Advanced Physical Metallurgy
"Amorphous Materials"

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Contents for previous class

Bonding type: covalent, ionic, metallic, van der waals, hydrogen bond
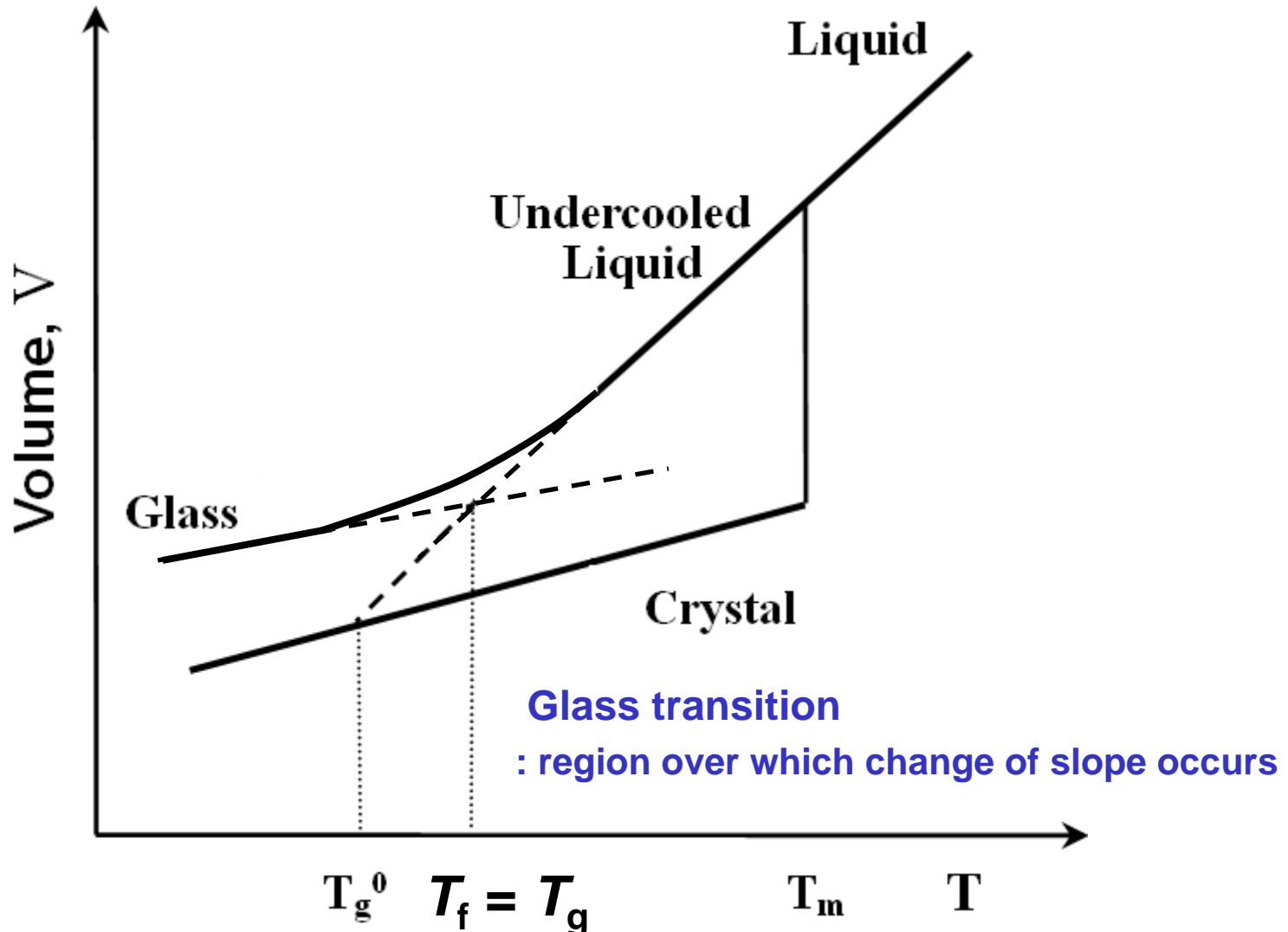
➡ Glass has one of those bonding.

Table 2.1 Examples of glass-formers for the major types of bonding

Type of bond	Material
Covalent	As_2Se_3, Se
Ionic	KNO_3–$Ca(NO_3)_2$
Metallic	Zr–Cu, Ni–Nb
Van der Waals'	*ortho* terphenyl
Hydrogen bond	$KHSO_4$, ice, aqueous solution of ionic salts (e.g. LiCl)

➡ Some examples which do not fit into any one category.

Ex) Silica : some ionic + predominant covalent

T_g = *fictive temperature, T_f*

Volume, V

Liquid

Undercooled Liquid

Glass

Crystal

T_g^0 $T_f = T_g$ T_m T

Glass transition
: region over which change of slope occurs

thermodynamic property ? **thermodynamic property**

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Ehrenfest Classification of Phase Transitions

- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

- Second Order Phase Transition at T_T:

