Welding Technology
ME692

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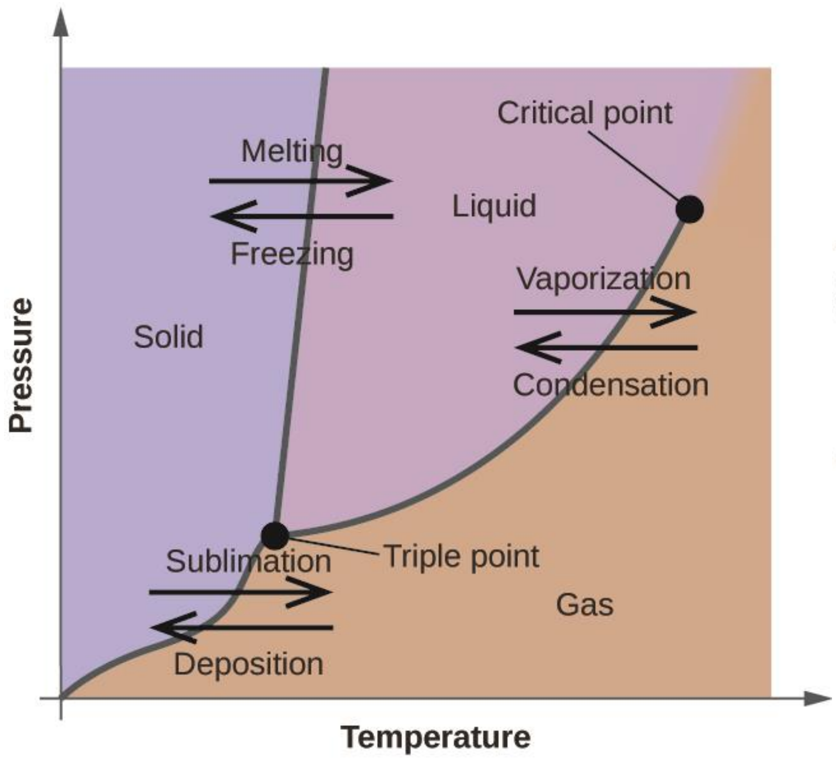
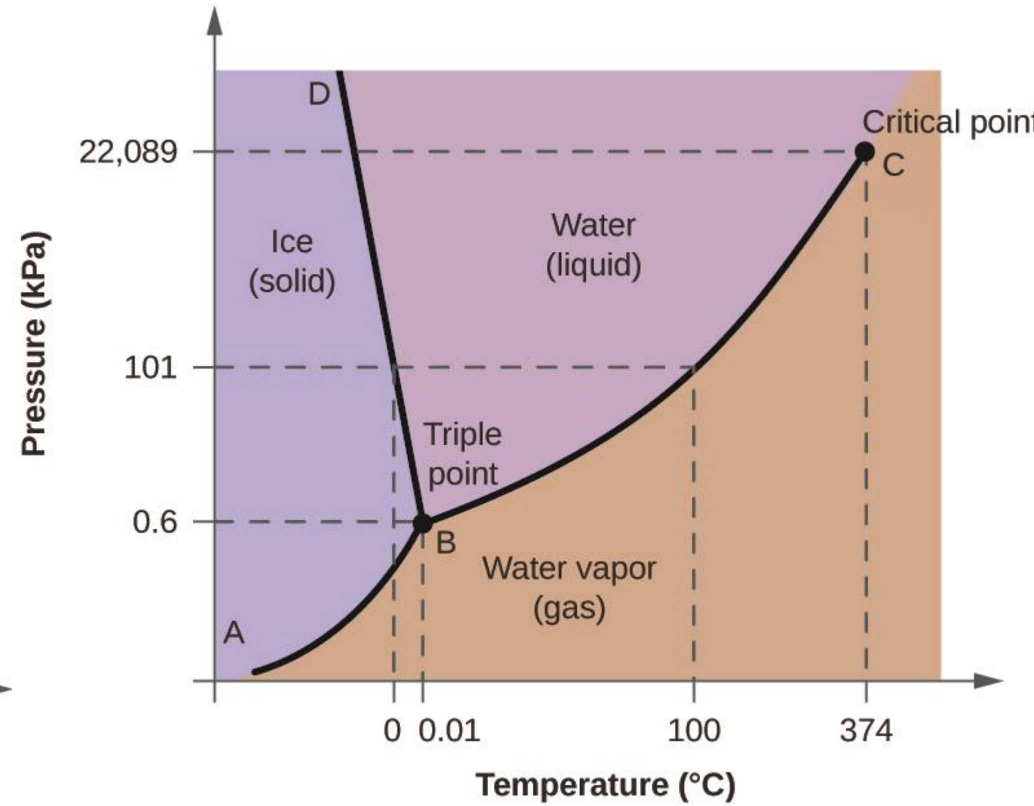
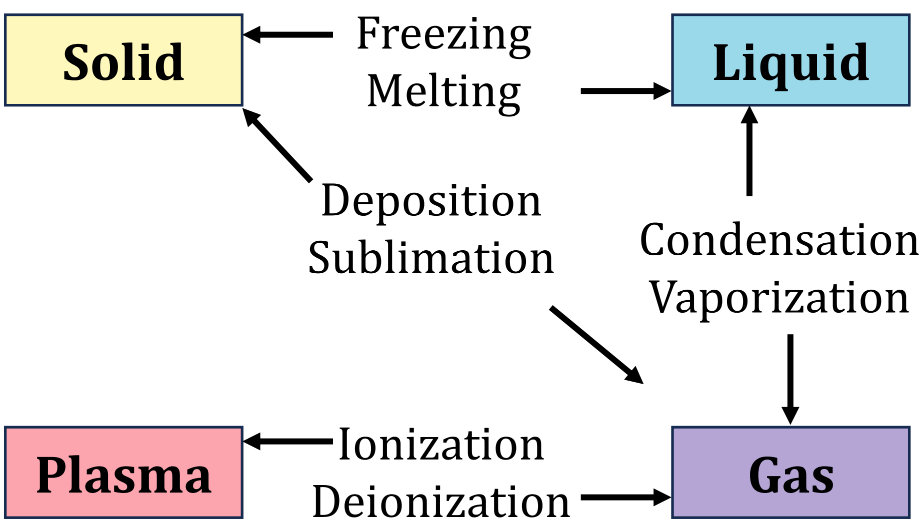
Solidification







Clausius-Clapeyron equation

$$\frac{\partial P}{\partial T_{eq}} = \frac{\Delta H}{T_{eq}\Delta V}$$

Phase

- ✓ A phase can be defined as a portion of the system whose properties and composition are homogeneous and physically distinct from other parts of the system.

✓ Why a transformation occurs at all?

- ✓ It is because the initial state of the alloy is unstable relative to the final state.

$G = H - TS$

✓ How is phase stability measured?

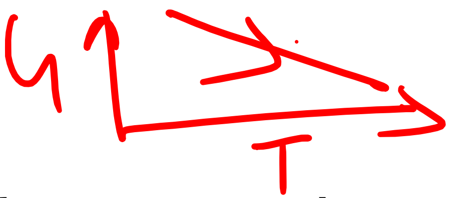
- ✓ The answer to this question is provided by thermodynamics. For transformations that occur at constant temperature and pressure, the relative stability of a system is determined by its Gibbs free energy (G).

Gibbs free energy

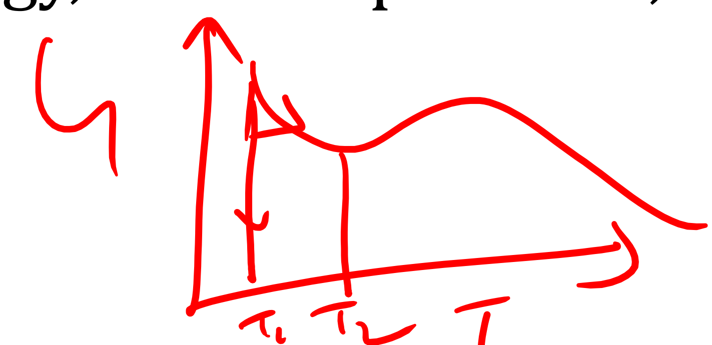
- ✓ Gibbs free energy (G) = H – TS
- ✓ H is the enthalpy, T is the absolute temperature, and S is the system's entropy.

$\Delta G < 0$ $G_2 - G_1$

- ✓ Entropy measures the system's randomness.
- ✓ Enthalpy is a measure of the heat content of the system



- ✓ H=E+PV
- ✓ E is the system's internal energy, P is the pressure, and V is the volume.



Equilibrium

Entropy

✓ $G=H-TS$, $H=E+PV$

Enthalpy

✓ The state with the highest stability will be the best compromise between low enthalpy and high entropy.

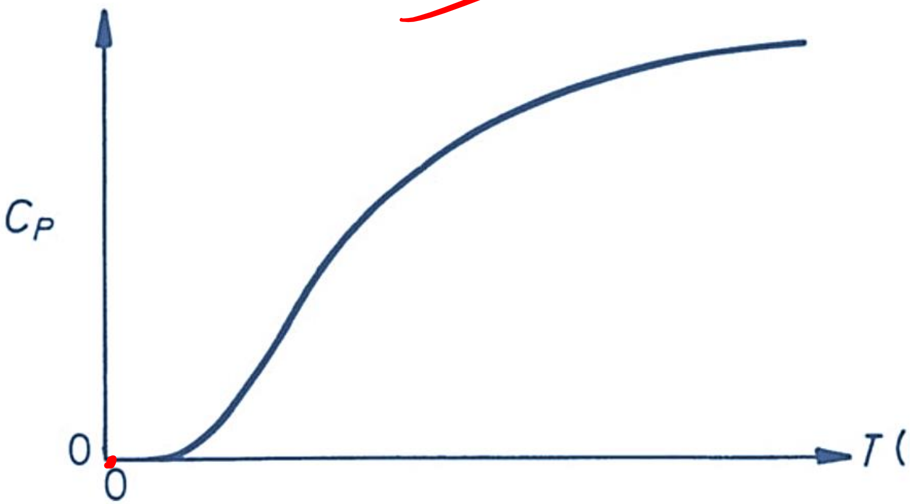
✓ At low temperatures, solid phases are most stable due to the strongest atomic bonding (the lowest internal energy (enthalpy)).

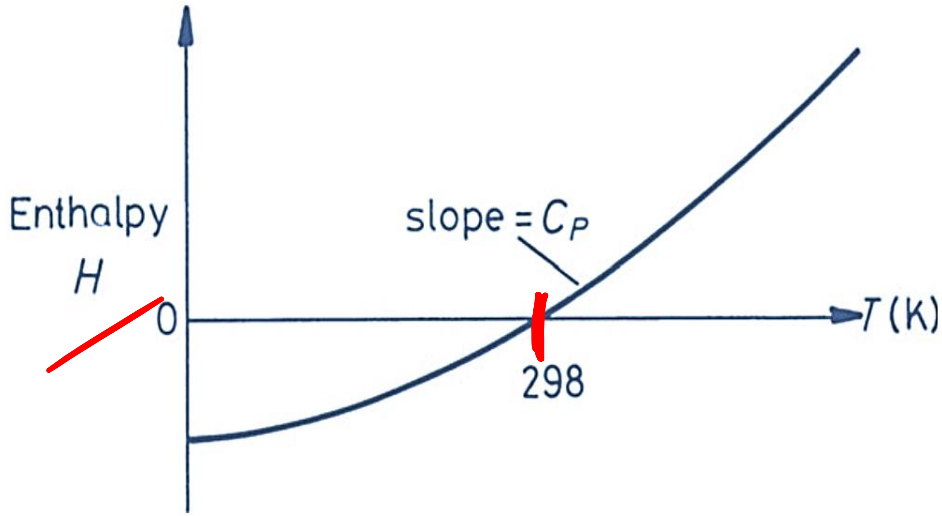
✓ At high temperatures, the -TS term dominates, and phases with more freedom of atom movement, liquids, and gases, become the most stable.

