2014 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

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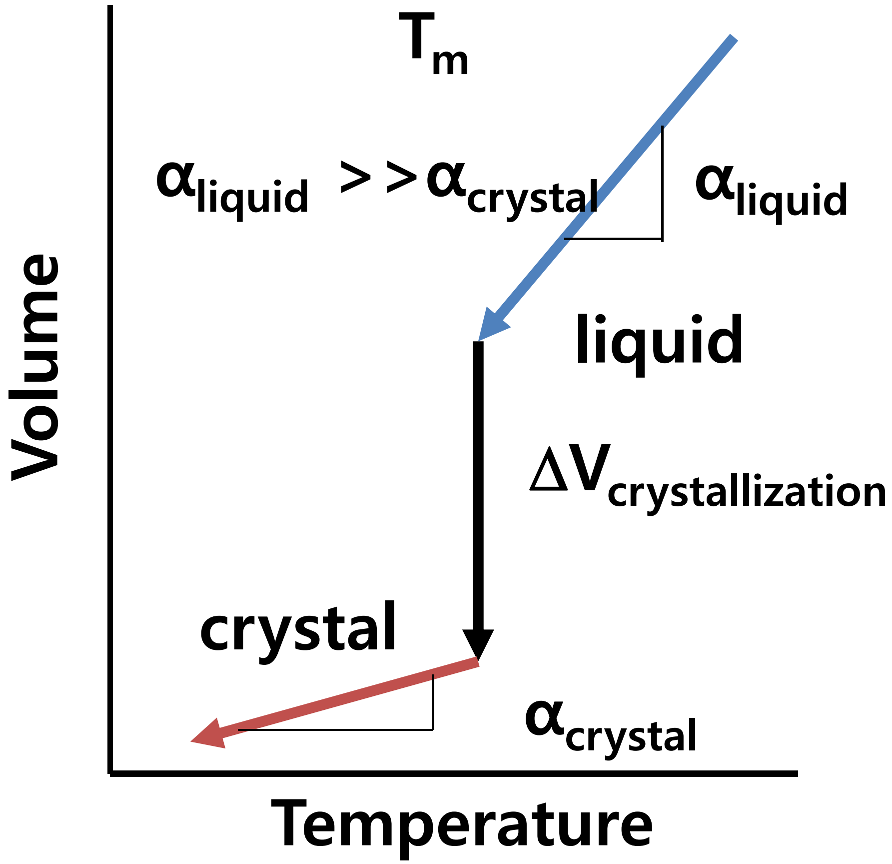
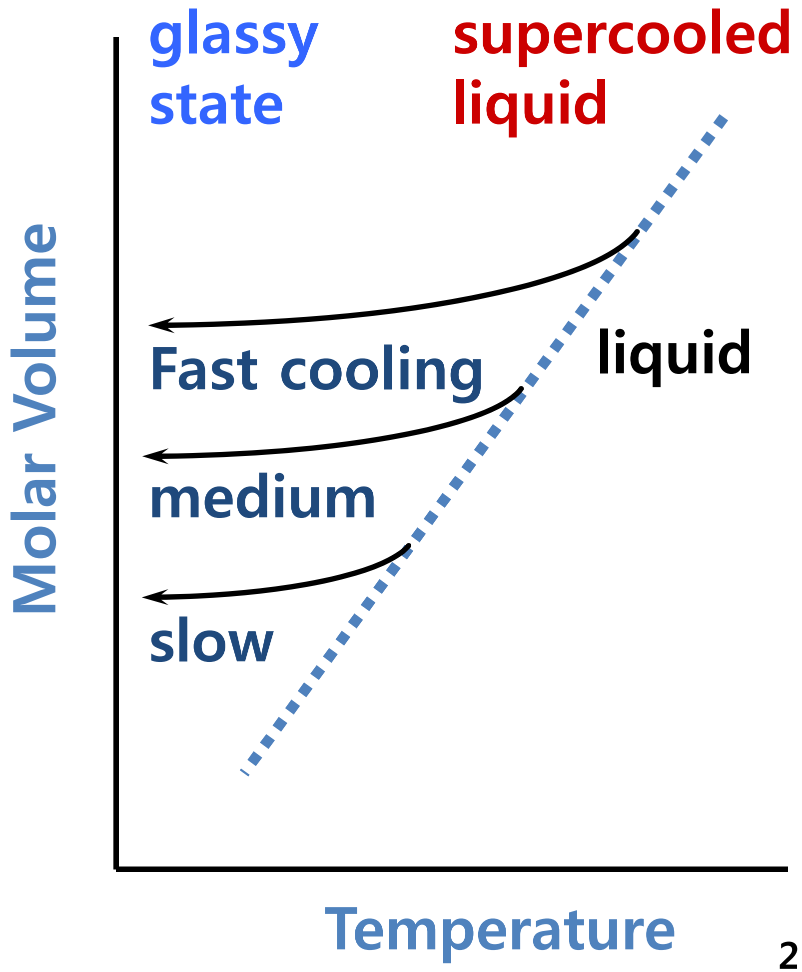
* Fundamentals of the Glass Transition

- Melting and Crystallization are **Thermodynamic Transitions**

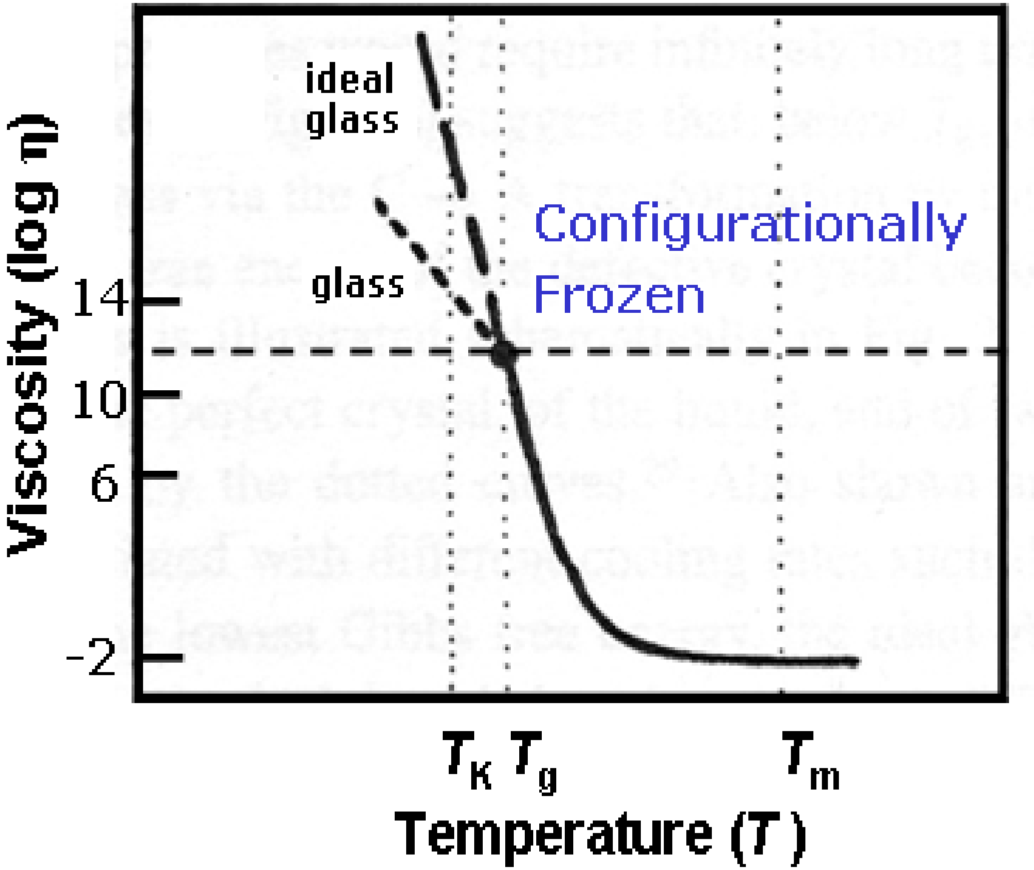


- The Glass Transition is a **Kinetic Transition**



Glass : undercooled liquid with high viscosity

The higher the structural relaxation, the closer it moves toward a "true" glass.

