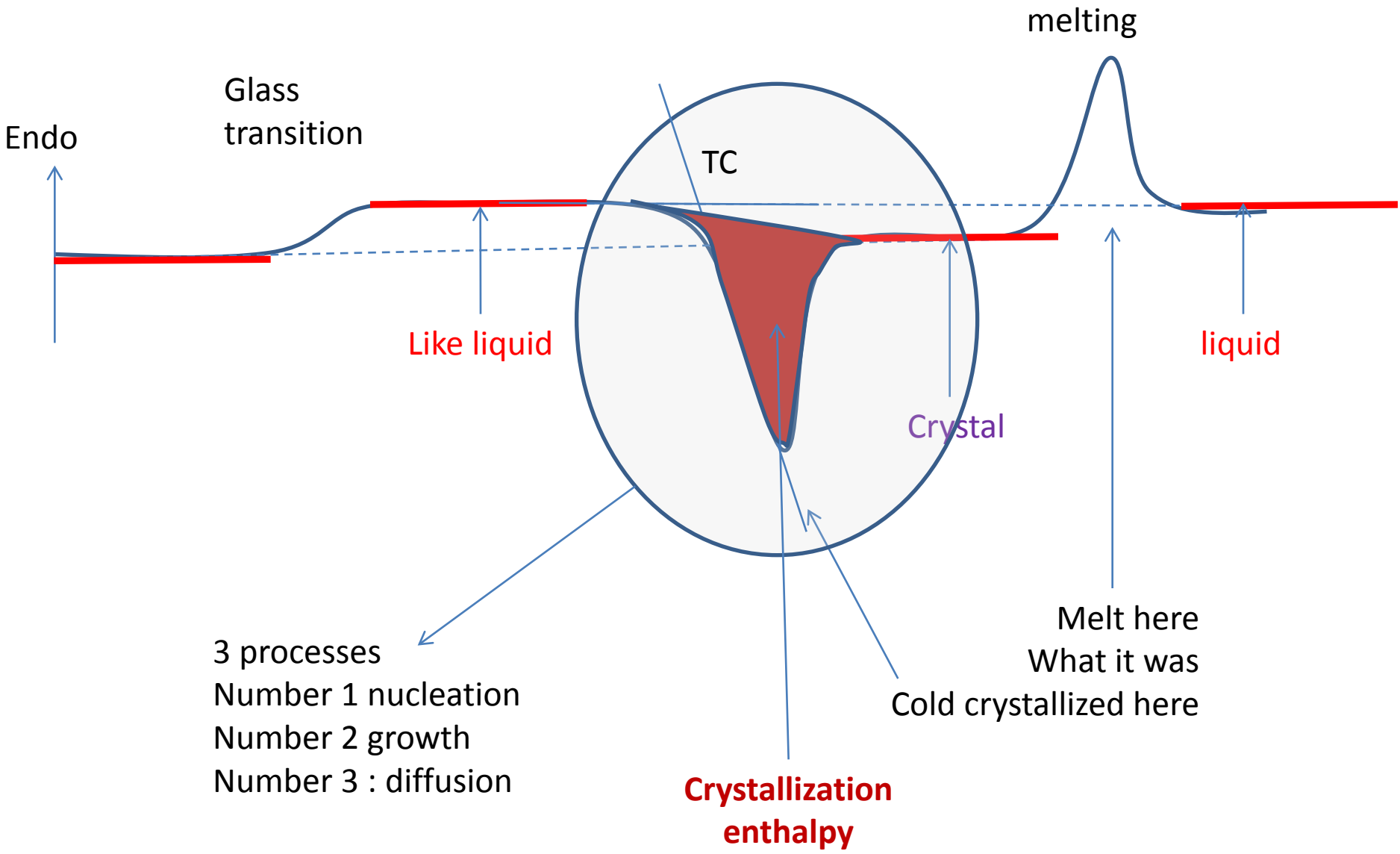
interesting

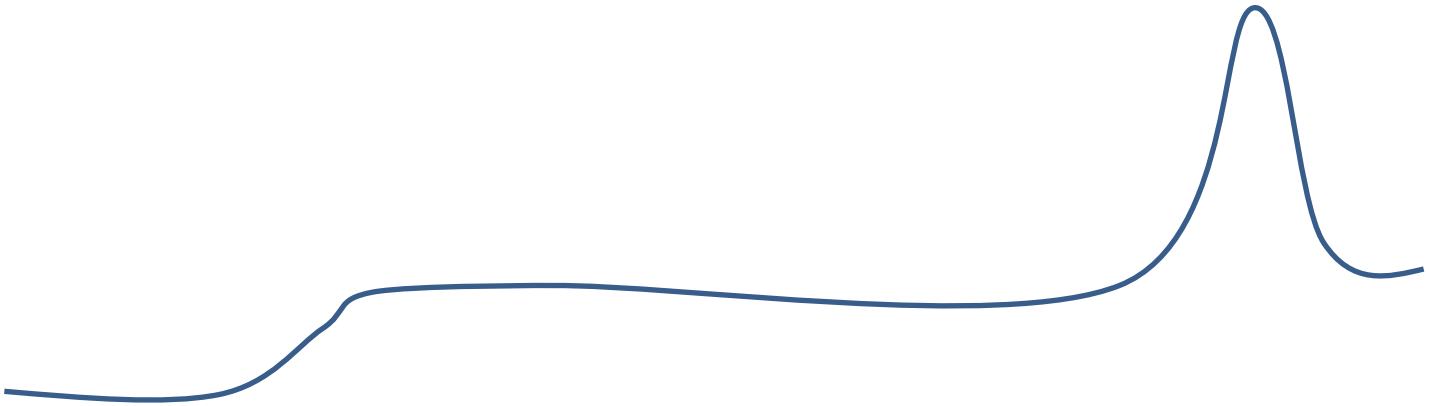
Effect of particle size of aged powder Selenium on measuring the glass transition. As seen, aged Selenium shows a large peak on glass transition.