Gibbs Free Energy as a Function of Temperature

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$H = \int_{298}^{T} CpdT$$





$H = \partial p$

$C_p = \frac{\partial H}{\partial T}$

$C_v = \frac{\partial U}{\partial T}$

Gibbs Free Energy as a Function of Temperature

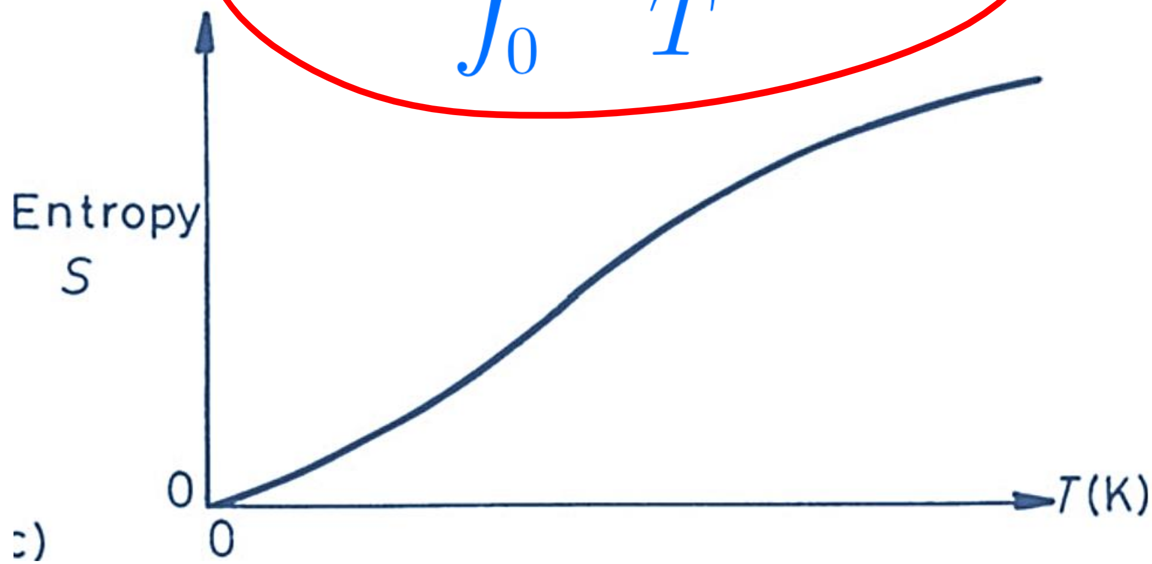
$$dS = \frac{dQ}{T}$$

$$= \frac{dH}{T} = \frac{CpdT}{T}$$

$$\frac{\partial S}{\partial T}\Big|_p = \frac{C_p}{T}$$

$$S = \int_0^T \frac{c_p}{T} dT$$

$Q = H$



Gibbs Free Energy as a Function of Temperature

- ✓ When temperature and pressure vary, the change in Gibbs free energy can be obtained from the following result of classical thermodynamics:

- ✓ **for a system of fixed mass and composition**
- ✓ **dG = -SdT + VdP**

at constant P. dP=0

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

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

$$T\uparrow, S\downarrow$$

G decreases with increasing T at a rate given by –S.