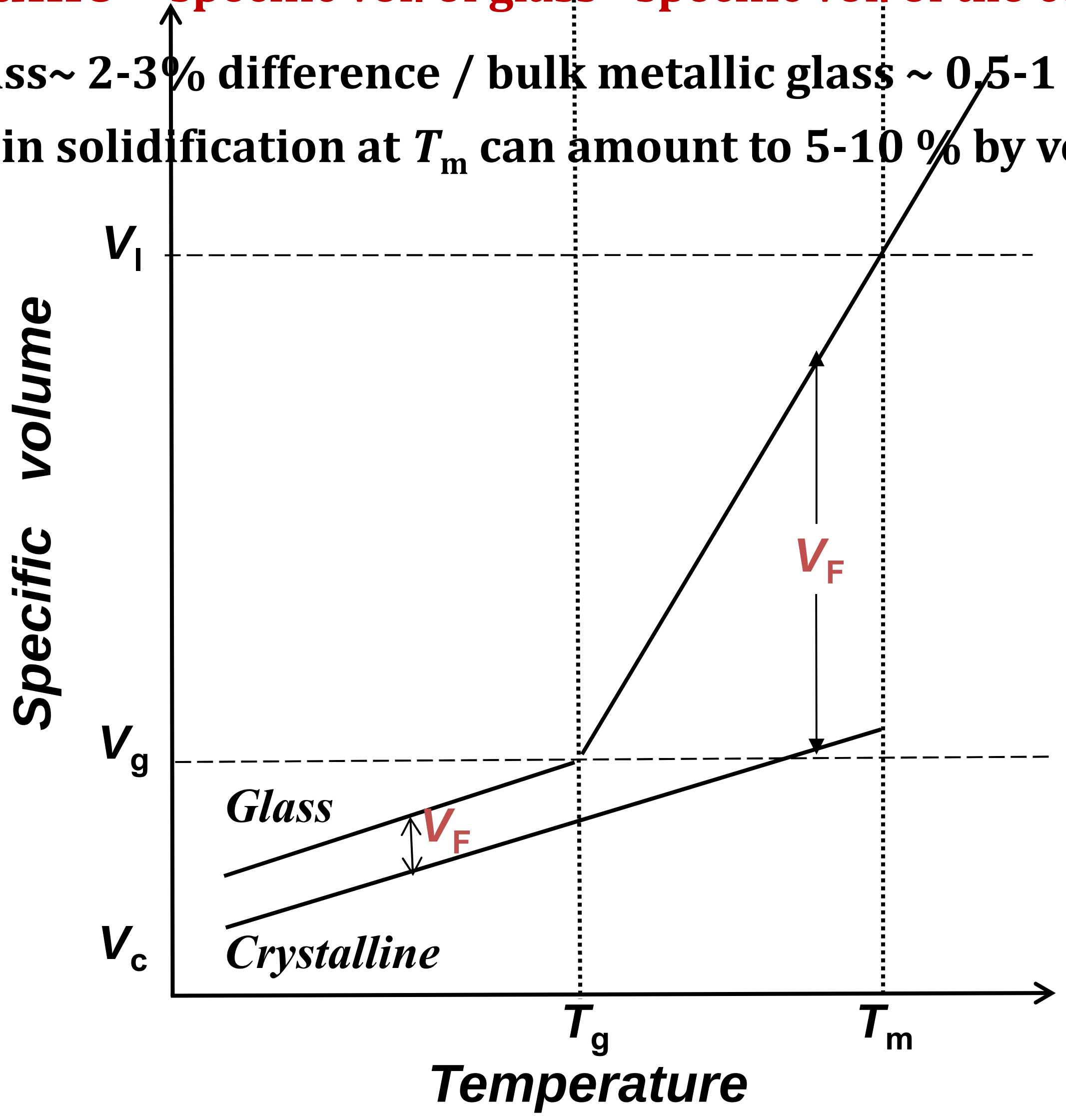


A solid is a materials whose viscosity exceeds $10^{14.6}$ centiPoise (10^{12} Pa s)

cf) liquid ~*10^{-2} poise*

* Free volume = specific vol. of glass - specific vol. of the corresponding crystal

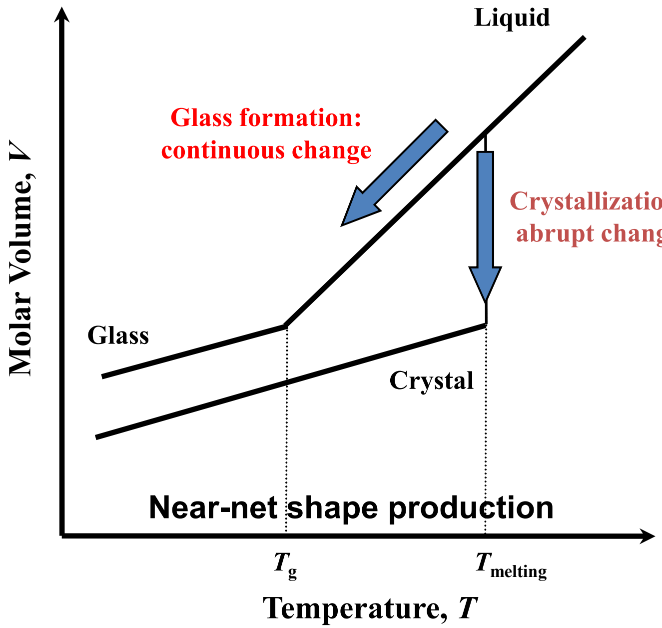
- normal glass~ 2-3% difference / bulk metallic glass ~ 0.5-1 % difference
- Shrinkage in solidification at T_m can amount to 5-10 % by volume.

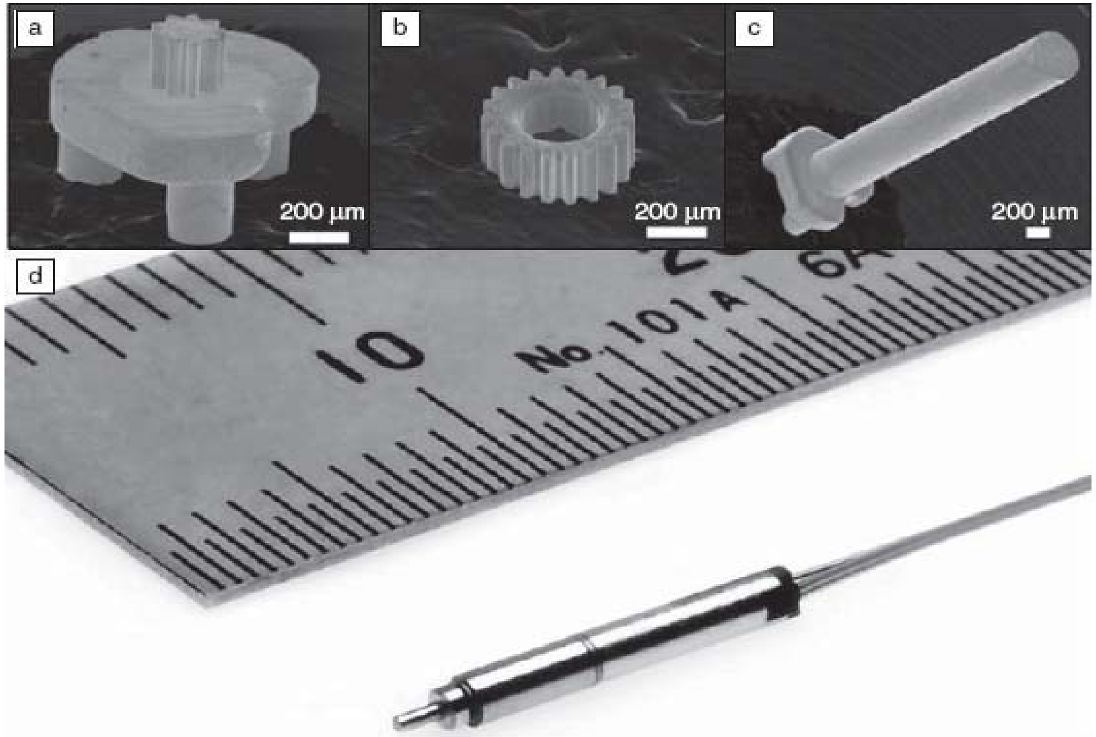


At the glass transition temperature, T_g, the free volume increases leading to atomic mobility and liquid-like behavior.