  - G is **continuous** at T_T
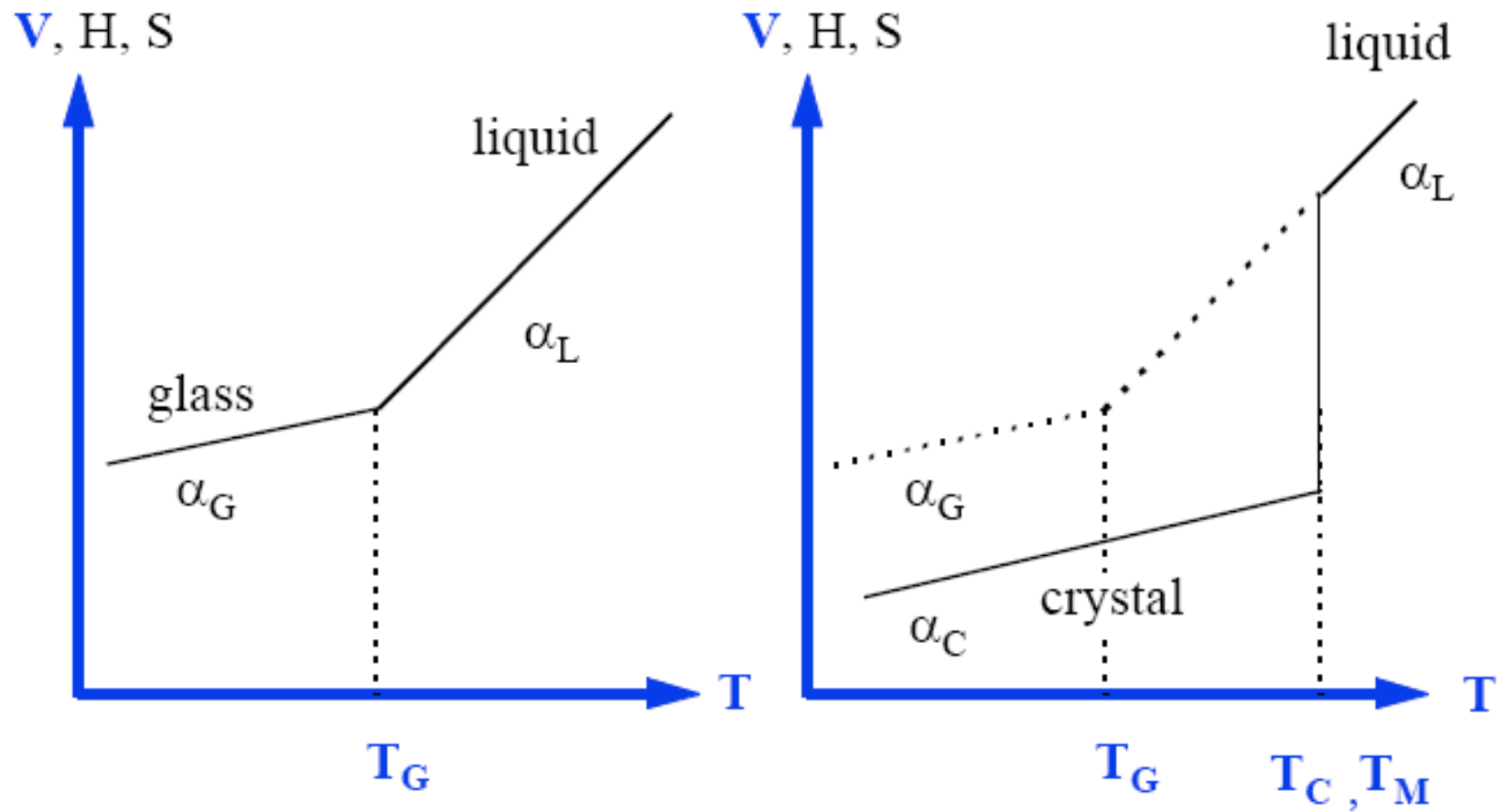 - First derivatives of G (V, S, H) are **continuous** at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

  - Second derivatives of G (α, β, C_p) are **discontinuous** at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Experimental Evidence: Dilatometry $V = f(T,P)$

Liquid to Glass Transition
"Second Order" Transition

Liquid to Crystal Transition
First Oder Transition

- Second Order Phase Transition at T_T:
    - G is <u>continuous</u> at T_T
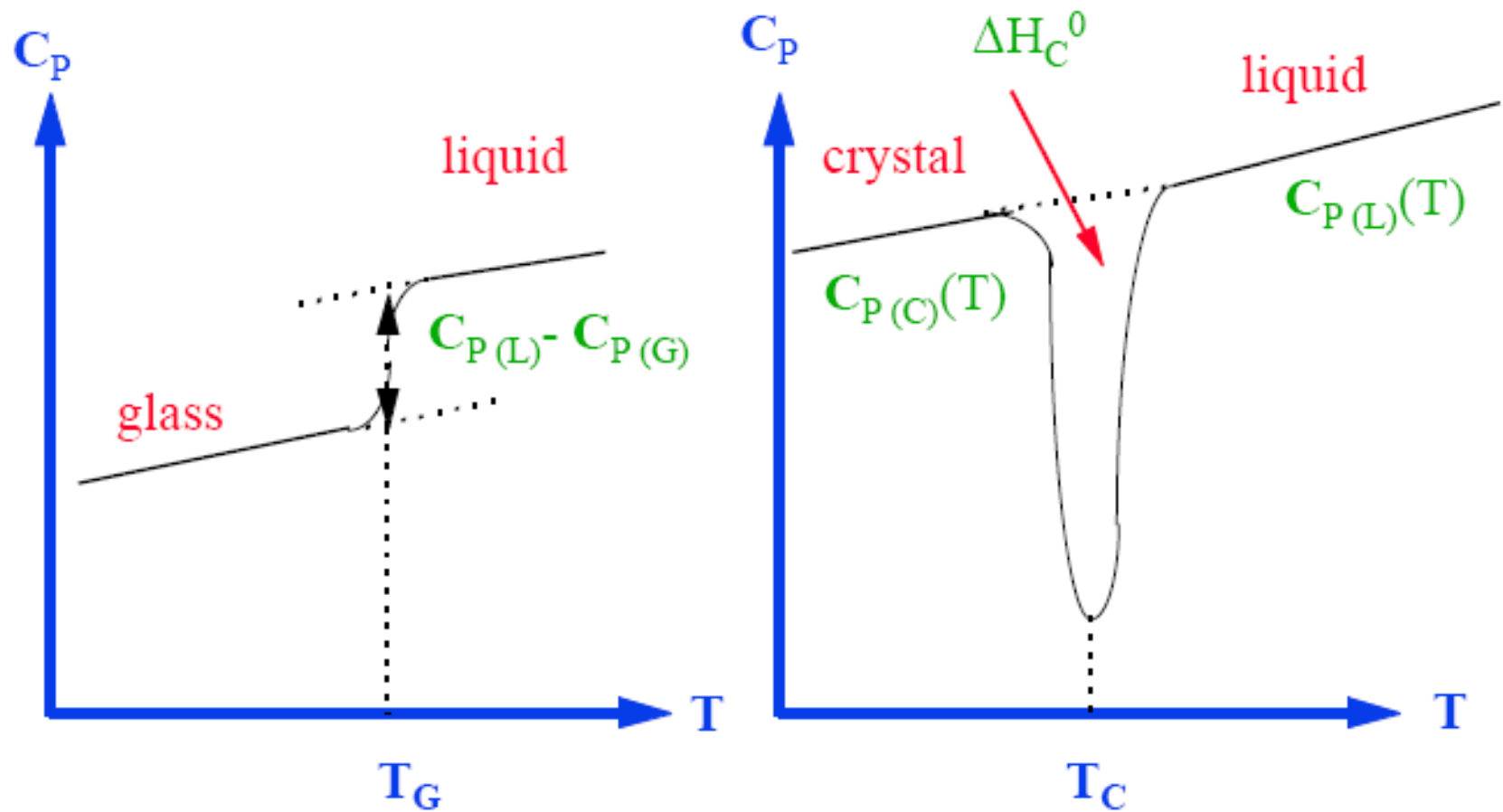   - First derivatives of G (V, S, H) are <u>continuous</u> at T_T