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = dH - TdS - SdT$$

$$H = E + PV$$

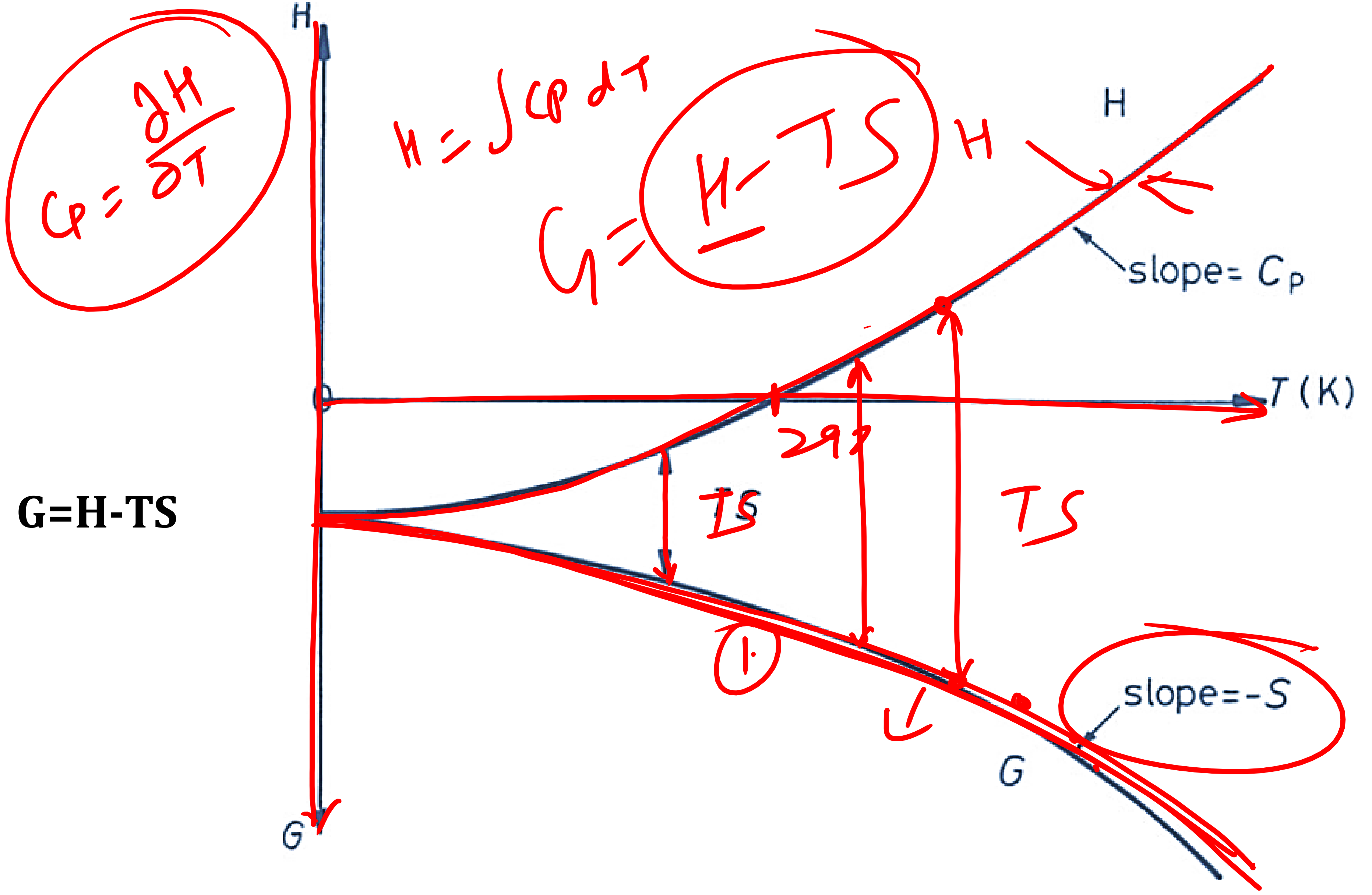
$$dH = dE + PdV + VdP$$

$$dG = dE + PdV + VdP - TdS$$
$$-SdT$$

$$dG = dQ + VdP - dQ - SdT$$

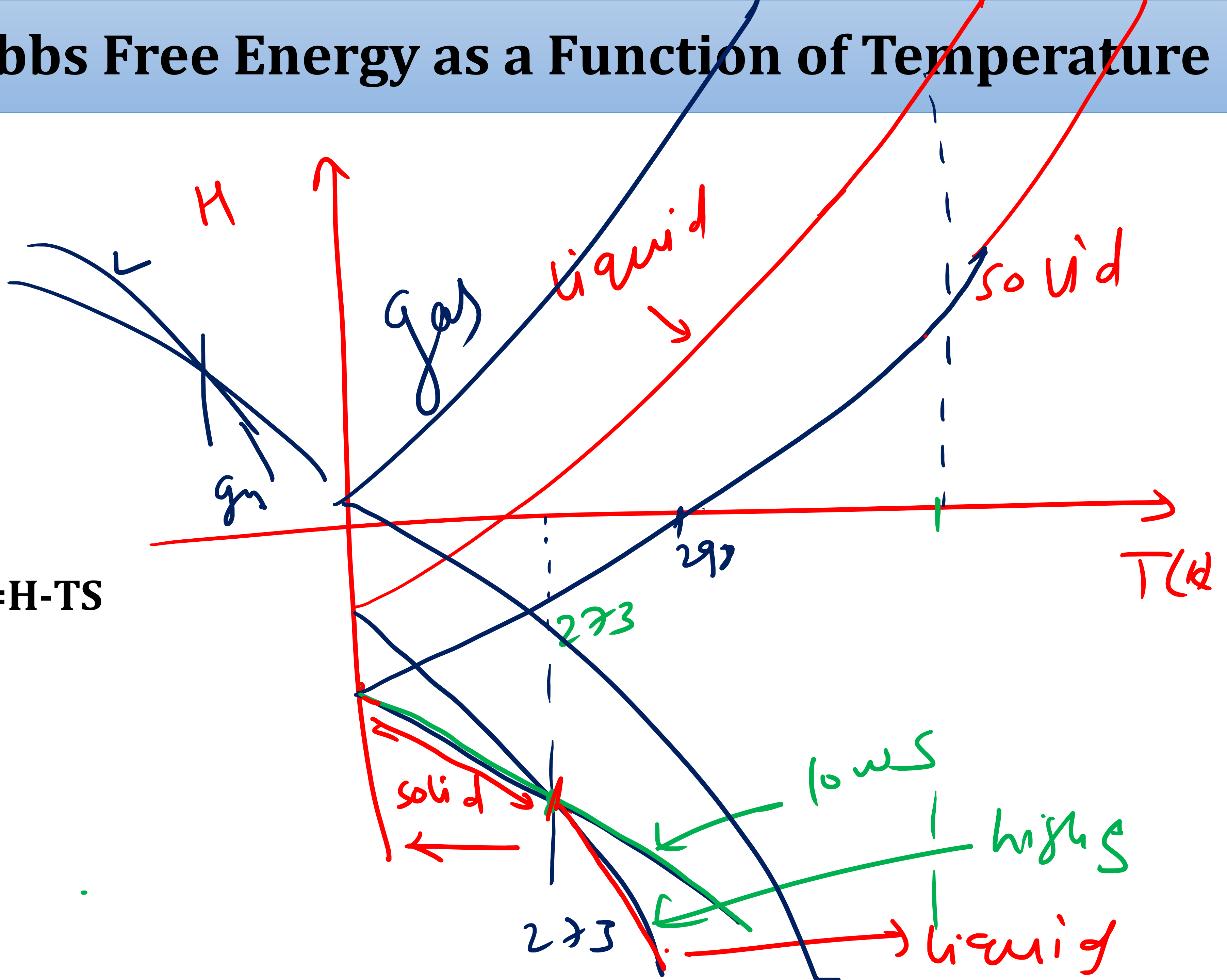
$$dG = VdP - SdT$$

Gibbs Free Energy as a Function of Temperature



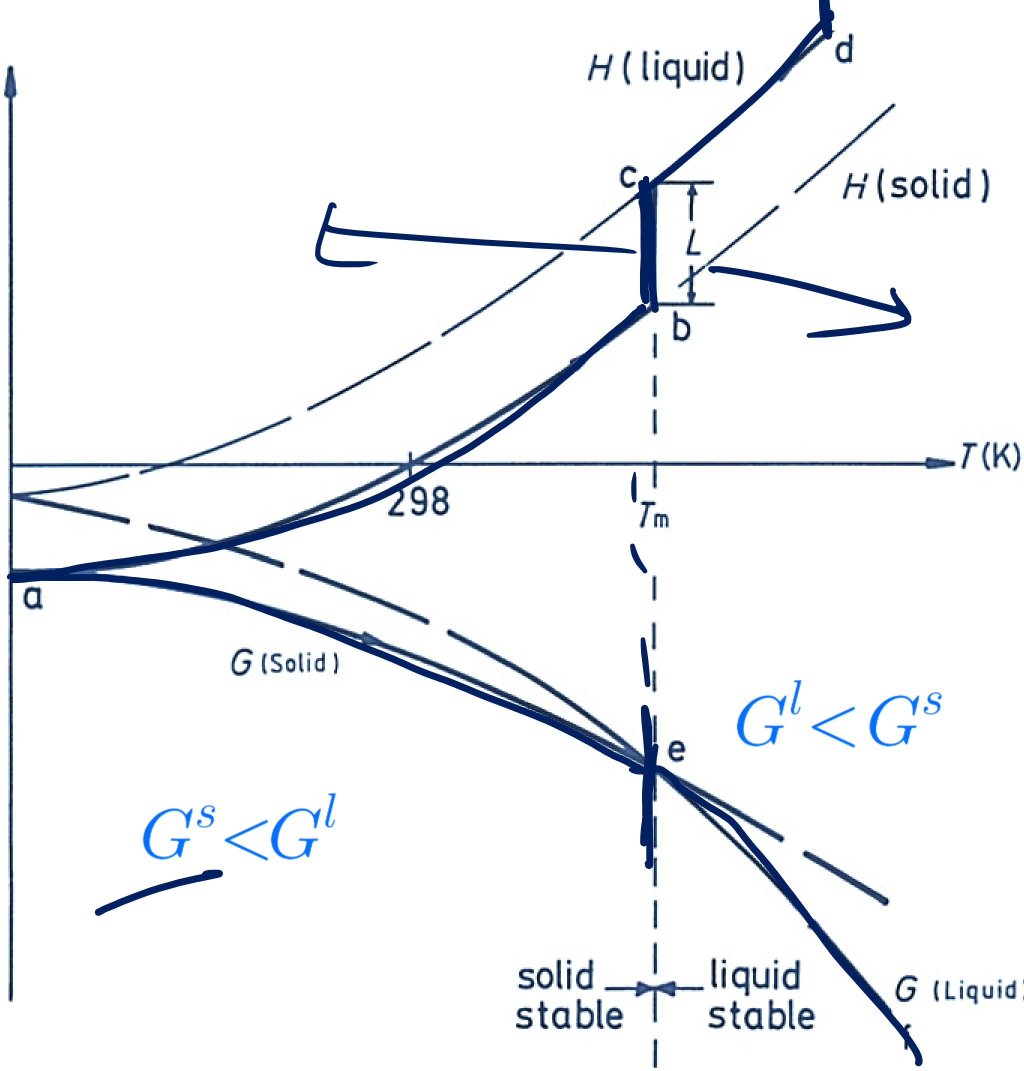
G=H-TS

Gibbs Free Energy as a Function of Temperature



G=H-TS

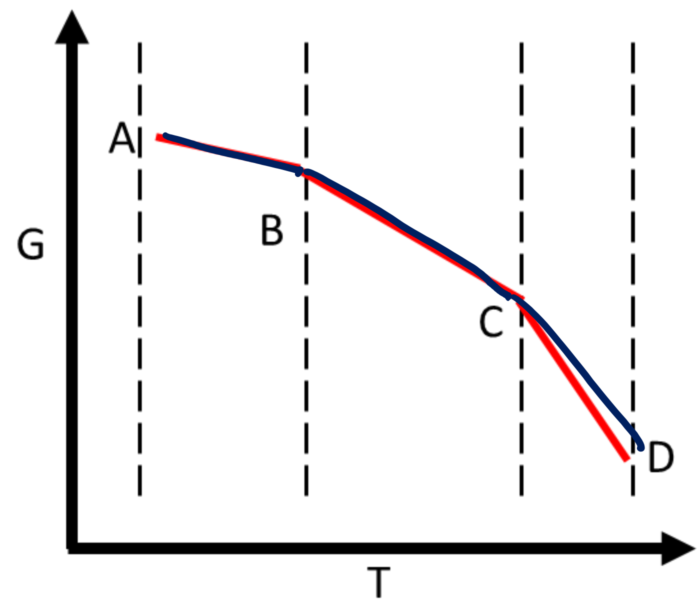
Gibbs Free Energy as a Function of Temperature



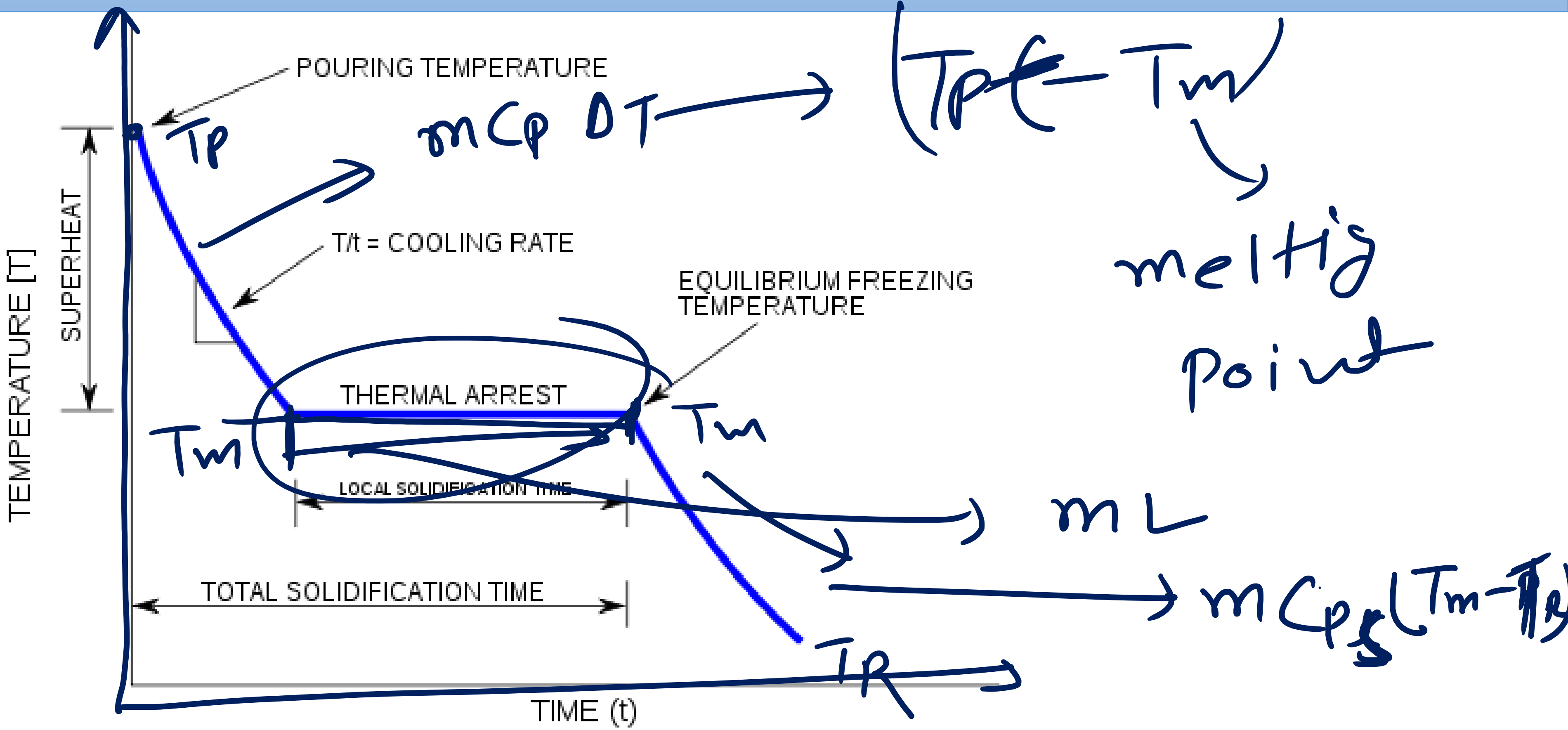
Liquid has a higher enthalpy (internal energy) than the solid.

Liquid phase has a higher entropy than the solid phase.

Gibbs free energy of the liquid decreases more rapidly with increasing temperature than that of the solid.



Cooling curve of pure metal

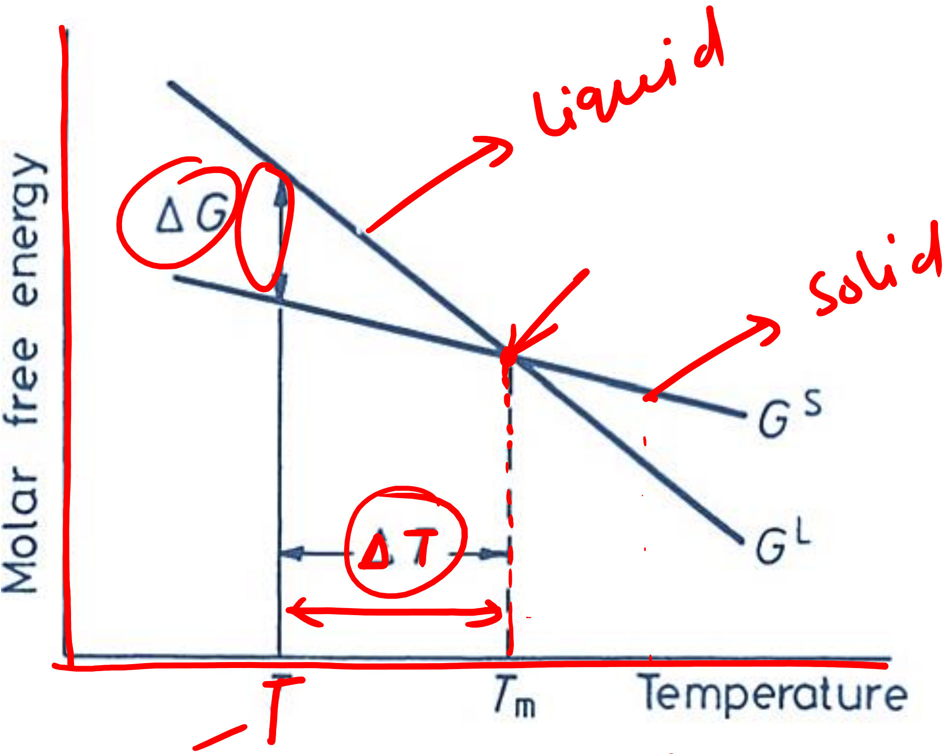


- ✓ The transformation from liquid to solid state begins only after it has cooled below its melting point.
- ✓ Once the process initiates, the latent heat that is released by the metal raises the temperature back to its melting point.
- ✓ Thereafter the temperature remains constant till the solidification is complete.