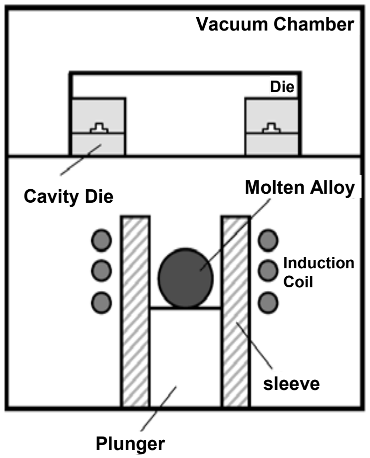
Below the glass transition temperature, atoms (ions) are not mobile and the material behaves like solid

* Micro/Nano casting

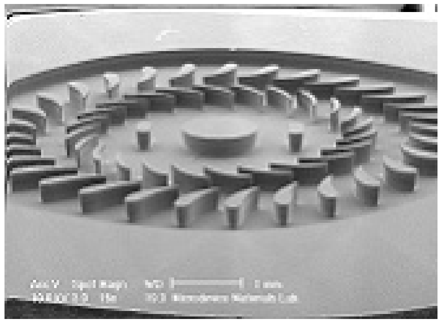


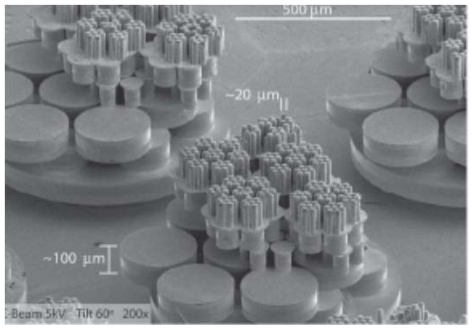


Precision Gears for Micro-motors



Precision die casting

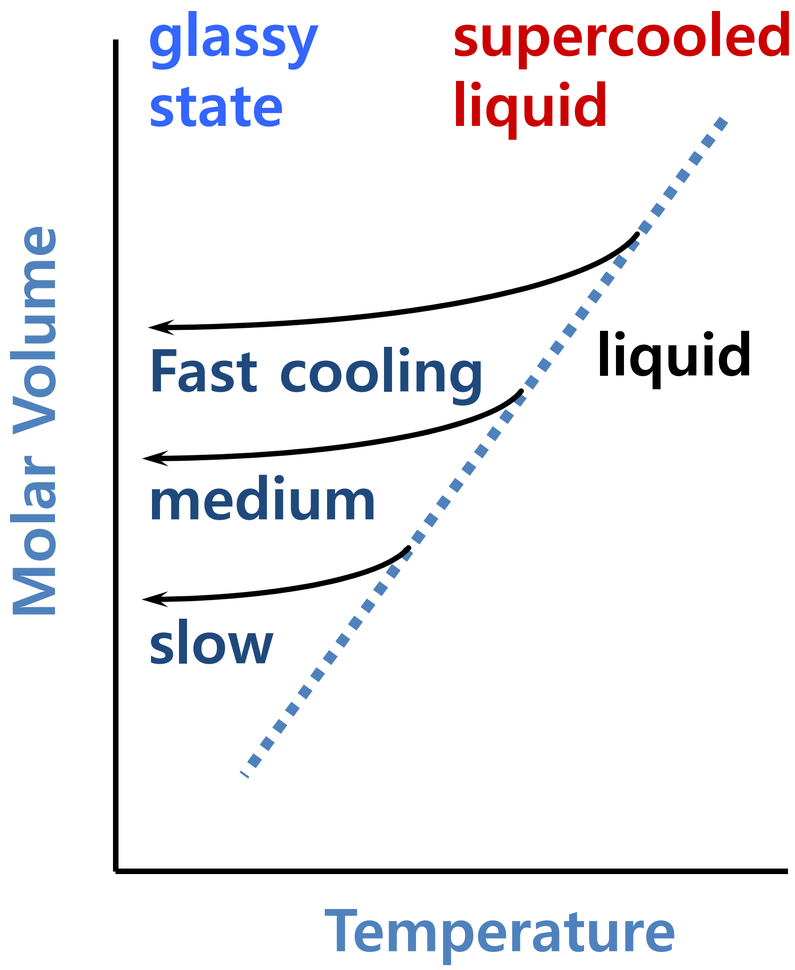




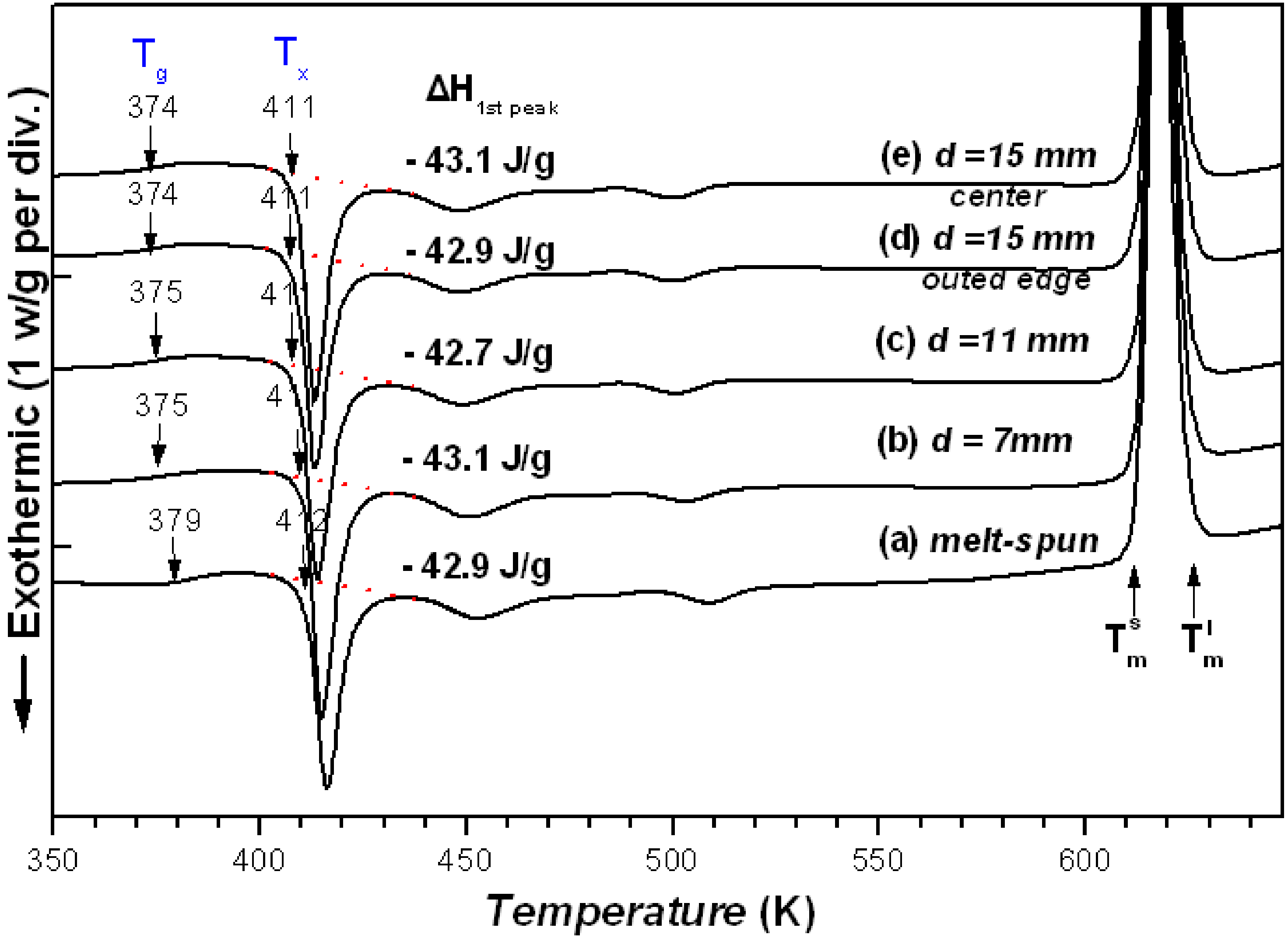
MRS BULLETIN ***32*** *(2007)654.*

The Cooling Rate Affects the Properties of Glass

- Faster cooling freezes in the glass at a higher temperature
- The temperature is lowered so fast that the liquid does not have time to relax to the properties at the next lower temperature, glass is formed at a high temperature
- Slower cooling freezes in the glass at a lower temperature
- The temperature is lowered slowly enough that the liquids can relax to properties at lower and lower temperatures, glass is eventually formed at a lower temperature