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

    - Second derivatives of G (α, β, C_p) are <u>discontinuous</u> at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

    - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

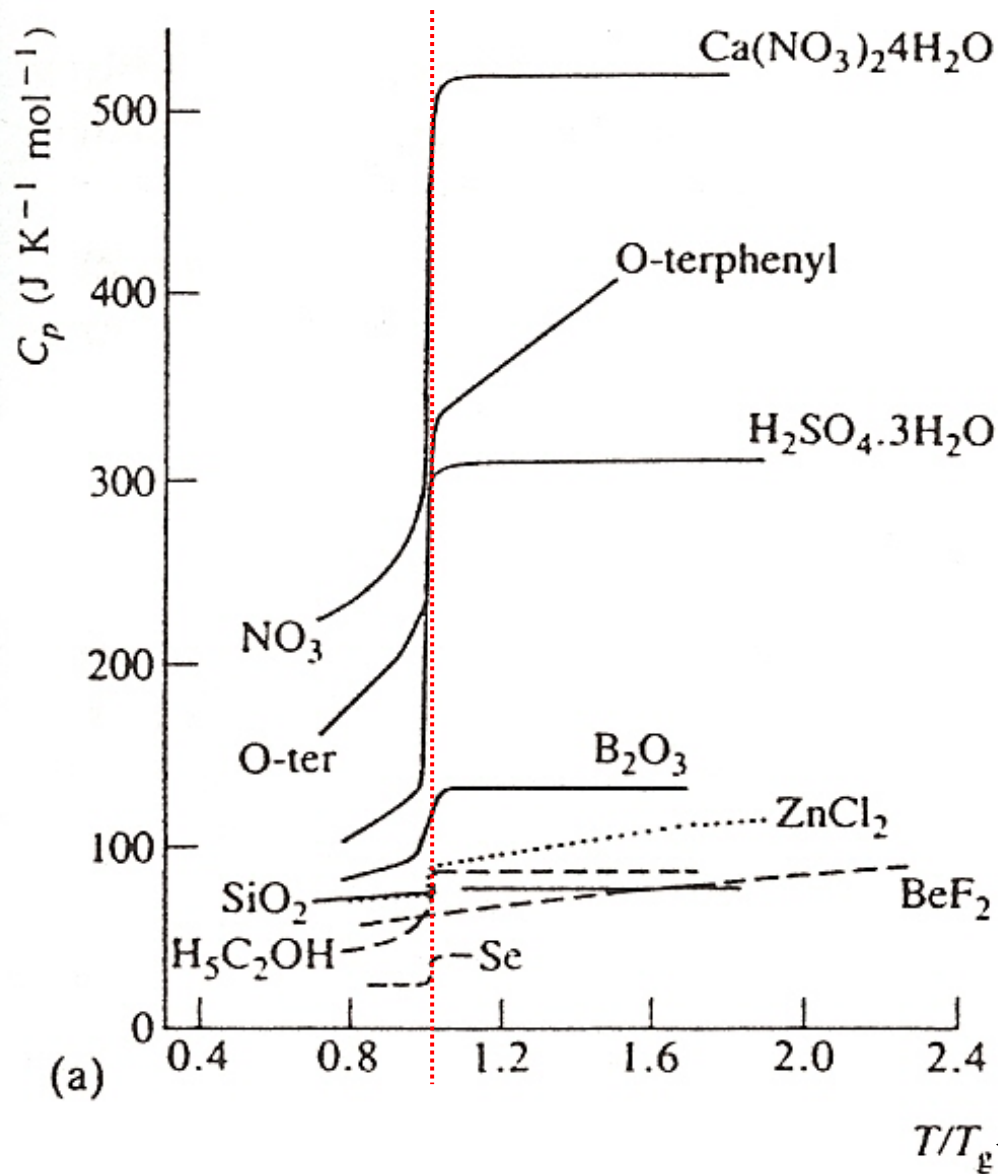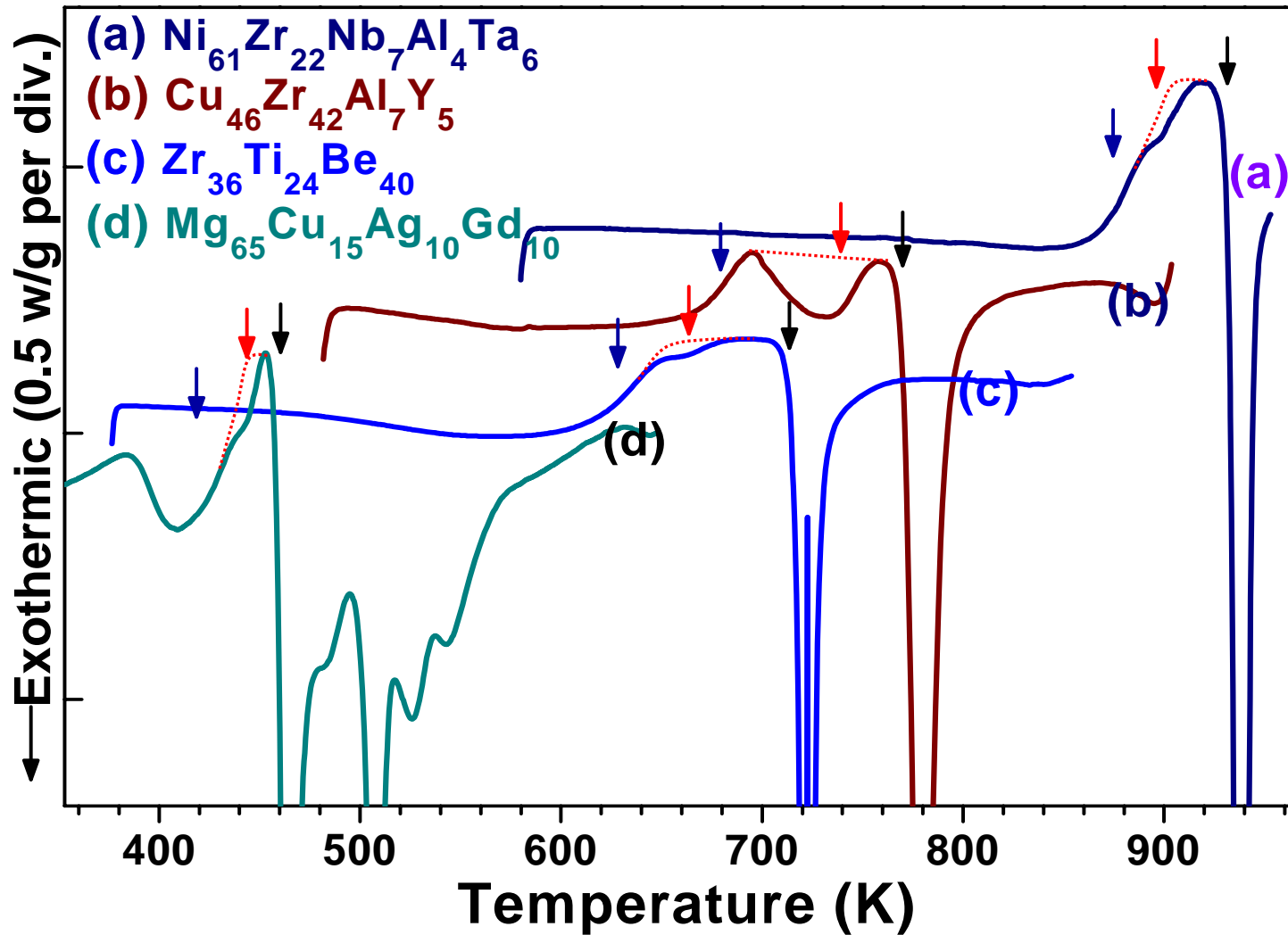# Experimental Evidence: Calorimetry $C_p = f(T)$

Liquid to Glass Transition