Nucleation

www.youtube.com/shorts/FdZIZH5ZvD4

The Driving Force for Solidification



T_m = melting point

at T

$$G^L = H^L - TS^L$$

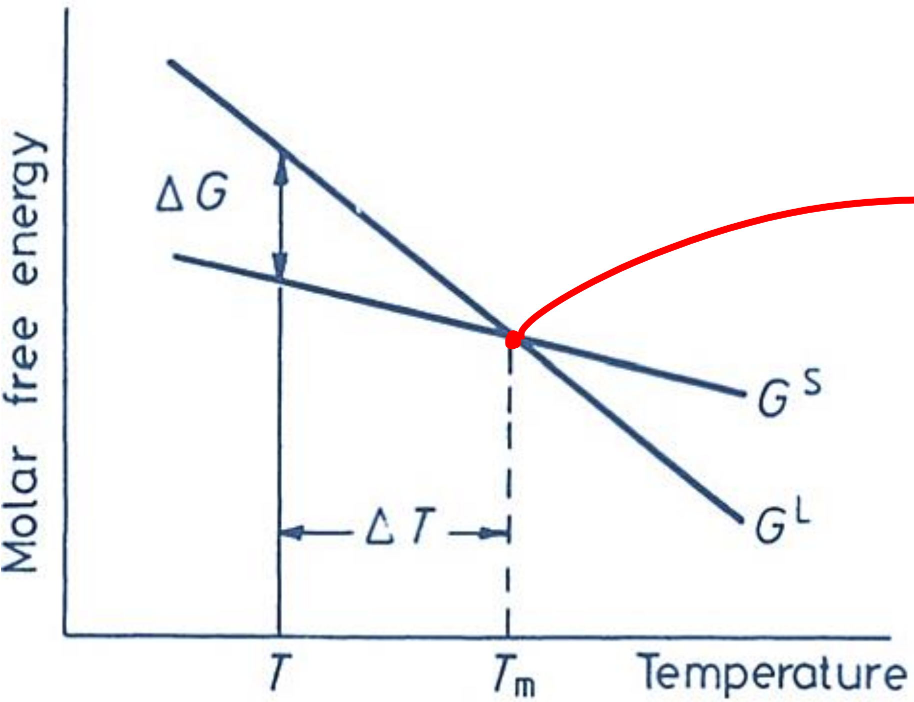
$$G^S = H^S - TS^S$$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

$$\Delta H = H^L - H^S$$

$$\Delta S = S^L - S^S$$

The Driving Force for Solidification



at T_m

$\Delta G = \Delta H - T_m \Delta S$

$0 = \Delta H - T_m \Delta S$

$\Delta S = \dfrac{\Delta H}{T_m}$

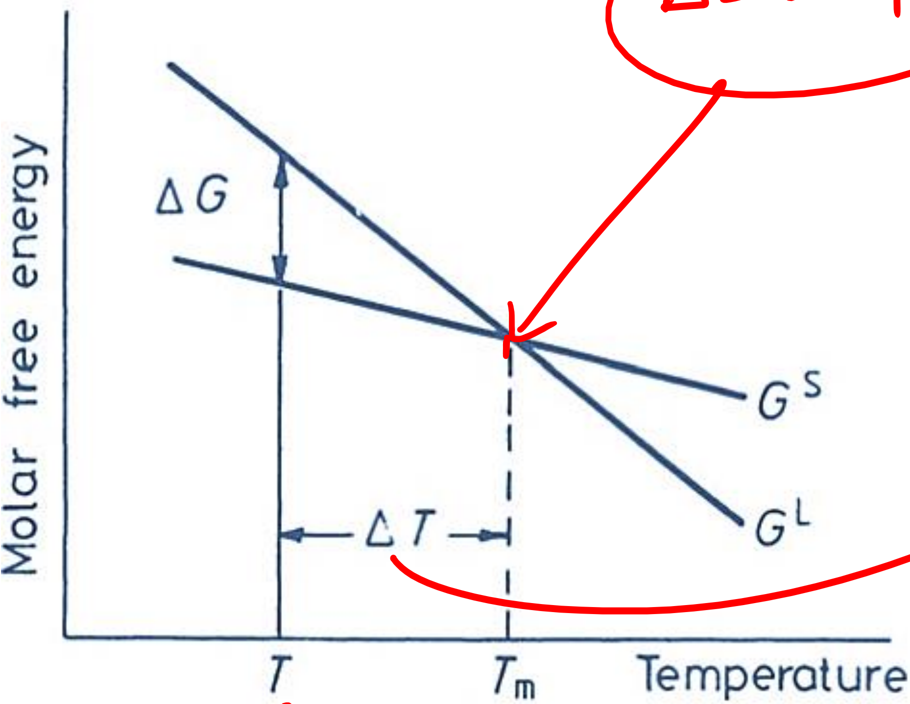
$= \dfrac{L}{T_m}$

Entropy for fusion

$R = 8.3\ J/mol^{-1}K^{-1}$

The Driving Force for Solidification

$$\Delta S = \frac{L}{T_m}$$



for small ΔT

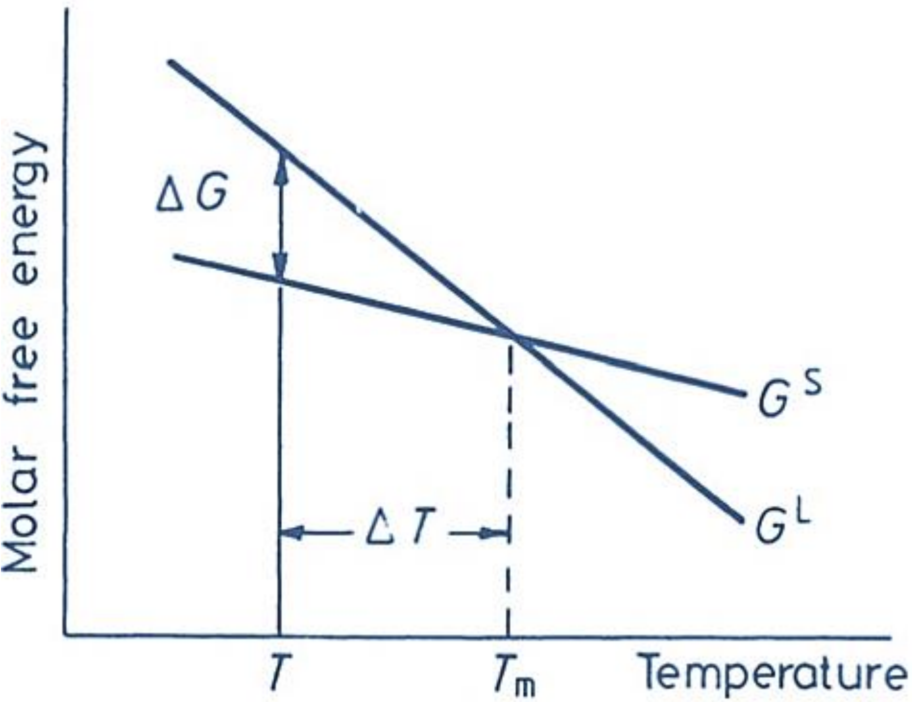
$C_p \sim C_L$

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

$$\simeq L - T\frac{L}{T_m}$$

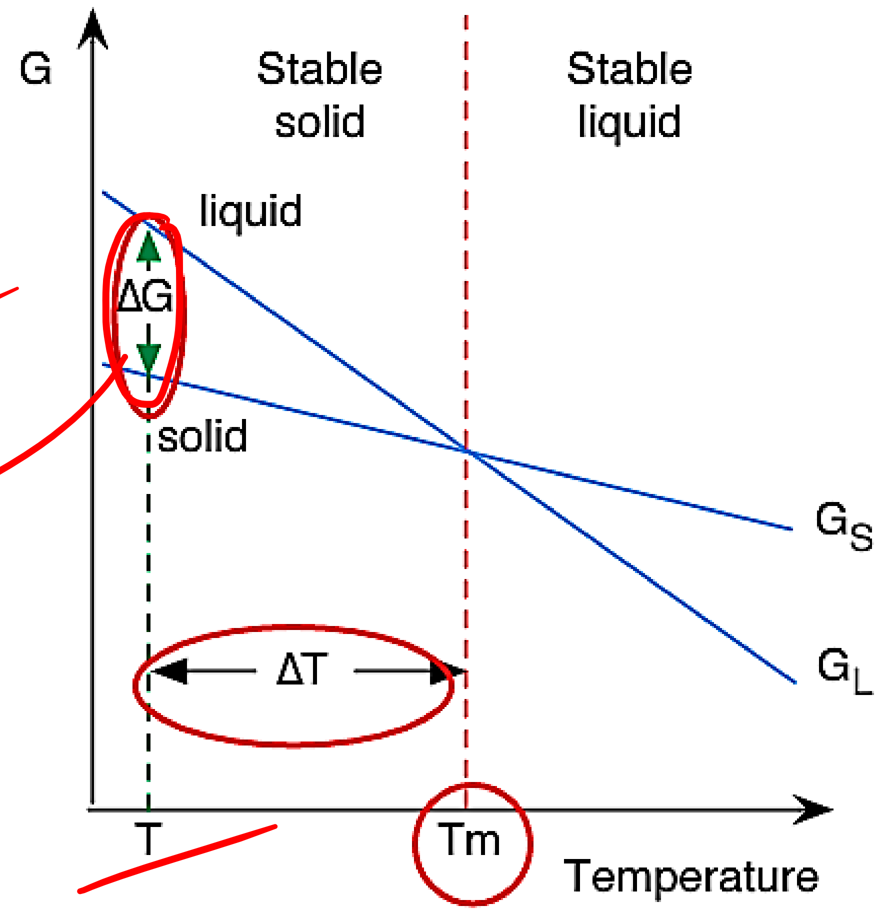
$$\Delta G \simeq L\left(\frac{T_m - T}{T_m}\right) \simeq \frac{L\Delta T}{T_m}$$

The Driving Force for Solidification



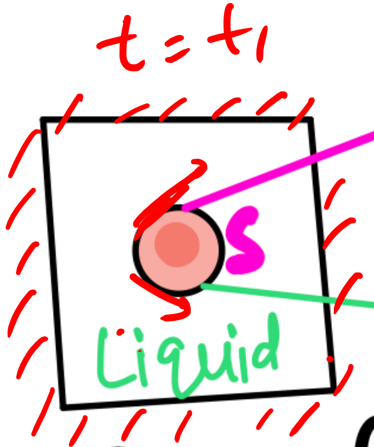
The Driving Force for Solidification

$$\Delta G \sim \frac{L\Delta T}{Tm}$$



Nucleation: Homogeneous

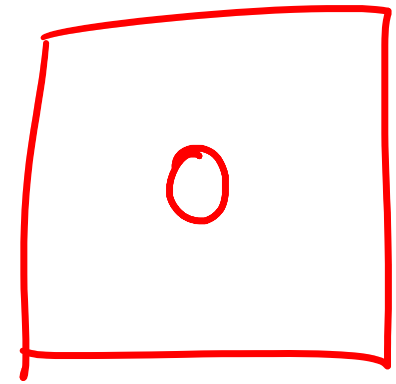
G_1



$A_{SL} = 4\pi r^2$

$V_S = \frac{4}{3}\pi r^3$

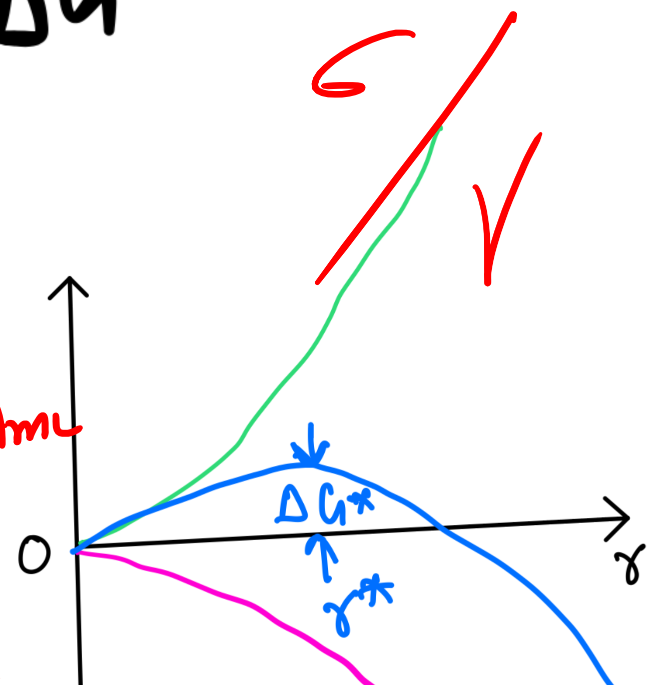
$G_2 = G_1 + \Delta G$



$\rho_s = \rho_L$

$t=0 \quad G_1 = (V_L + V_S)\, G_V^L + \gamma_{mL} A_{mL}$

$t=t_1 \quad G_2 = V_L G_V^L + V_S G_V^S + \gamma_{SL} A_{SL} + \gamma_{mL} A_{mL}$