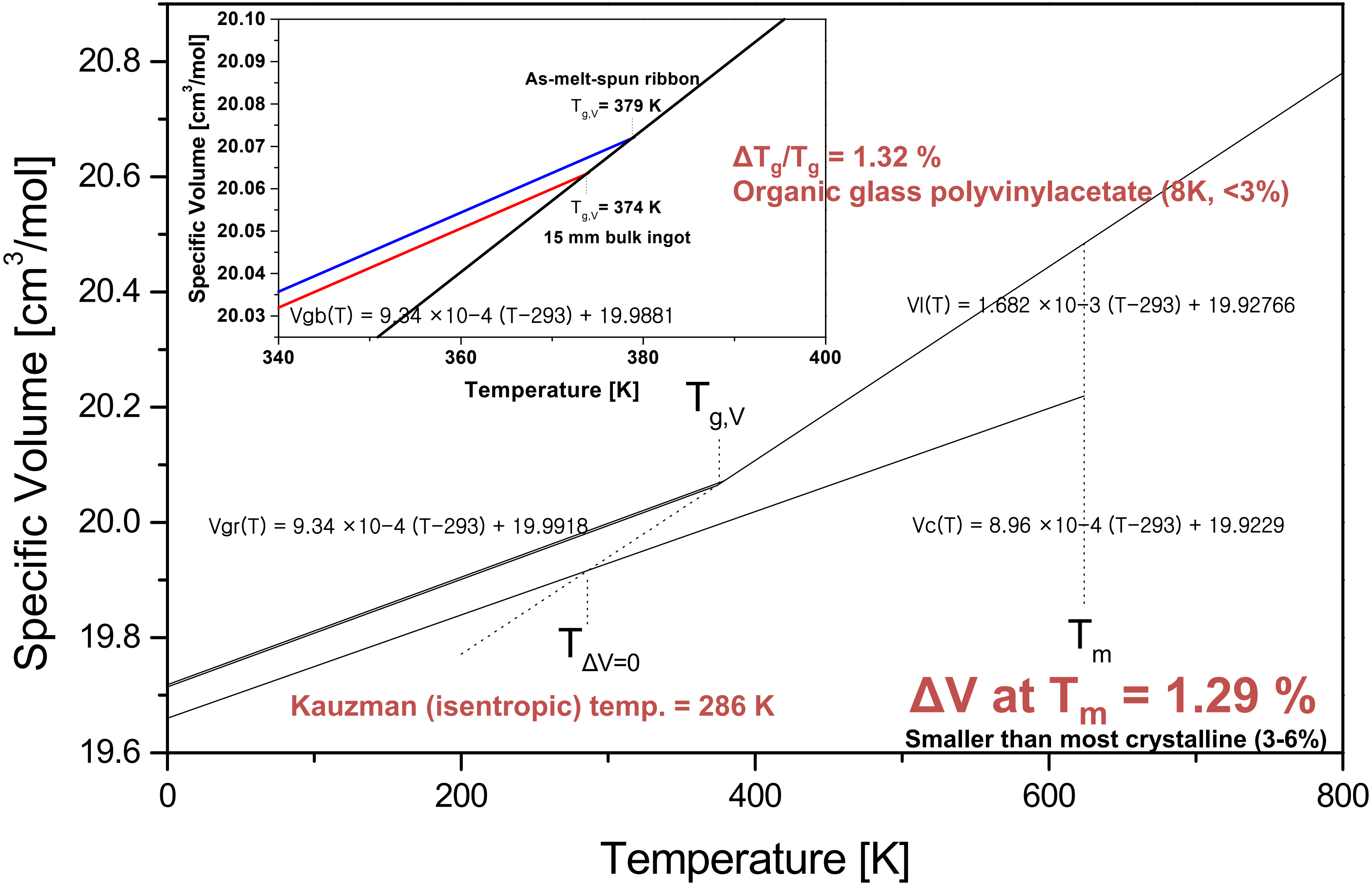


❖ Typically T_g is ~ 50-60% of the melting point. ($0.6T_m$)



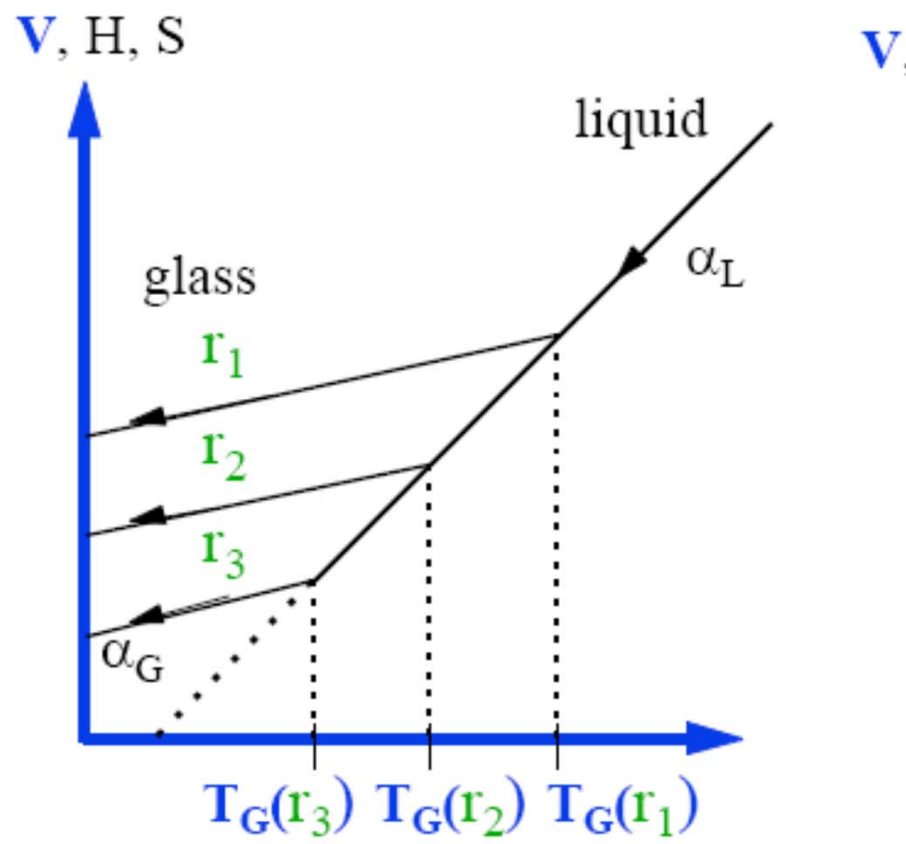
* J Mater Res, 19 (2004) 685.

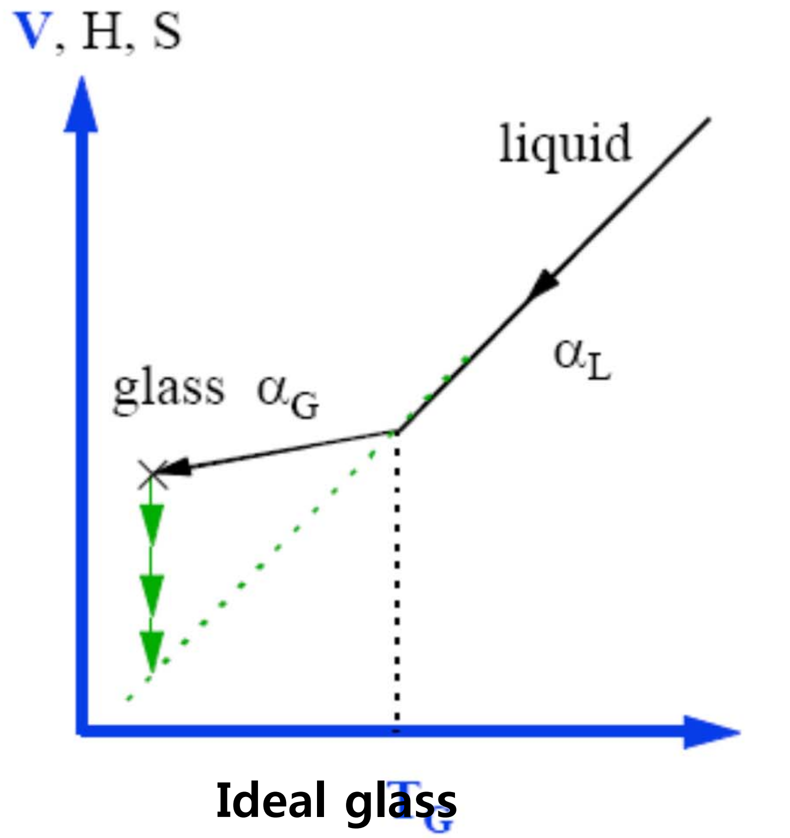
* T_g depends on thermal history even in same alloy composition.