"Second Order" Transition

Liquid to CrystalTransition
First Order Transition

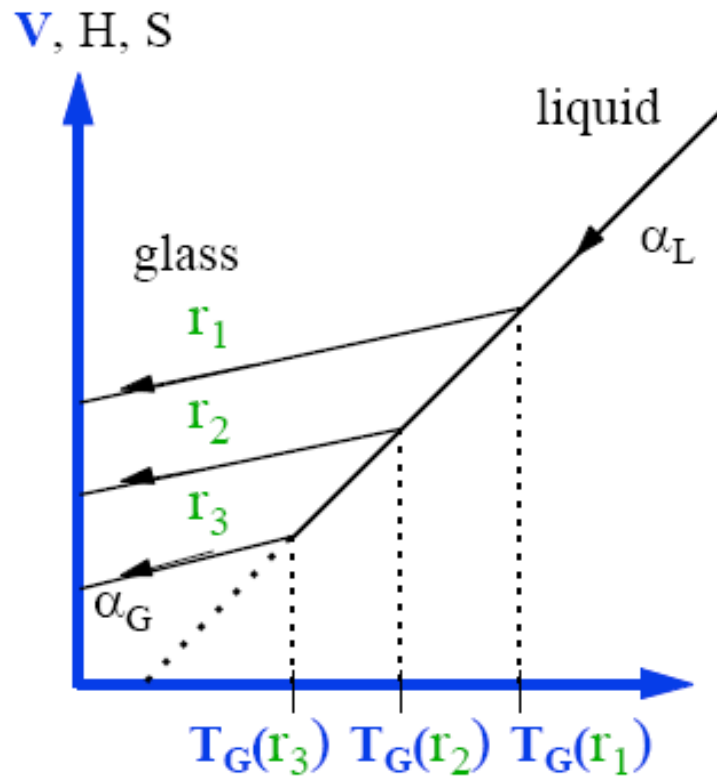# 1) *Difference of C_p at T_g depending on materials*

(a)

T/T_g ←—— **Normalizing as T_g**

2) change of T_gs depending on alloy compositions

(a) $Ni_{61}Zr_{22}Nb_7Al_4Ta_6$
(b) $Cu_{46}Zr_{42}Al_7Y_5$
(c) $Zr_{36}Ti_{24}Be_{40}$
(d) $Mg_{65}Cu_{15}Ag_{10}Gd_{10}$

Exothermic (0.5 w/g per div.)