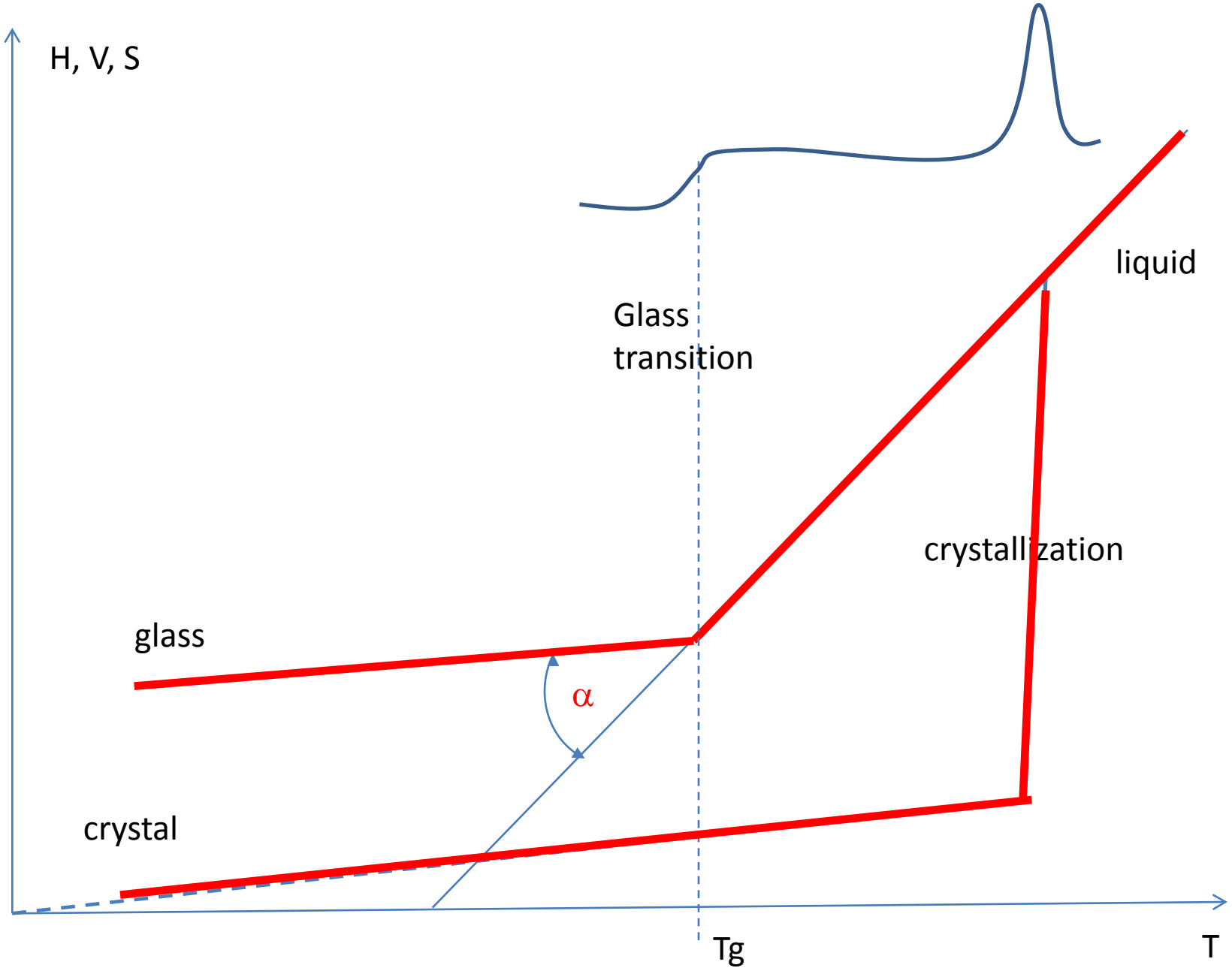


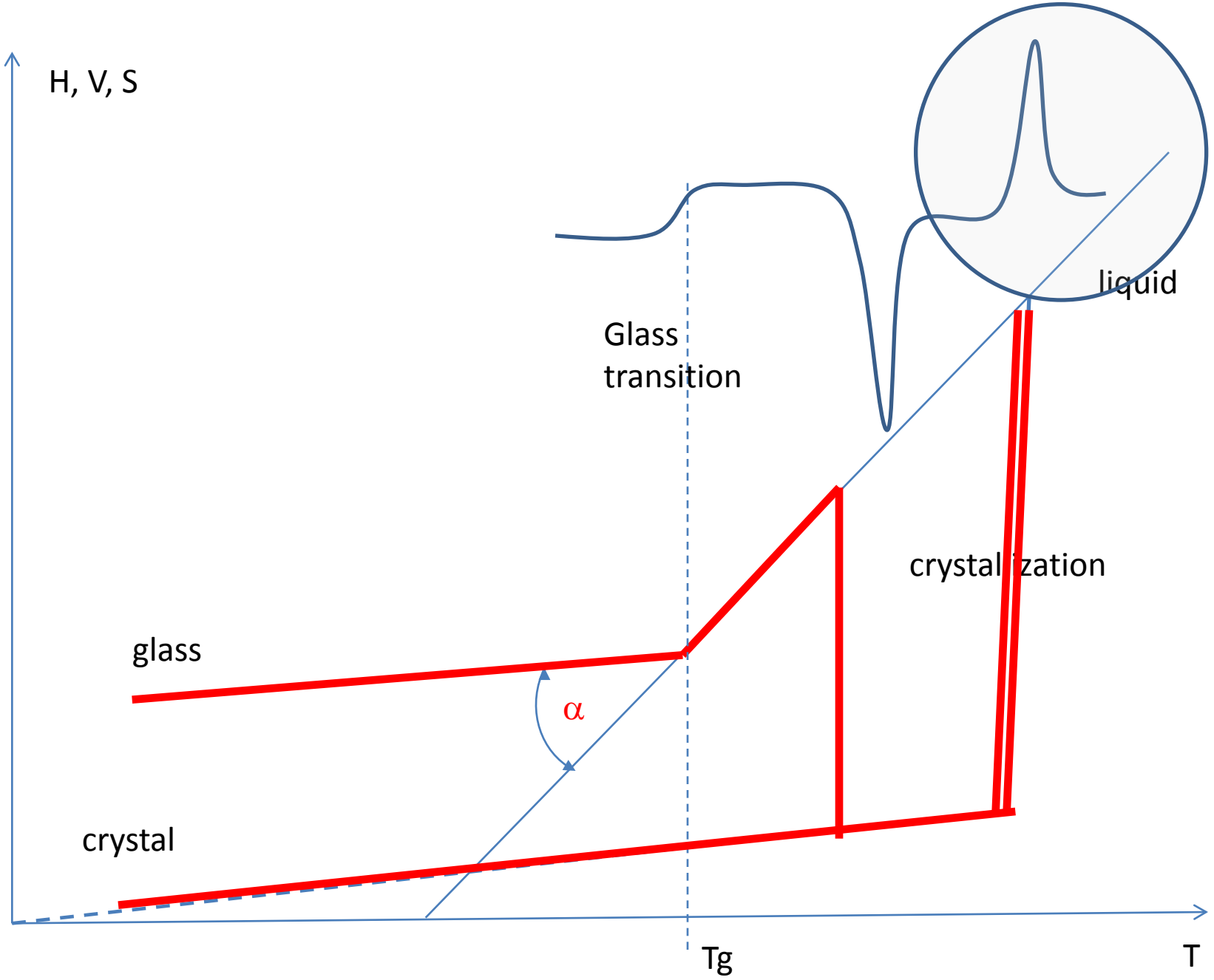


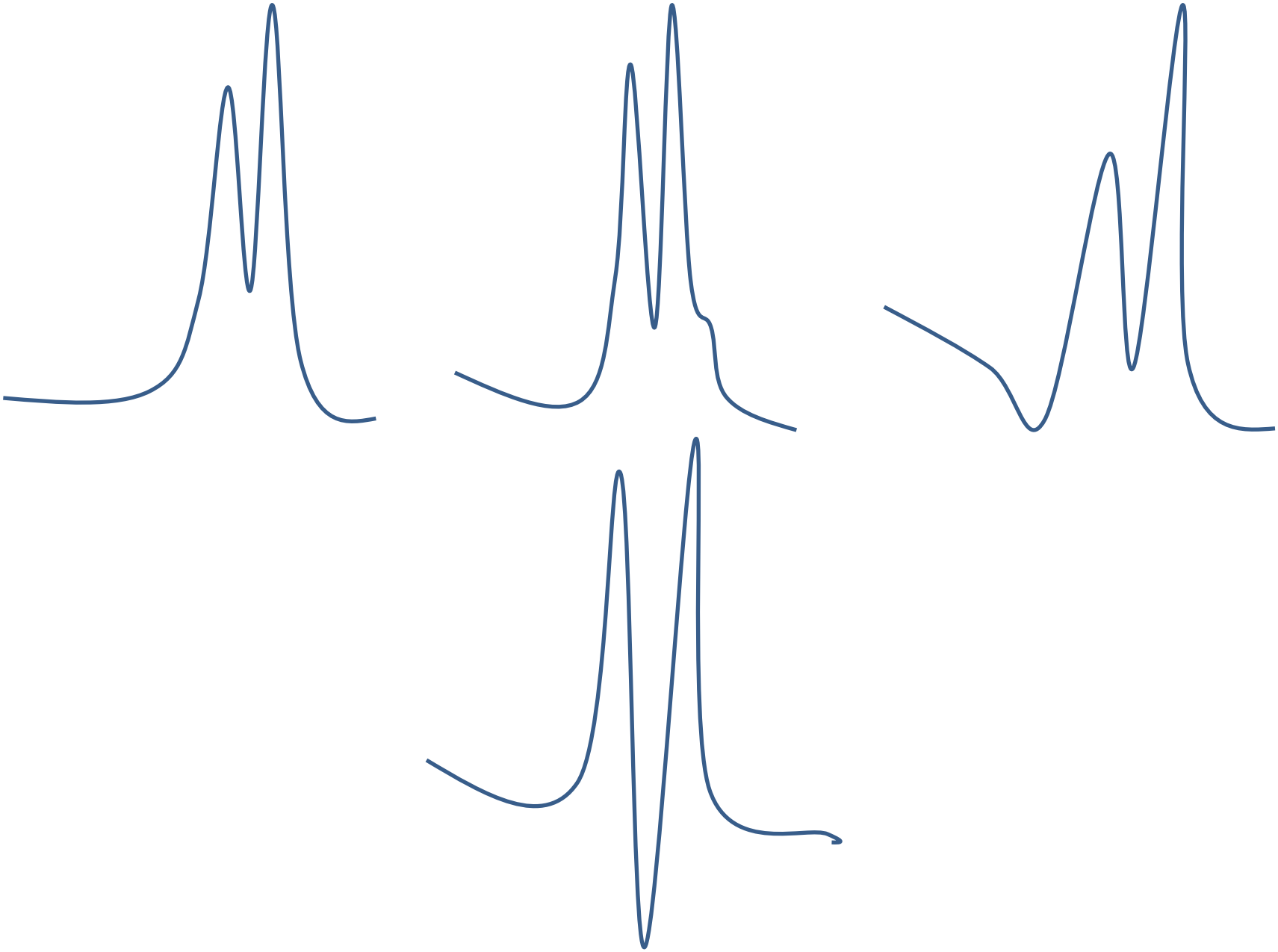












Cp mesurement

More difficult

Requires an excellent knowledge of the apparatus performances

Requires an excellent calibration procedure

Requires a long experimental time to be good

Why ?