* **APL, 92 (2008) 091915.**

* Kinetic Nature of the Glass Transition





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

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

*** Glass → exited state –(sufficient time)→ relax and eventually transform to crystalline ground state**

2.5 Thermodynamics and Kinetics of Glass Formation

"Phase Transition"

Thermodynamically: what is possible!
Kinetics: speed/rate of the transition

Thermodynamical classification: first order & second order

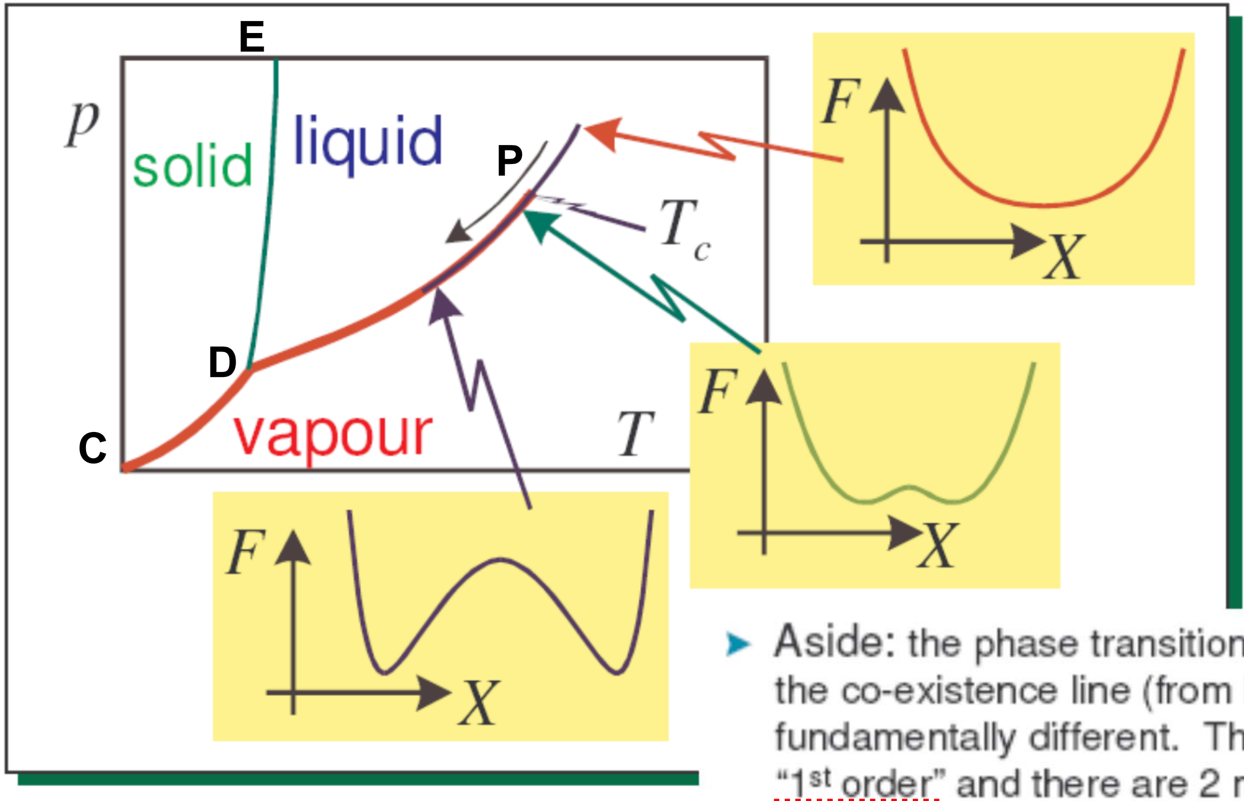
$$\Delta G = \Delta H - T\Delta S = 0$$

• Order (degree) of transition

***Continuous phase transitions*:**

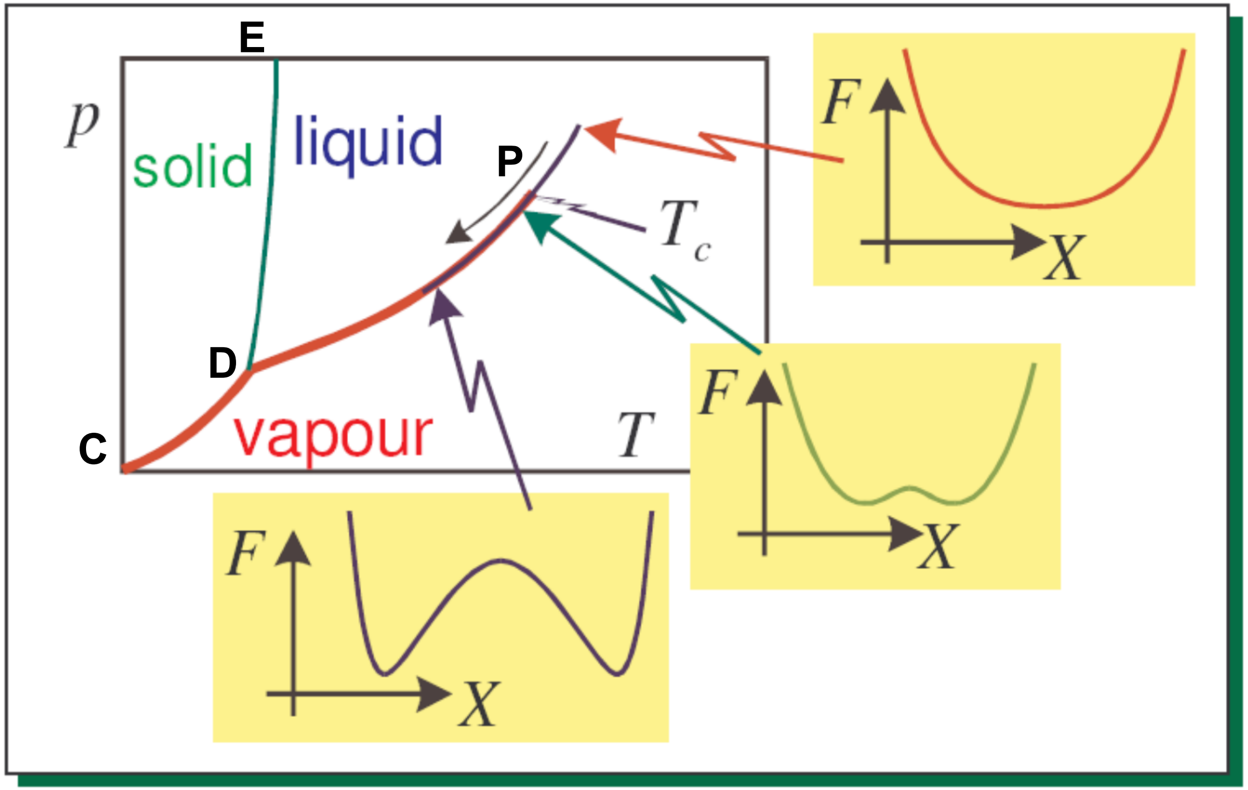
occur when the minimum in the thermodynamic potential evolves smoothly into two equal minima.

An example is seen in the model of phase separation, along the co-existence line.



➤ Aside: the phase transition as one moves across the co-existence line (from liquid to vapour) is fundamentally different. That transition is known as "1st order" and there are 2 minima in the potential throughout. In the transition the lowest minimum changes from liquid to vapour (and vice-versa).

- **Order (degree) of transition**



- **CD, DE, DP: Equilibrium of 2 phases**
  - → latent heat
  - → Volume change
  - → 1st order transition

- **T and P beyond point p**
  : vapor and liquid are indistinguishable.
  - → Single phase: only property changes.
  - → No boiling pt. / no latent heat
  - → Higher order transition

First-order transition:
a discontinuity occurs in the first derivative of the free energy with respect to T and P.

Discontinuous enthalpy, entropy and volume

$$\frac{dG}{dT} = -S$$

$$\frac{dG}{dP} = V$$

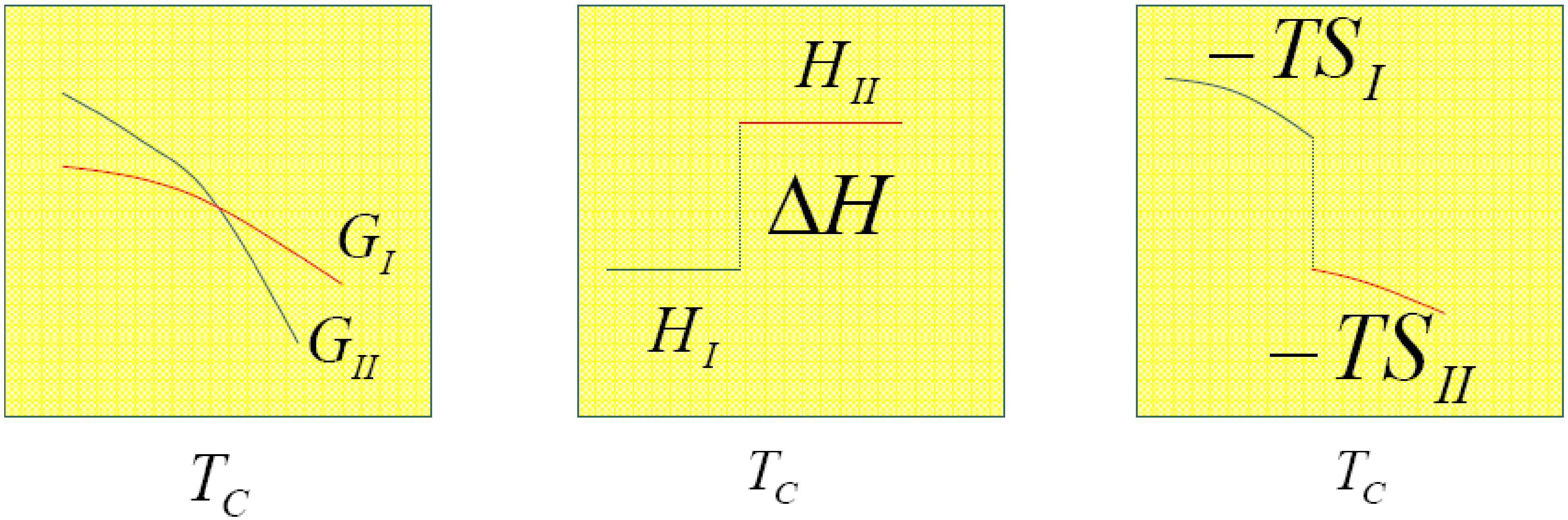
Examples: CsCl structure to NaCl structure; T =479 C.