Temperature (K)

3) T_g depends on thermal history.

Kinetic Nature of the Glass Transition

V, H, S

liquid

glass

r_1

r_2

r_3

α_L

α_G

$T_G(r_3)$ $T_G(r_2)$ $T_G(r_1)$

Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$

V, H, S

liquid

glass α_G

α_L

T_G
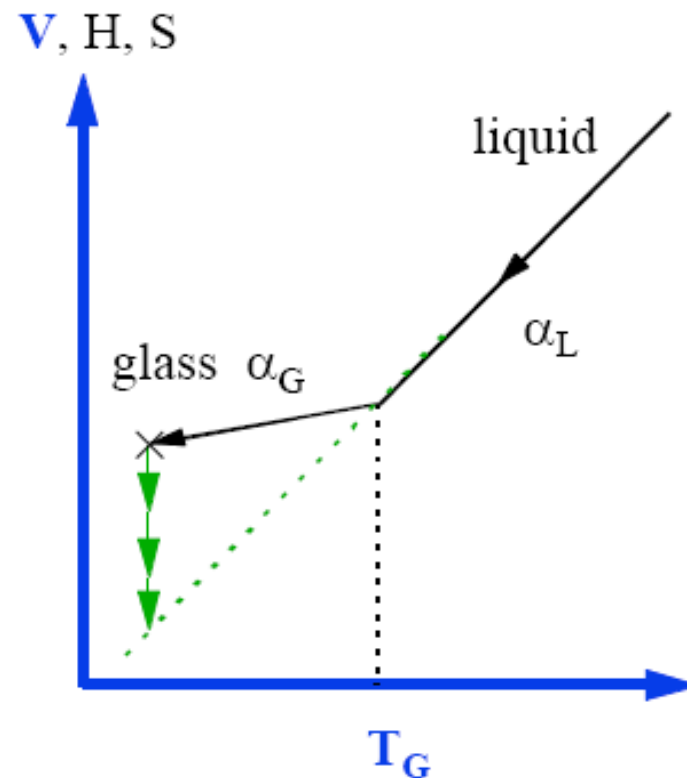
Specific Volume (density) of the glass depends on the time at a given $T < T_g$

# Kinetic Nature of the Glass Transition (cont.)

- The glass transition is not a true second order transition but only a "pseudo" second order phase transition

  - 1) the glass is not an equilibrium phase (i.e. its properties depend on time)

  - 2) the glass transition temperature depends on the rate at which it is measured. The glass transition will therefore be defined over a range of temperatures and pressures.

- An approximate but useful relationship is $T_G = (2/3)\ T_M$

- What is the origin of the kinetic nature of T_G ?
  The answer to this question is associated with the time scale for "relaxation of the structure" (return to equilibrium after a perturbation is communicated to the material: change in T or P). It is therefore related to whether or not the material properties (e.g density) can preserve their equilibrium value during the perturbation.