Nucleation: Driving force

$$\Delta G = G_2 - G_1$$

$$= \cancel{V_L G_V^L} + V_S G_V^S + \gamma_{SL} A_{SL} + \cancel{\gamma_{mL} A_{mL}}$$

$$- \left((\cancel{V_L} + V_S) G_V^L + \cancel{\gamma_{mL} A_{mL}} \right)$$

$$= V_S G_V^S - V_S G_V^L + \gamma_{SL} A_{SL}$$

$$= - V_S \underline{\Delta G_V^{L \to S}} + \underline{\gamma_{SL} A_{SL}}$$

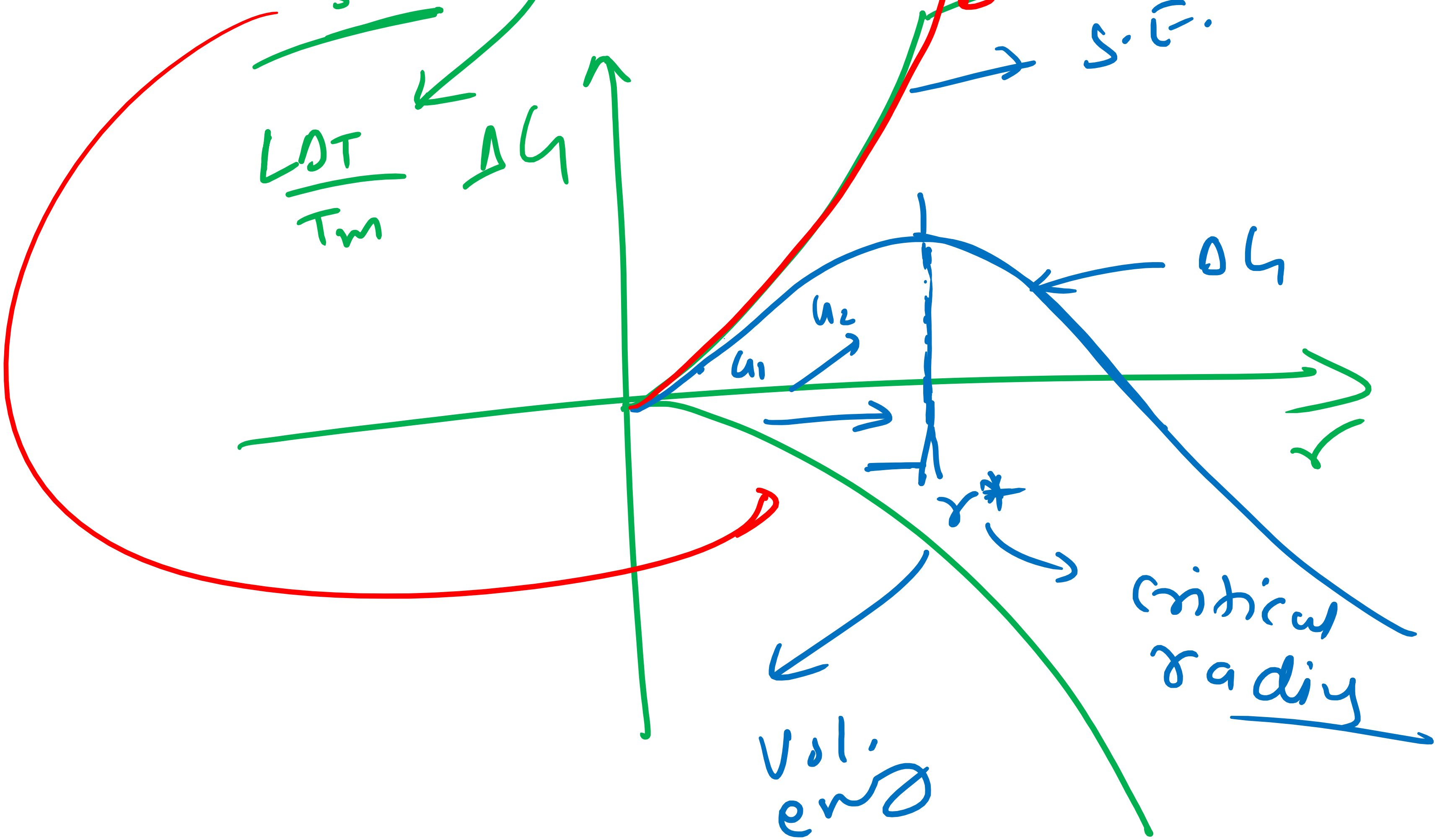
$$\frac{L \Delta T}{T_m}$$

$$V_S = \frac{4}{3} \pi r^3$$

$$A_{SL} = 4 \pi r^2$$

Nucleation: Homogeneous

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$



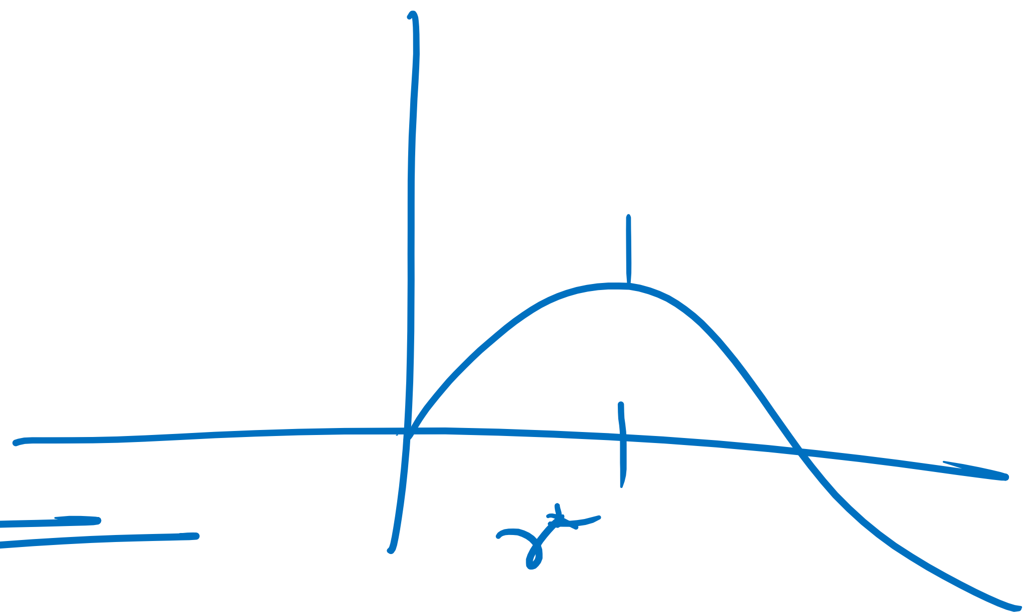
Nucleation: Homogeneous

$r < r^*$ Then Not sustain of Nuclei

Known as Embryos

$r > r^*$

Nuclei



Nucleation: Homogeneous

what is r^*

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v^{L\to S} + 4\pi r^2 \gamma_{SL}$$

$$\frac{\partial \Delta G}{\partial r} = 0$$

$$-\cancel{4}\pi \cancel{r^2}\,\Delta G_v^{L\to S} + \overset{\cancel{8}}{2}\pi \cancel{r}\,\gamma_{SL} = 0$$

$$r\,\Delta G_v^{L\to S} = 2\gamma_{SL}$$

$$\boxed{r^* = \frac{2\gamma_{SL}}{\Delta G_v^{L\to S}} = \frac{2\gamma_{SL} T_m}{L\,\Delta T}}$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\,\Delta G_v^{L\to S\,2}}$$

Nucleation: Homogeneous

I) $r < r^*$, System can lower its free energy by dissolution of solid.

Known as Embryos

II) $r > r^*$, free energy of system decrease if solid grow.

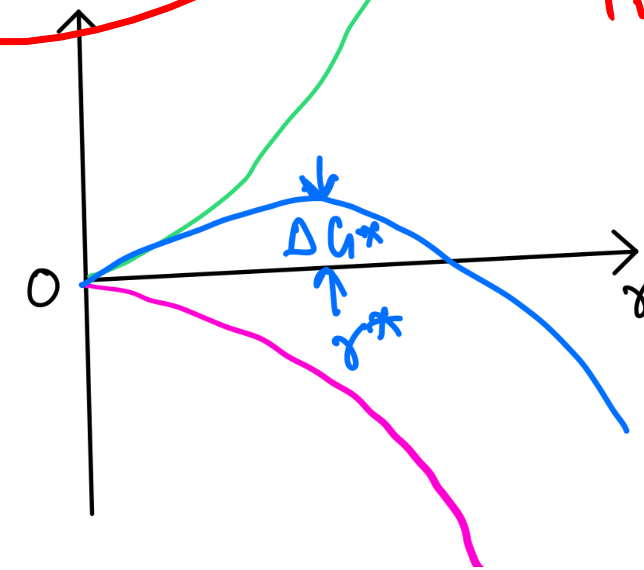
Nuclei.