Because we want an absolute value for Cp,

and we are only able to make a comparison

TAKE CARE

$\Delta P = d\,\Delta W/dt = f(T)$ ← DSC curve

$= d\Delta H/dt$ ← Heating rate

$= d\Delta H.dT/dt.dT$ $= q^{+}.d\Delta H/dT$

~~$= q + C_p$~~

NO That is WRONG

$\Delta P_{(Tg)} = q^{+}((Cpl\_C_{pref1})-(Cpg-C_{pref2})$

Not known

⟹ (Cpl-Cpg) at Tg = $\Delta Cp_{(Tg)} = \Delta P/q^{+}$

if $Cp_{ref1} = Cp_{ref2}$

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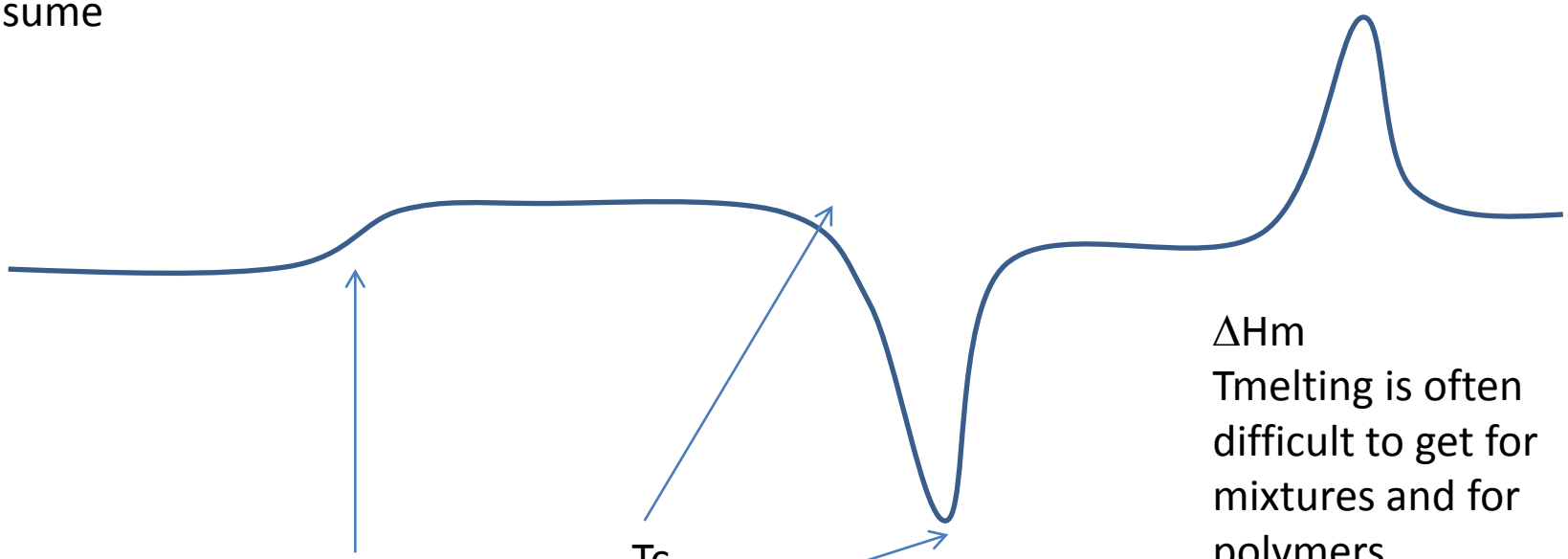
Quantitative and Transient DSC Measurements
I. Heat Capacity and Glass Transition

Jean-Marc Saiter
, Mehrdad Negahban
Philippe dos Santos Claro
Pierre Delabare
Marie-Rose Garda

To resume



ΔCP at Tg

Tg

Tc
Tm
ΔHC

ΔCP at TC is very difficult to determine

ΔHm
Tmelting is often difficult to get for mixtures and for polymers
Often taken at the maximum of the main peak,

Heating rate
Cooling rate
Age
Annealing temperature