Temperature Dependence of Liquid Viscosity
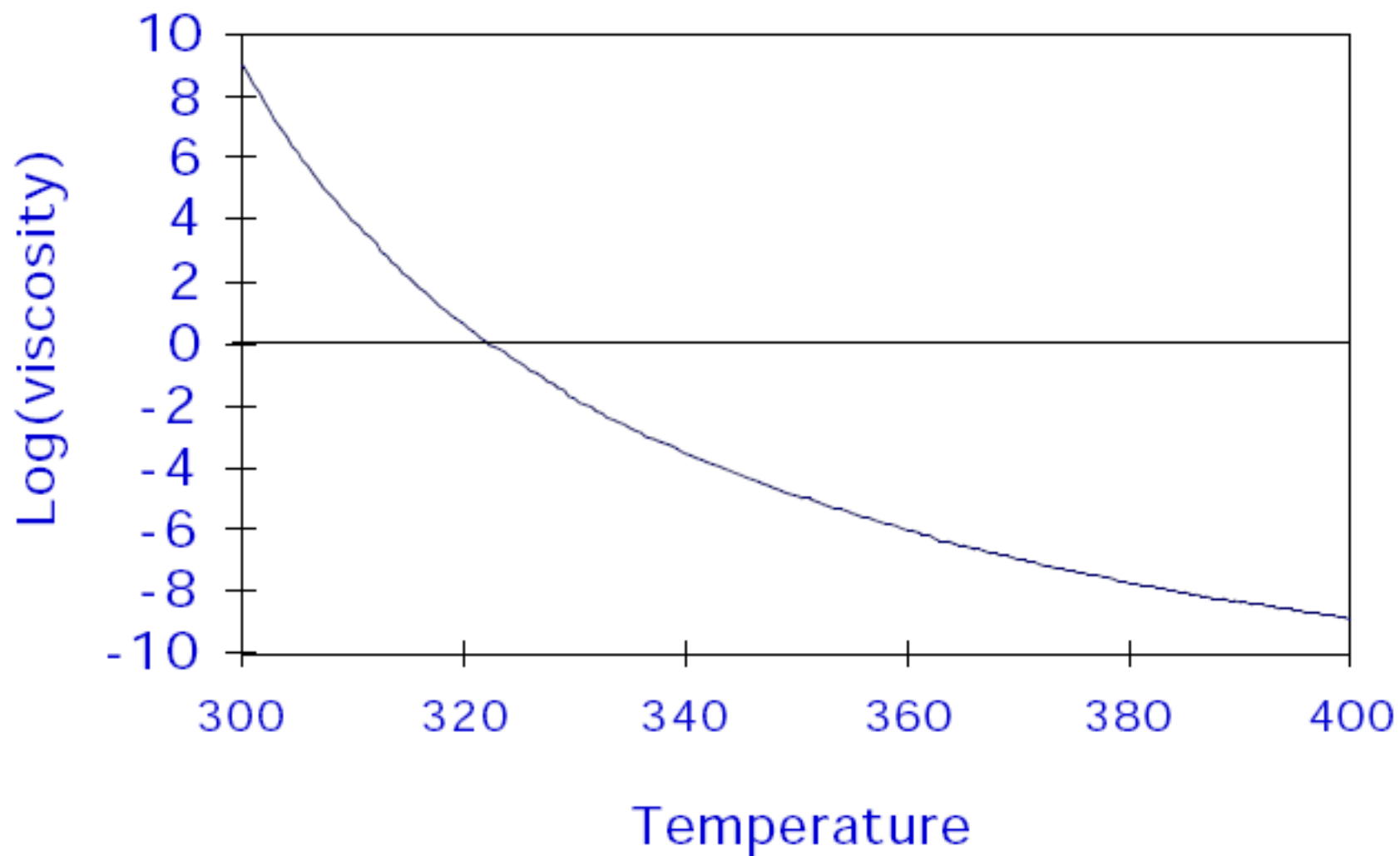
Temperature Dependence of Liquid Viscosity
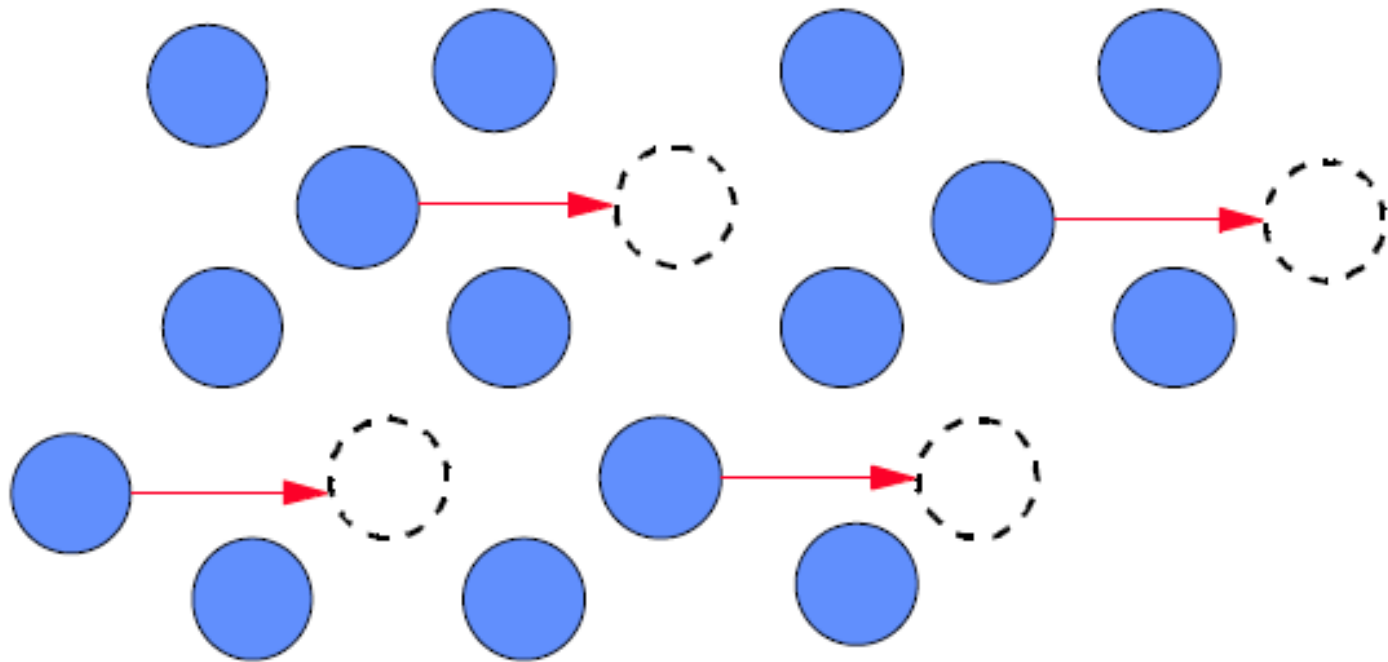
Viscosity is a measure of the resistance to flow. The higher T, the larger the average size of the holes and the larger the energy of the molecules, the easier the molecule move past oneanother, the lower the resistance to flow.

- ## *Formation of glass during cooling*

- At high T, molecular motion in the liquid is very fast and a change in T can lead to rapid ("instantaneous") molecular rerrangements. During cooling at high temperatures, the system's average free energy is always minimum (i.e. the liquid is at equilibrium at all times during cooling).

- At lower T, the rate of molecular motion becomes lower. The material preserves equilibrium properties during cooling as long as the rate of molecular rearrangement (required by the change in T) is larger than the rate at which the perturbation is exerted on the material (i.e. cooling rate).

- At some temperature (which we will denote as T_g), molecular motions become slower than the rate at which the temperature is changed. The material has no longer sufficient time during cooling to remain in equilibrium (i.e. to exhibit the equilibrium properties, e.g. specific volume) : the relaxation time scale is larger than the experimental time scale, the material does not respond instantaneously to the perturbation.