$$\frac{2\gamma_{SL} T_m}{L \Delta T}$$

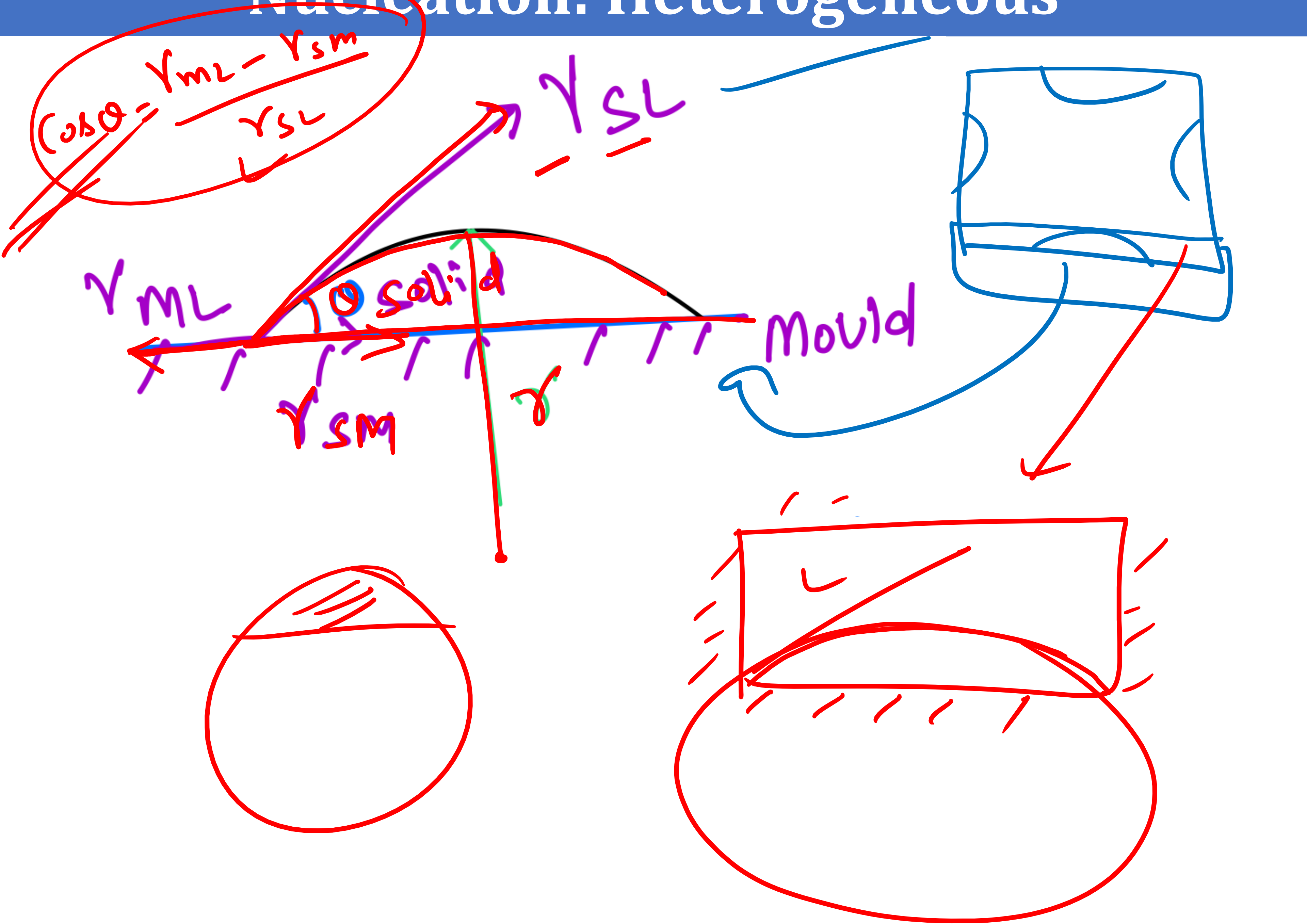
$$\frac{L \Delta T}{T_m}$$

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V}$$

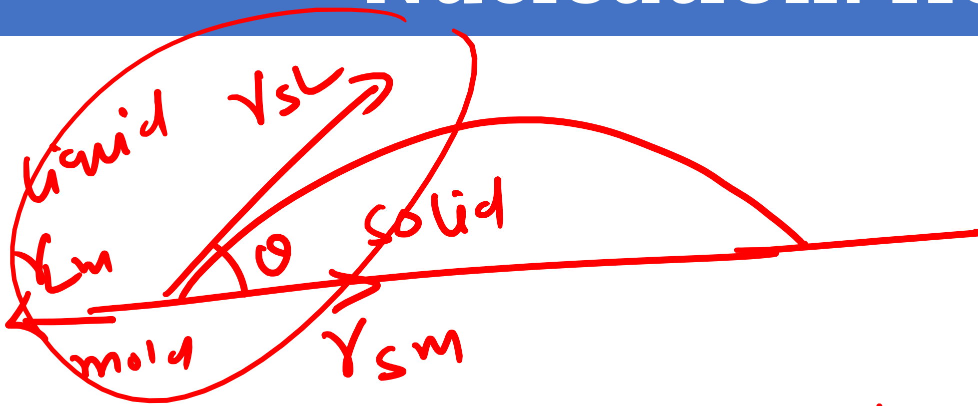
$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}$$



Nucleation: Heterogeneous



Nucleation: Heterogeneous

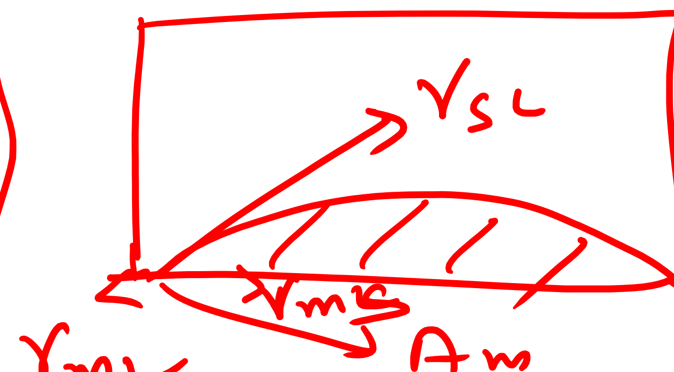


$t = 0$

$$G_1 = (V_L + V_s)\, G_v^L + \gamma_{mL} A_{ml}$$

$t = t_1$

$$G_2 = V_L G_v^L + V_s G_v^S + \left\{ \begin{array}{l} \gamma_{sL} \times A_{sL} \\ + \gamma_{ms} \times A_m \\ + \gamma_{mL} (A - A_m) \end{array} \right\}$$



Nucleation: Heterogeneous

$$\Delta G = G_2 - G_1$$

$$= \cancel{G_L G_V^L} + V_S G_V^S + \gamma_{SL} A_{SL}$$

$$+ \gamma_{mL} (\cancel{A} - A_m) + \gamma_{mS} A_m$$

$$- G_V^L (\cancel{V_L} + V_S) - \cancel{\gamma_{mL} A}$$

$$= -V_S \Delta G_V^{L \to S} + \gamma_{SL} A_{SL} + \gamma_{Sm} A_m$$

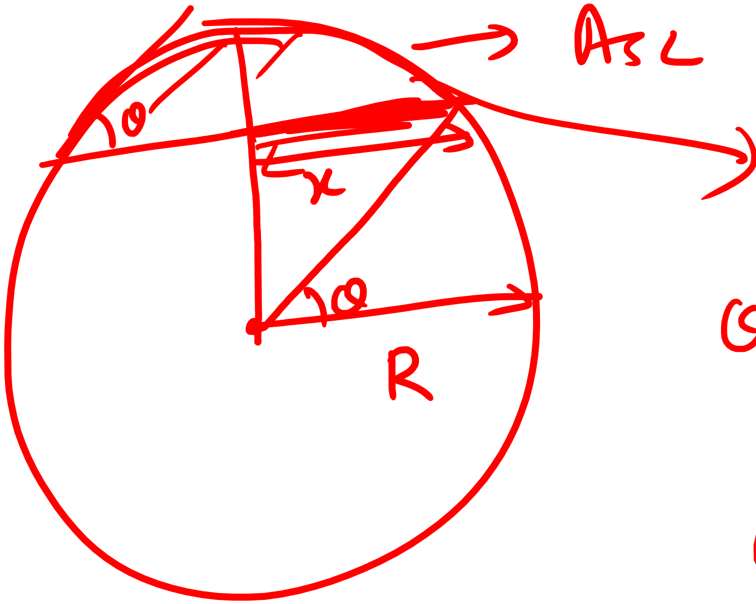
$$- \gamma_{mL} A_m$$

Nucleation: Heterogeneous

$A_m = \pi x^2$

$x \;\; r\sin\theta$

r_{circle}



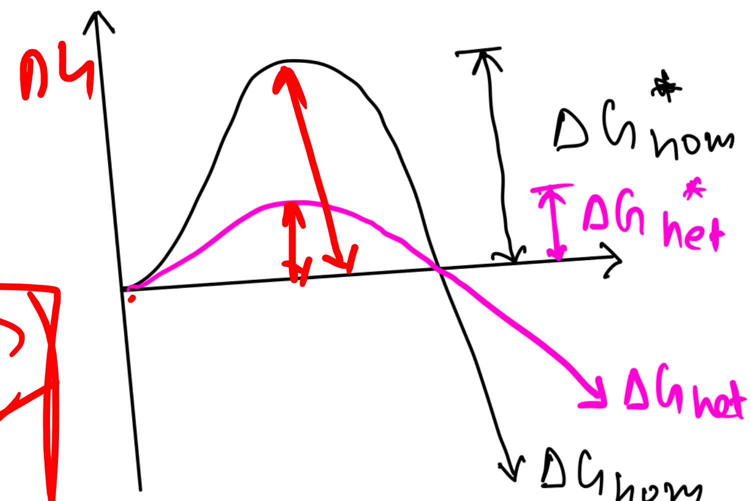
$\theta = 0,$ $S(\theta) \to 0$

when $\theta =$

$S(\theta) = 1$

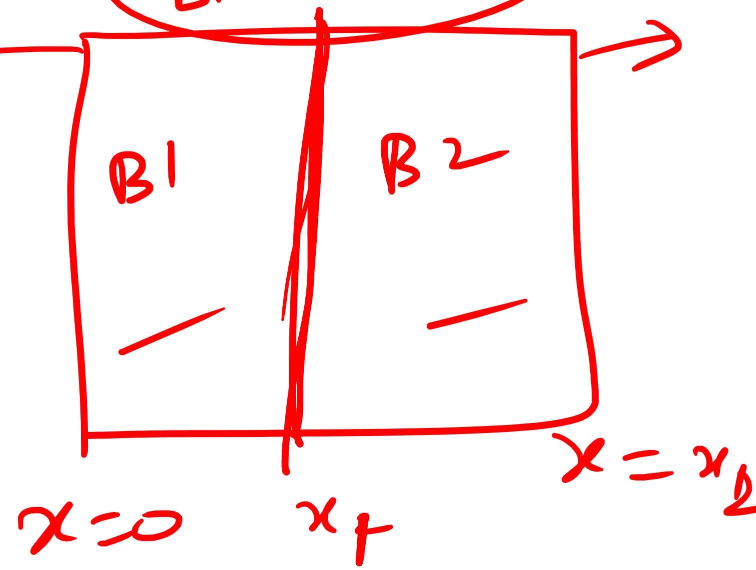
$$\Delta G^*_{het} = \Delta G^*_{hom} \cdot S(\theta)$$

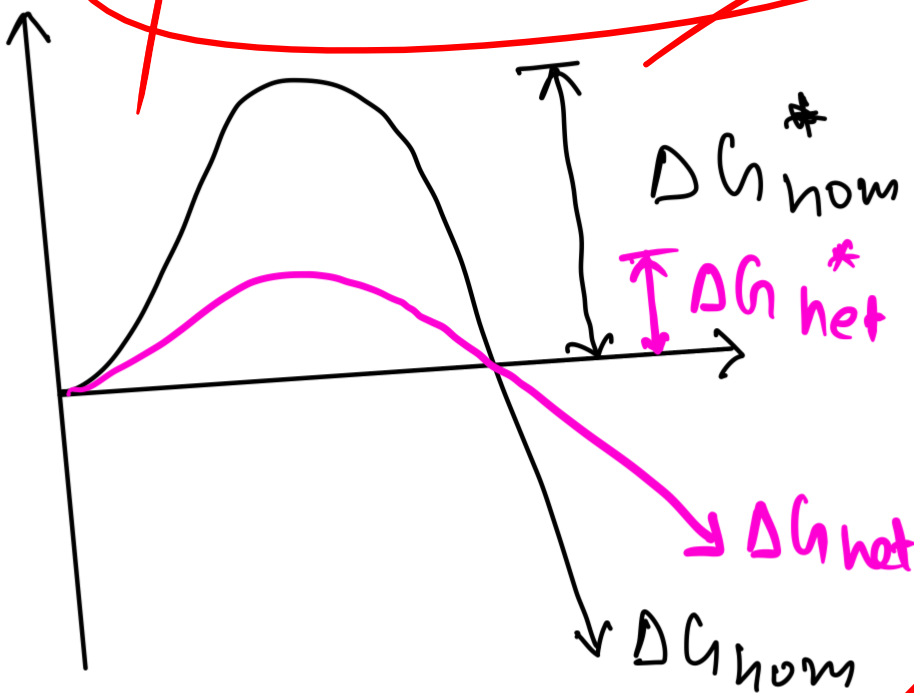
$$\boxed{S(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}}$$



$$-k_{B_1}\frac{dT_{B_1}}{dx} = -k_{B_2}\frac{dT_{B_2}}{dx}$$

$$T_{B_1} = T_{B_2}$$





$$\Delta G^*_{het} = \Delta G^*_{hom}\cdot S(\theta)$$

$T = T_A \Rightarrow x = 0$

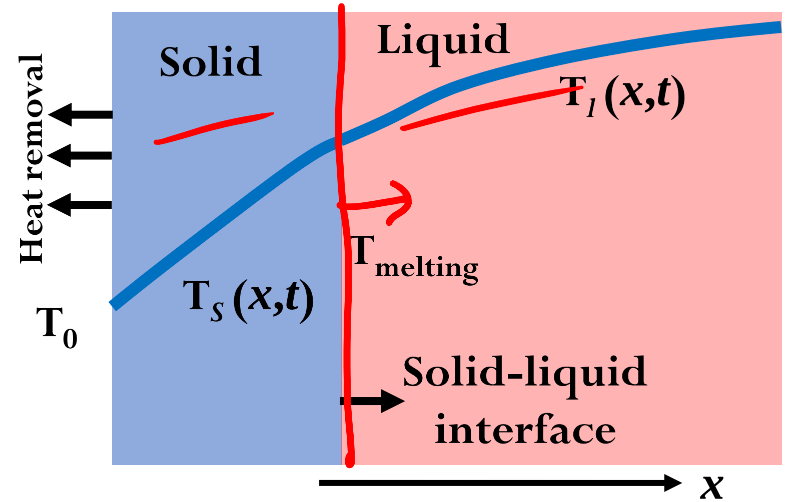
$T = T_B \Rightarrow x = x_2$

Application of thermal analysis

Conduction heat flux into the solid phase in the negative in *x* direction **−** Conduction heat flux from the liquid phase in the negative in *x* direction = Rate of heat liberated during solidification per unit area of interface