$$\Delta V = 10.3 cm^3$$

$$\Delta H = 2.424 kJ / mol$$

Melting, freezing, vaporization, condensation…

First-order transition:



Second order transition: Discontinuities in the second derivatives of the free energy, i.e. heat capacity, thermal expansion, compressibility.

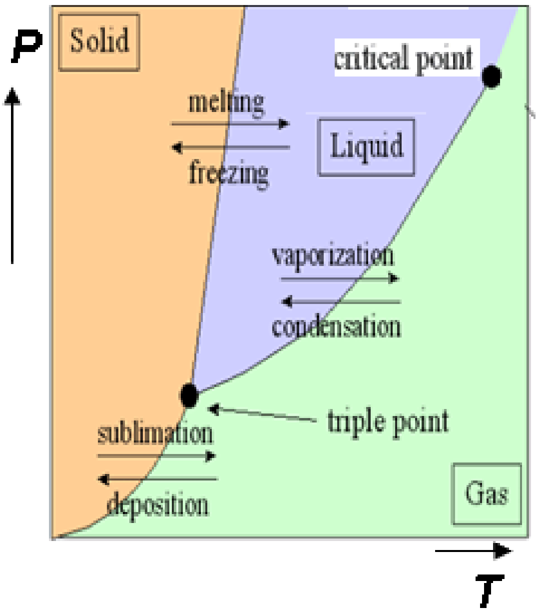
Enthalpy, entropy and volume, continuous functions of T

$$\frac{\partial^2 G}{\partial P_T^2} = \frac{\partial V}{\partial P_T} = -V\beta(compressibility)$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial V}{\partial T_P} = V\alpha(thermal\,\exp ansion)$$

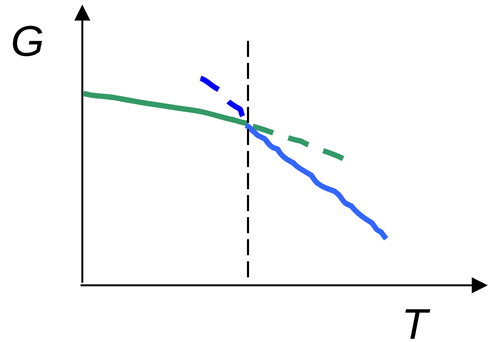
$$\frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T_P} = -\frac{C_p}{T}$$

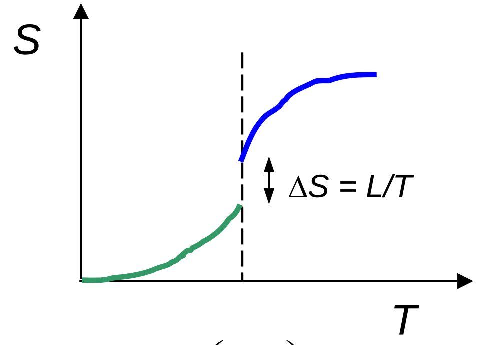
Measurement of heat capacities (calorimetry)



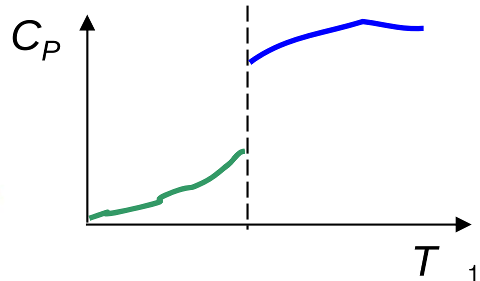
The First-Order Transitions

Latent heat
Energy barrier
Discontinuous entropy, heat capacity





$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$



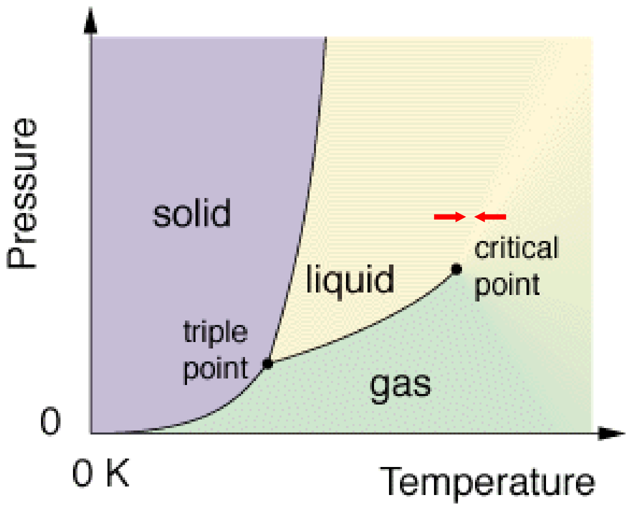
- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

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

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

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

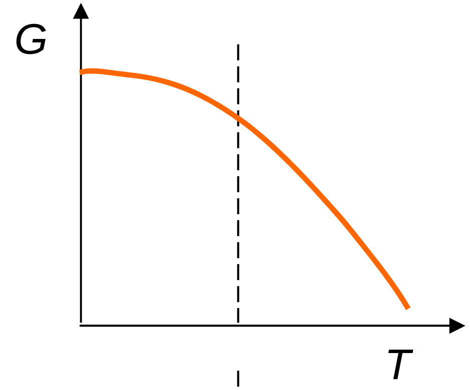
  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