- The above statements explain the dependence of the measured glass transition temperature on the rate of cooling.

- A similar discussion can be applied to the effect of pressure.

- The fact that the rate of molecular motion decreases with temperature can be qualitatively explained on the basis of free volume concepts* (molecular motion is afforded by the existence of empty spaces between molecules). The higher the temperature, the higher the specific volume of the material (for a given number of molecules), the higher the free volume in the material, the higher the rate of molecular motion.

- The fact that the material is not in equilibrium below Tg because it did not have sufficient time to reach the equilibrium configuration (S) and density, therefore energy or enthalpy (H) during cooling explains why the specific volume decreases with time at a given $T < T_G$ (phenomenon of physical aging of glasses)

* free volume theory will be expanded upon later.

# Controversies in Amorphous Solids: The Kauzmann Paradox

If we extrapolate the specific volume of the liquid from above T_M to temperatures much below T_G, one must accept that at some temperature T_K well above 0 K, the specific volume, the enthalpy and the entropy of the equilibrium liquid would become lower than that of the crystal... Since the above statement is not possible (Kauzmann paradox) , two solutions are possible:

1) at some temperature (T_K), there is a true 2nd order phase tansition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!
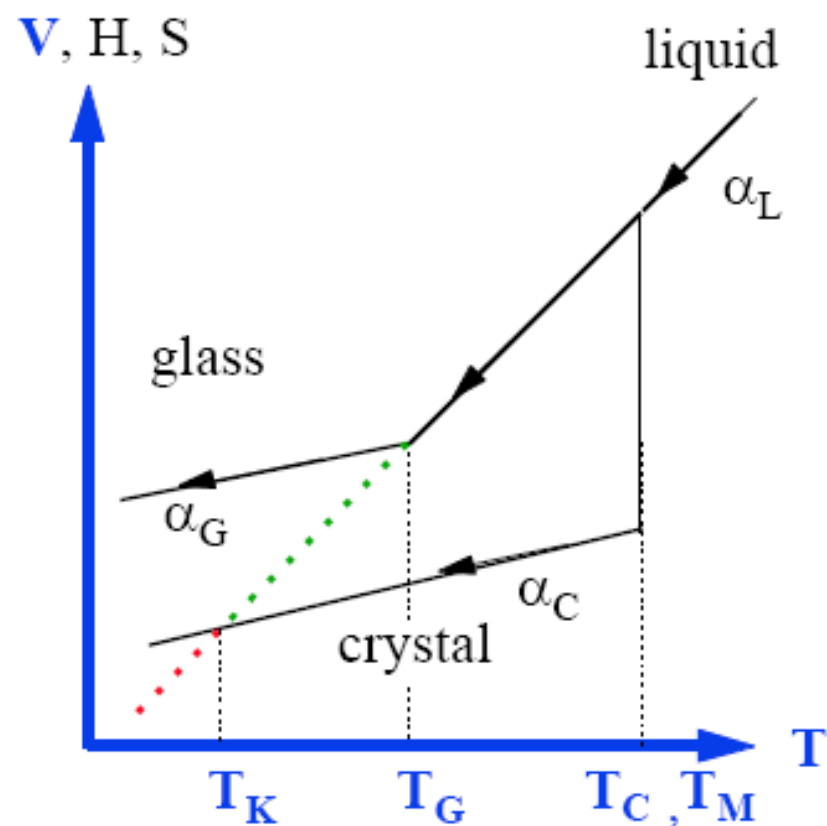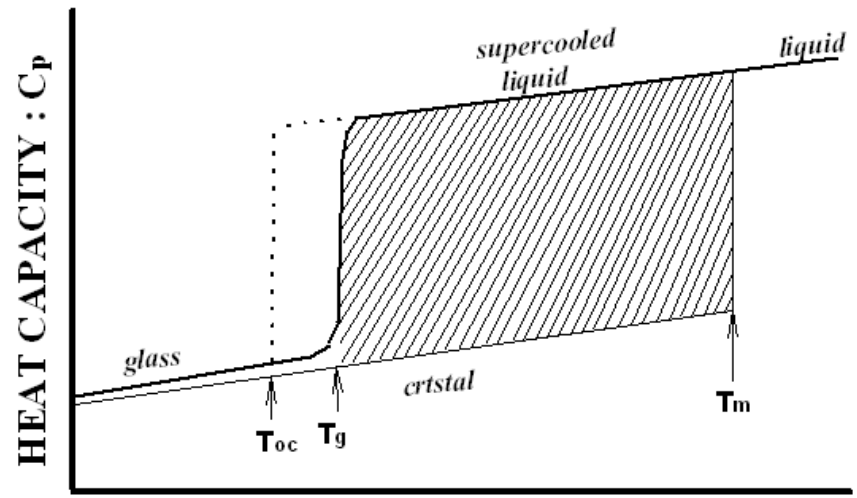
Ideal glass transition temperature (T_{oc})