$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t}$$

ρ = of Solid density



Effects of Convection: If the interface is controlled by convection

$$k_S \frac{\partial T_S}{\partial x} - h(T_\infty - T_m) = \rho L \frac{\partial x}{\partial t}$$

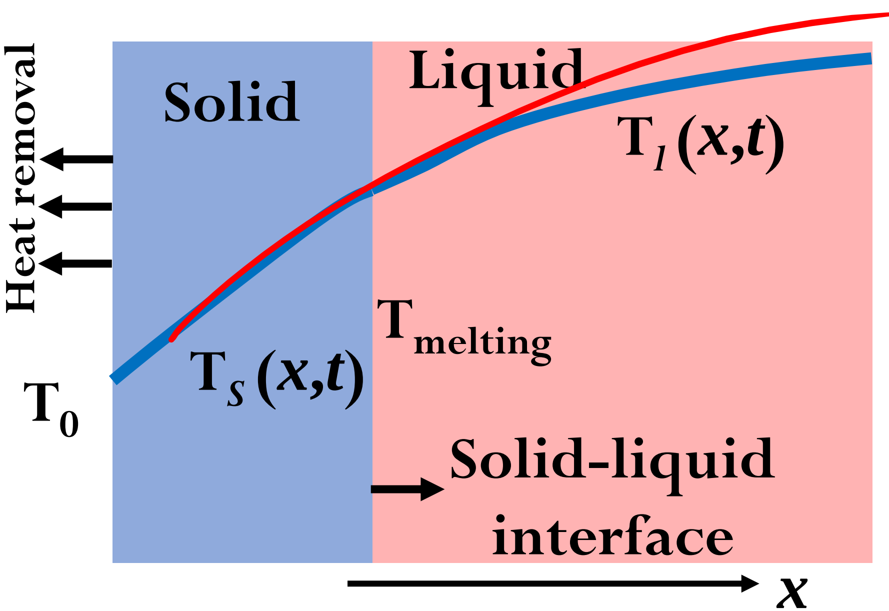
T_∞ is bulk liquid temperature

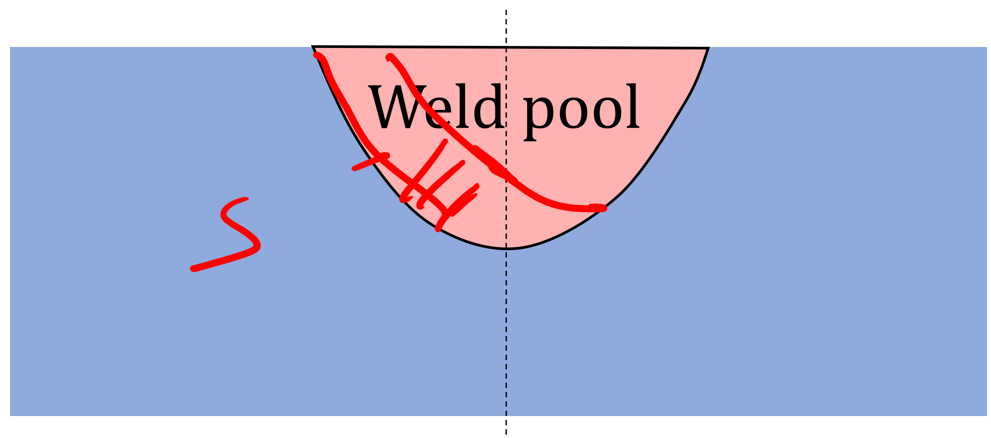
T_m is freezing point

Application of thermal analysis

Conduction heat flux into the solid phase in the negative in x direction	-	Conduction heat flux from the liquid phase in the negative in x direction	=	Rate of heat liberated during solidification per unit area of interface

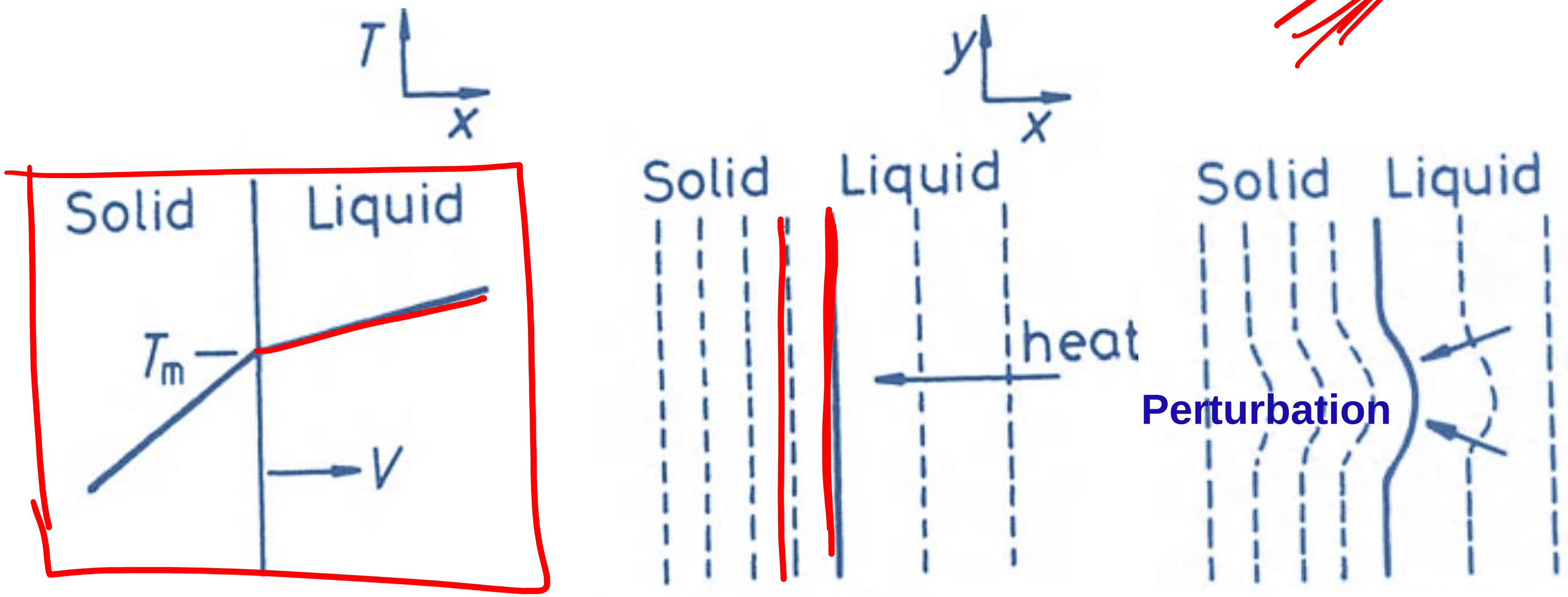
$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t}$$

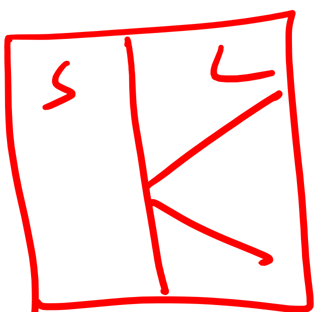




Solidification of pure material: + Gr.

Positive thermal gradient in the liquid

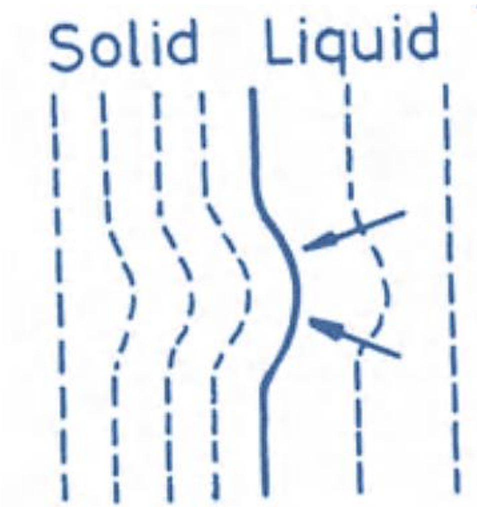




$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t}$$

Phase transformations in metals and alloys

Solidification of pure material: + Gr.



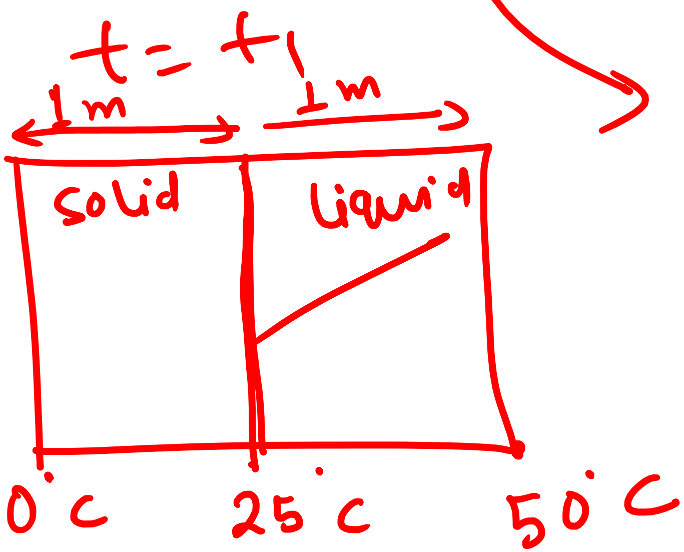
$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t} = \rho L v$$

$T_m = 25^\circ C$

$K_s = 2$

$K_l = 1$

$\rho L = 100 \times 1000$

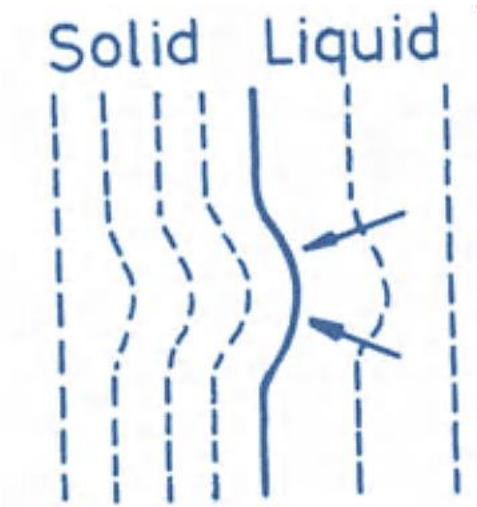


$$2 \times \frac{25-0}{1} - 1\,\frac{50-25}{1} = 100 \times 1000 \times v$$

$$\boxed{V = 0.25 \times 10^{-3}\ m/s}$$

$= 0.25\ mm/sec$

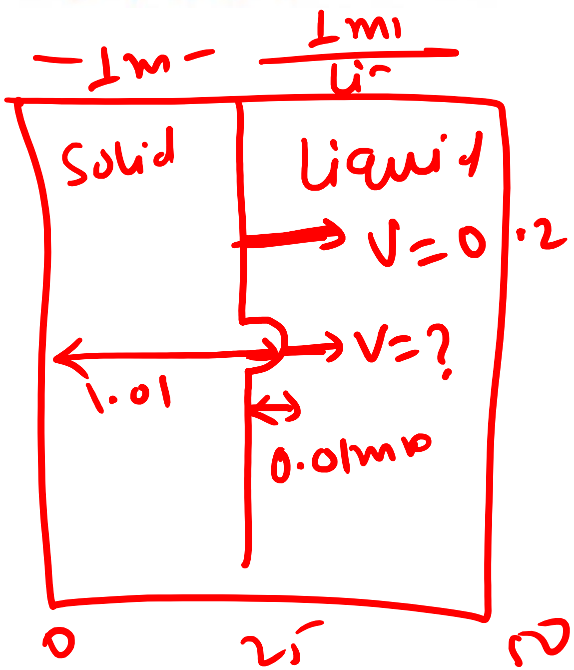
Solidification of pure material: + Gr.