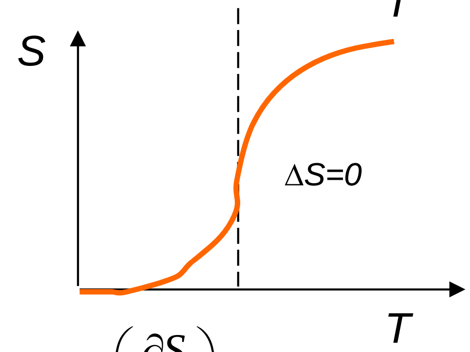


The Second Order Transition

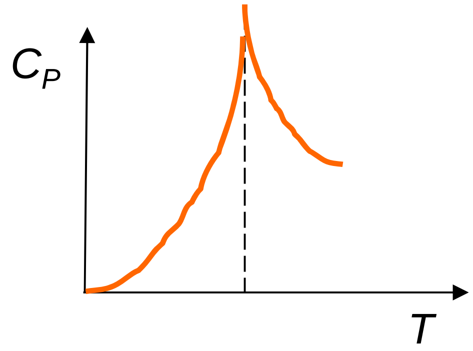
No Latent heat
Continuous entropy

Second-order transition





$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \to \infty$$



- 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

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

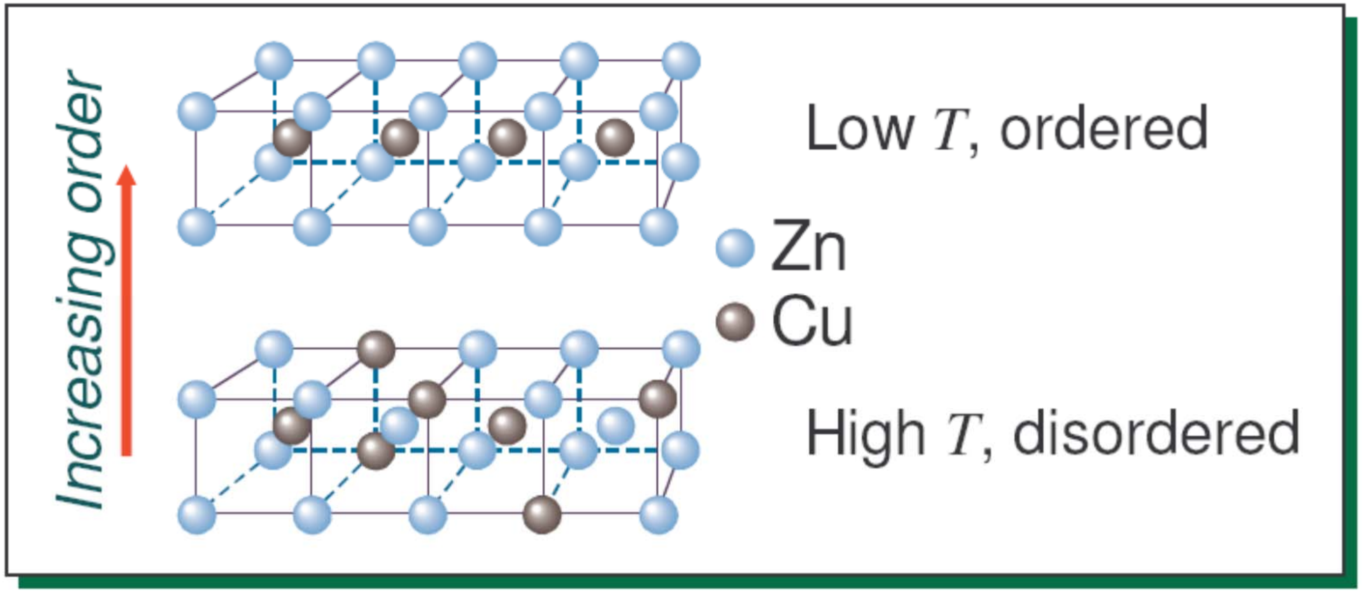
  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Order-disorder transition: 2nd order transition

- β-brass.

~ **Brass is a 50:50, Cu:Zn alloy with a b.c.c structure.**

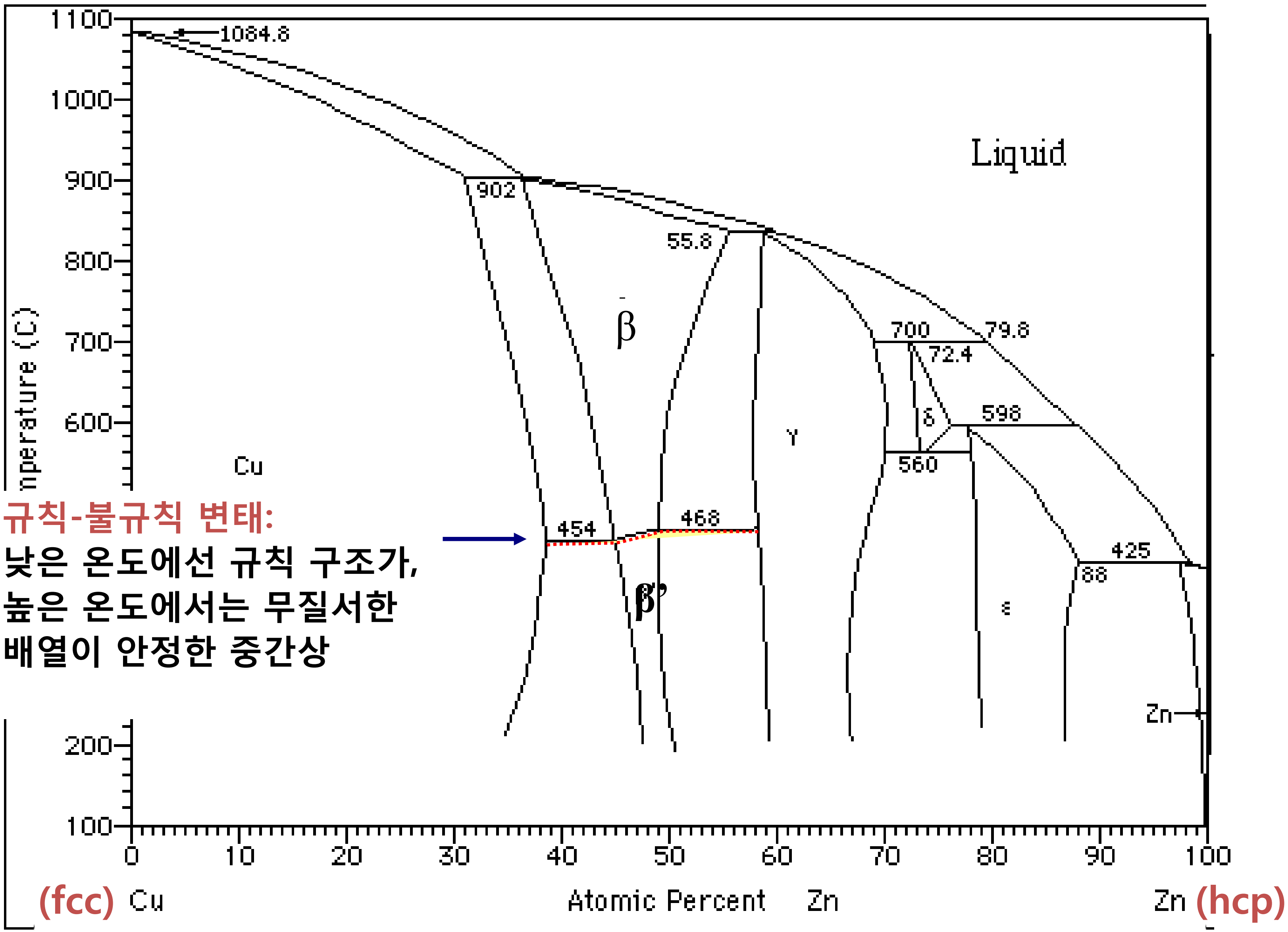
~ **At low temperatures, T<460K, the Zn and Cu atoms for an ordered structure (eg. Cu atoms in the body-centre sites in top diagram)**



- Two types of site call them: A-sites and B-sites.
- At high T, equal probability for any site to be occupied by Cu or Zn.

Intermediate Phase

$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim -21$ kJ/mol



- α and η are terminal solid solutions
- β, β', γ, δ and ε are intermediate solid solutions.

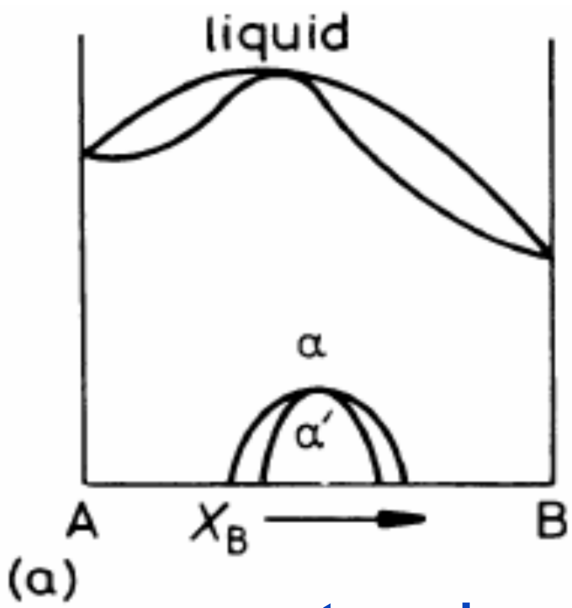
Ordered Alloys $\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} < 0$

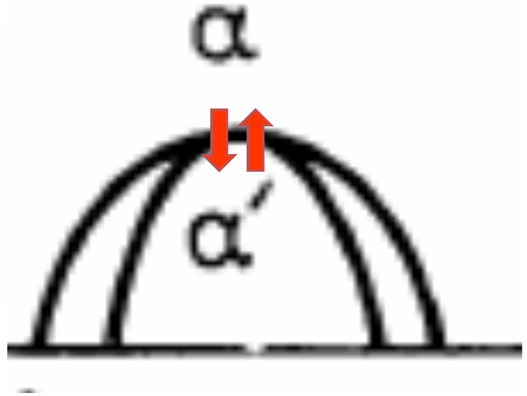
a. **$\Delta H_{mix} < 0 \rightarrow$ A atoms and B atoms like each other.**

How does the phase diagram differ from the previous case?

b. **What would happen when $\Delta H_{mix} << 0$?**

$\rightarrow$ The ordered state can extend to the melting temperature.