: lower temperature limit to occur glass transition thermodynamically
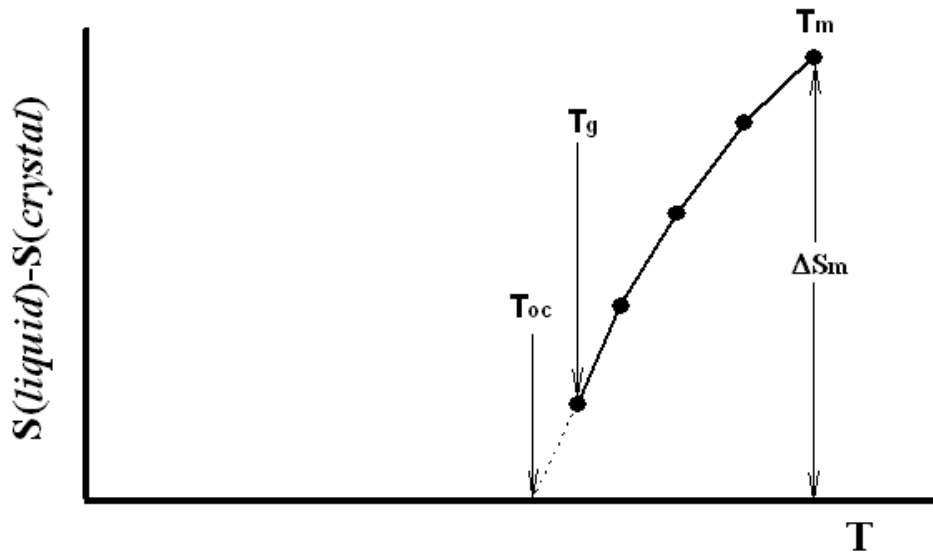
Variation of (a) C_p and (b) excess entropy, S depending on temp. for glass, crystal and liquid. Ideal glass transition temp, T_{oc}. is the temperature when excess entropy is disappeared.

Value of the Prigogine Defay Ratio: R

- Continuity conditions for G or μ at a first order phase transition allowed us to derive the Clapeyron equation $\left(\dfrac{dP}{dT}\right) = \dfrac{\Delta S}{\Delta V} = \dfrac{\Delta H}{T\Delta V}$

- If T_G is a second order transition, continuity of V and S at T_G leads to two similar relations between materials parameters and state variables.

$V_G = V_L \qquad dV_G = dV_L$
$dV_G = \alpha_G V_G dT - \kappa_G V_G dP$
$dV_L = \alpha_L V_L dT - \kappa_L V_L dP$

$\Longrightarrow \left(\dfrac{dP}{dT}\right) = \dfrac{\Delta C_p}{VT\Delta\alpha}$

$S_G = S_L \qquad dS_G = dS_L$
$dS_G = (C_p{}^G / T)dT - \alpha_G V_G dP$
$dS_L = (C_p{}^L / T)dT - \alpha_L V_L dP$

$\Longrightarrow \left(\dfrac{dP}{dT}\right) = \dfrac{\Delta\alpha}{\Delta\kappa}$

The Prigogine-Defay ratio, R, defined by: must be equal to unity.

$$R = \dfrac{\Delta C_p \Delta\kappa}{VT(\Delta\alpha)^2}$$

The Clapeyron equation

For stable equilibrium states it holds:

$$dg - vdP + sdT = 0 \qquad \& \qquad d\mu - vdP + sdT = 0$$

<p style="color:red; text-align:center">**specific Gibbs function**   **Gibbs-Duhem relation**</p>

i.e. the chemical potential coincides with the specific Gibbs function for a unary system. During a phase change, neither pressure nor temperature vary, hence
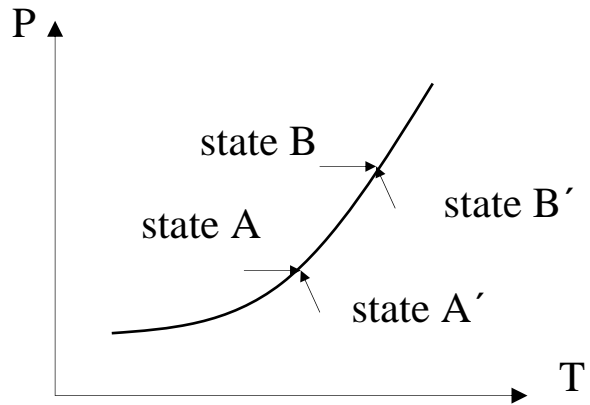
$$dg = 0 \Leftrightarrow g_1 = g_2 \qquad \& \qquad d\mu = 0 \Leftrightarrow \mu_1 = \mu_2$$

We will demonstrate that the Clausius-Clapeyron Eq. represents the inclination of the locus of points in the *PT* plane for which it holds $\mu_1 = \mu_2$.

Nota Bene: the specific volume and entropy, defined as $\quad v = \left(\dfrac{\partial g}{\partial P}\right)_T \quad$ and $\quad s = -\left(\dfrac{\partial g}{\partial T}\right)_P$ may be discontinuous at the interface.

The situations described here are the so called *first-order* phase change, because discontinuity occurs not in the specific Gibbs function but in its first derivative.

The Clapeyron equation

P

state B

state B′

state A

state A′

T

assuming $\quad dP_{AB} = dP_{A'B'} \approx 0 \atop dT_{AB} = dT_{A'B'} \approx 0 \quad$ we have:

$\mu_A = \mu_{A'} \ \& \ \mu_B = \mu_{B'}$ **phase equilibrium**

$\mu_B - \mu_A = -sdT + vdP$ **Gibbs-Duhem**

$\mu_{B'} - \mu_{A'} = -s'dT + v'dP$ **for each phase**

$$\frac{dP}{dT} = \frac{s'-s}{v'-v} \quad \Longrightarrow \quad \frac{dP}{dT} = \frac{\Delta s}{\Delta v}$$

where Δv, Δs represent the discontinuity in specific entropy and volume. Since the latent heat is equal to $L = T \Delta s$, it yields

$$\frac{dP}{dT} = \frac{L}{T(v'-v)} \qquad \textbf{Clausius-Clayperon}$$

for thermally perfect gases $v << v'$, hence

$$\frac{dP}{dT} = \frac{L}{Tv'} = \frac{PL}{R_v T^2}$$

$$\ln P_{S,\infty} = -\frac{L}{R_v T} + const.$$

good approximation of sublimation & evaporation curves, although the Eq. of perfect gases is much more accurate near the triple point than at the critical point.