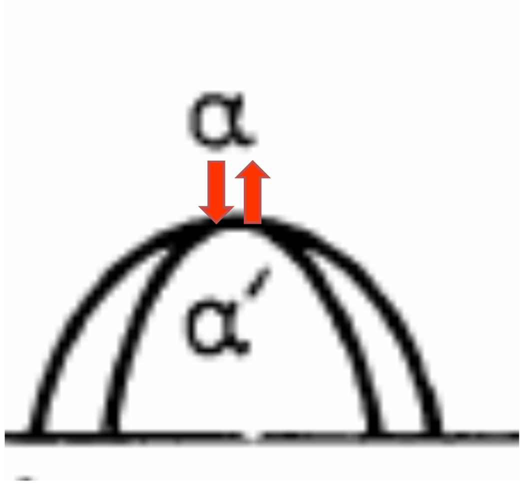


congruent maxima

Order-disorder phase transformation

- Not classical phase change=~not depend on diffusion process
- change of temperature allowed a continuous re-arrangement of atoms without changing the phase
- boundary: ordered lattice & disordered lattice/phase rule could not applied

  there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.
- Simple composition of the type AB or AB_3 can the transformation (i.e. at the temperature maximum) be considered diffusionless.



* Solid solution

→ random mixing

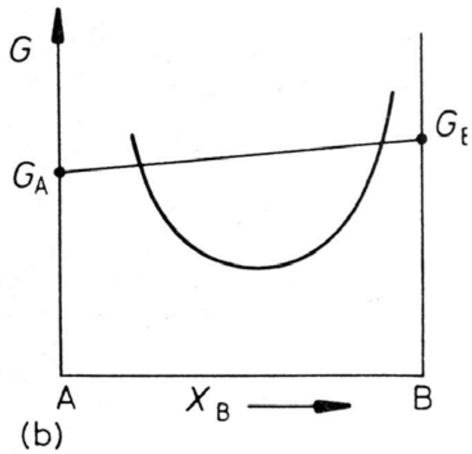
→ entropy ↑

negative enthalpy ↓

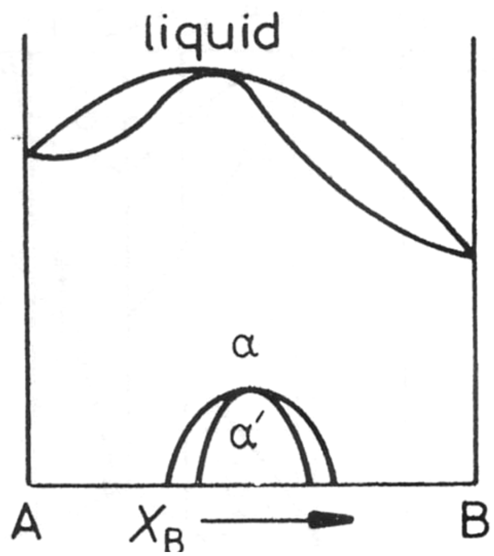
$$\Delta H^{S}_{mix} < 0$$

Large composition range

➔ G ↓



diate phases: (a) for an intermetallic com-
(b) for an intermediate phase with a wide



* Compound : AB, A_2B...

→ entropy↓

→ covalent, ionic contributioi

→ enthalpy more negative ↓

$$\Delta H^{S}_{mix} << 0$$

Small composition range

➔ G ↓

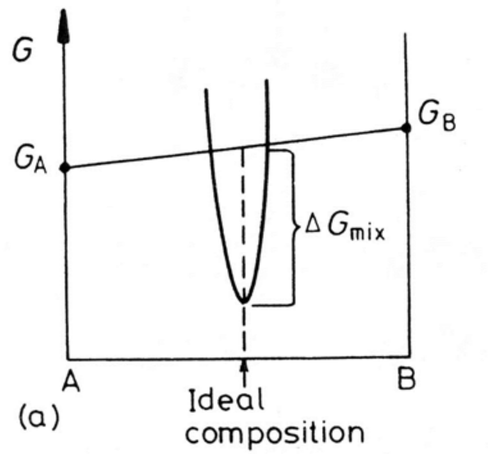
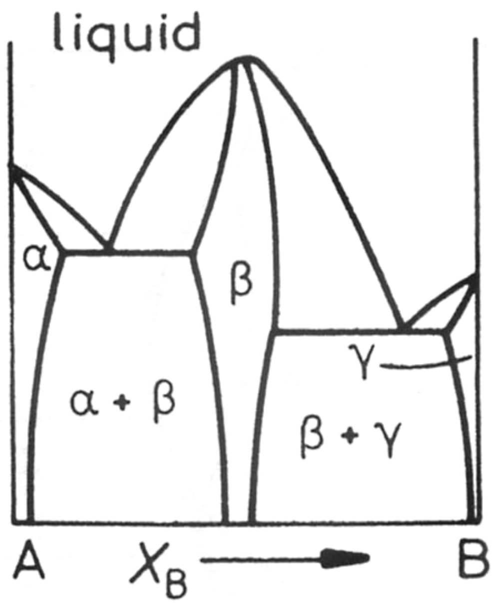


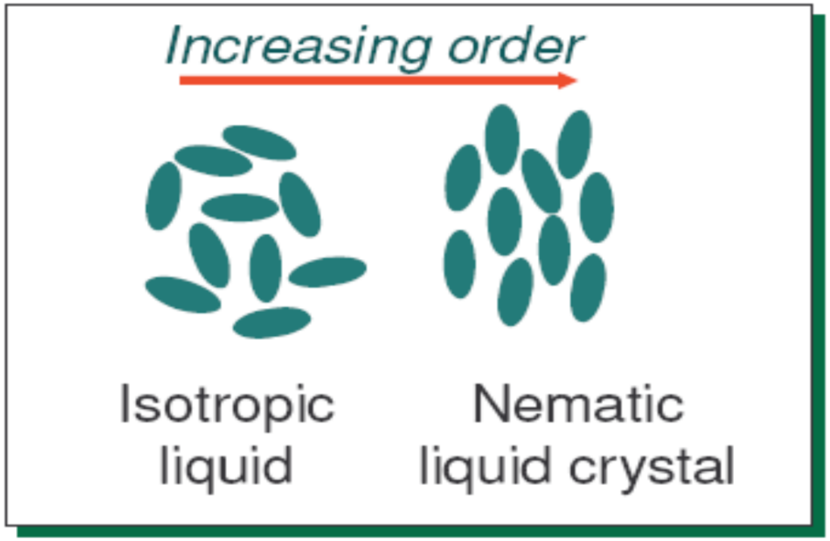
Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.



Order-disorder transition: 2nd order transition

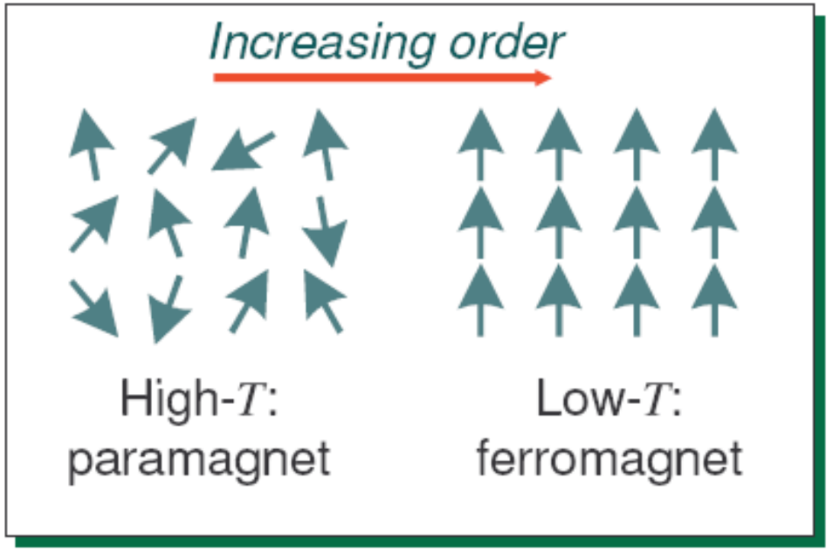
♦ Other examples (there are many):

➤ Isotropic – nematic transition in liquid crystals: appearance of orientational order (liquid crystals have no long-range, positional order).



액정의 가는 분자가 서로의 위치는 불규칙하지만
모두 일정방향으로 향하고 있는 상태

➤ Ferromagnetic - paramagnetic transition: manifests itself as a spontaneous polarisation, in zero external field.



- **Thermodynamics for glass transition**

~ not thermodynamic nature
~ close to second order phase transition

➡ *at T_g* → *G changes continuously.*

→ *V, H. S changes continuously.*

– First derivatives of G (V, S, H) are continuous at T_T

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

→ *α_T C_P K_T changes discontinuously.*

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

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

❖ **The glass transition is 'pseudo' second-order phase transition. And the transition depends on kinetic factors.**