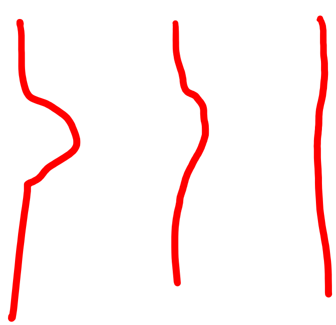


$$K_s \frac{dT_s}{dx} - K_l \frac{dT_l}{dx} = \rho L v$$

$$2 \times \frac{25-0}{1.01} - 1 \times \frac{50-25}{0.99} = 100 \times 1000 \times v$$

$$v = 0.2425 \text{ mm/sec}$$

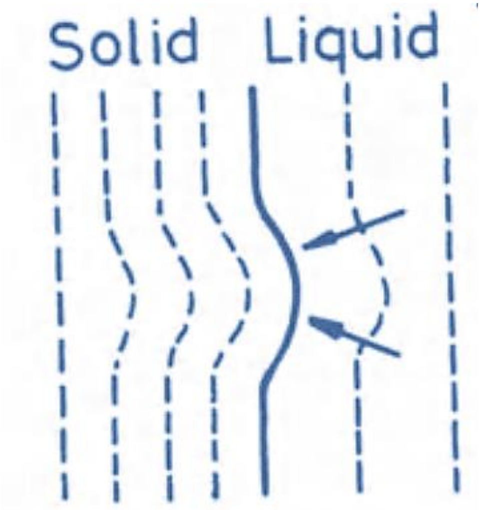




$v = 0.2425 <$ v flat

0.25 mm/s

Solidification of pure material: + Gr.



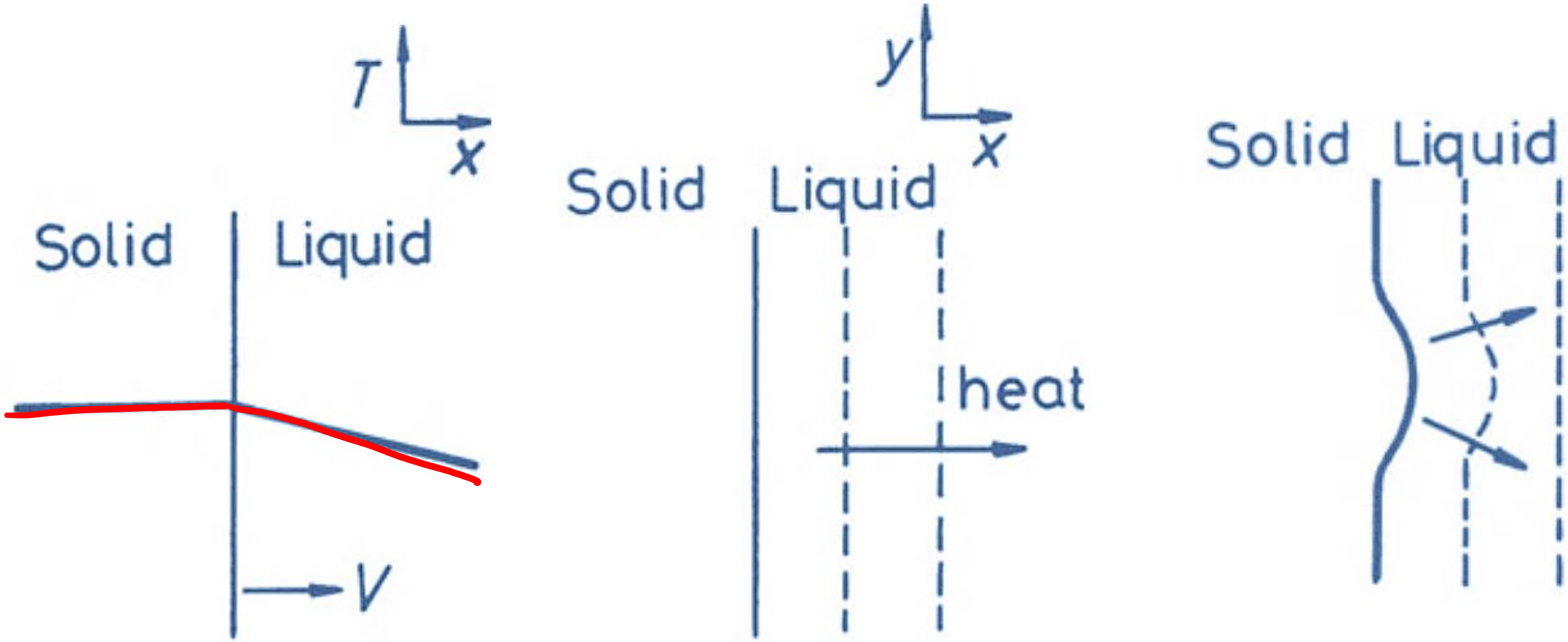
$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t} = \rho L v$$

- The temperature gradient in the liquid will increase
- The temperature gradient in the solid will decreases.

- More heat will be conducted into the protruding solid
- The growth rate will decrease below that of the planar regions, and the protrusion will disappear.
- Planar interface

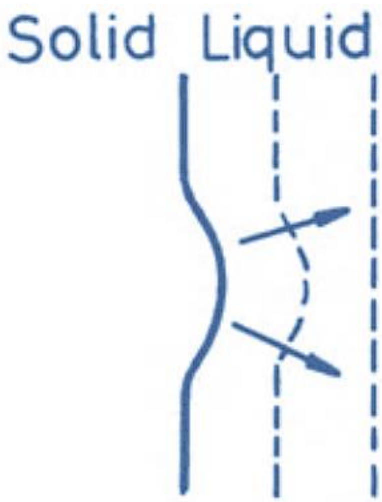
Solidification of pure material: - Gr.

Negative thermal gradient in the liquid



$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t} = \rho L v$$

Solidification of pure material: - Gr.

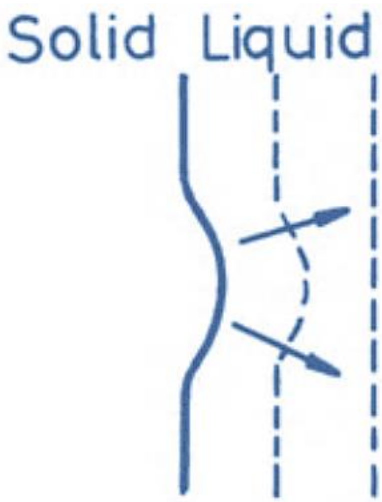


$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t} = \rho L v$$

- The negative temperature gradient in the liquid becomes even more negative when a protrusion forms on the solid.
- Heat is removed more effectively from the tip of the protrusion than from the surrounding regions allowing it to grow preferentially.

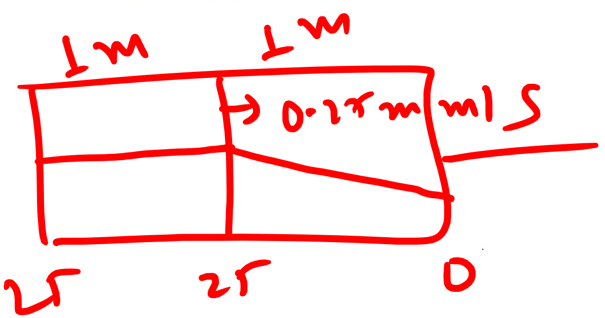
- Protrusion will grow.

Solidification of pure material: - Gr.



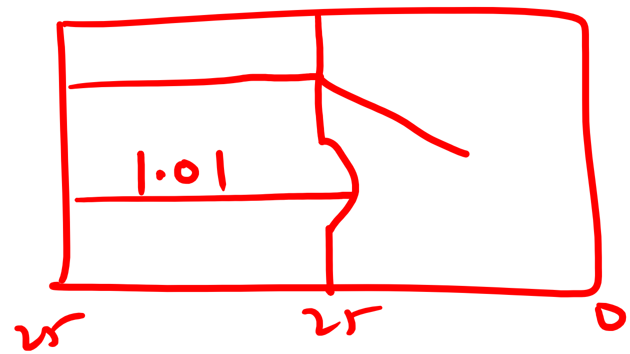
$$k_S\frac{\partial T_S}{\partial x} - k_l\frac{\partial T_l}{\partial x} = \rho L\frac{\partial x}{\partial t} = \rho L v$$

flat interface
at $t = t_1$



$$2\times 0 - 1\times\frac{0-25}{1} = 100\times 1000\times v$$

$v = 0.25$ mm/s

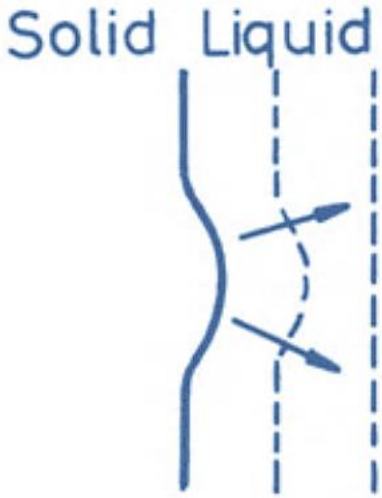


$$2\times 0 - 1\times\frac{0-25}{0.99} = 100\times 1000 v$$

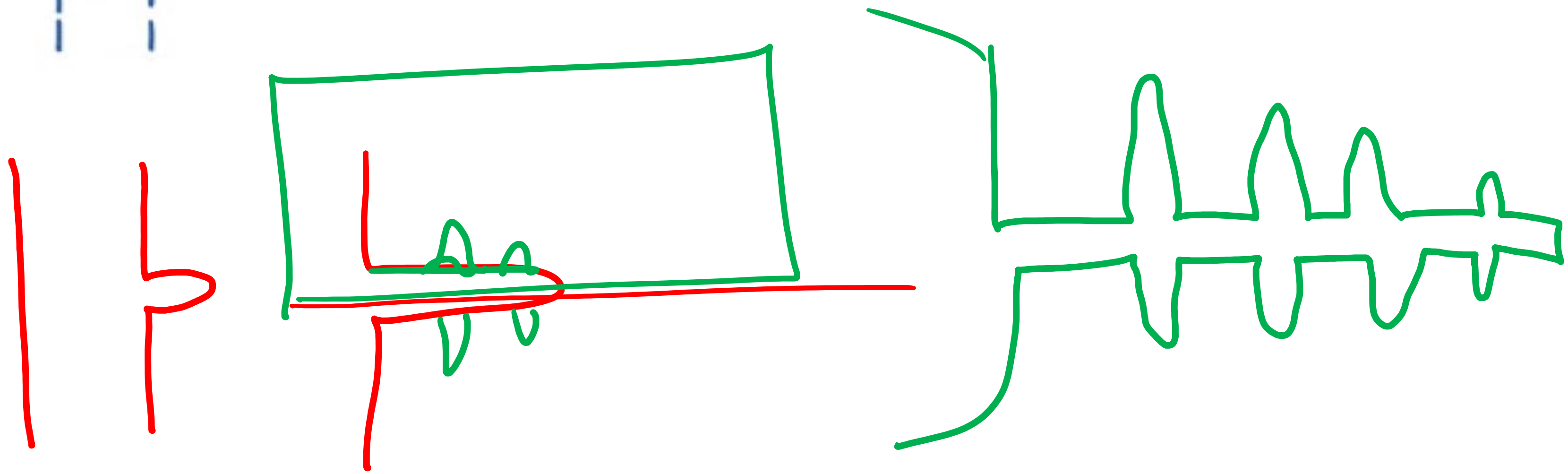
$v = 0.2525$ mm/s

Pe

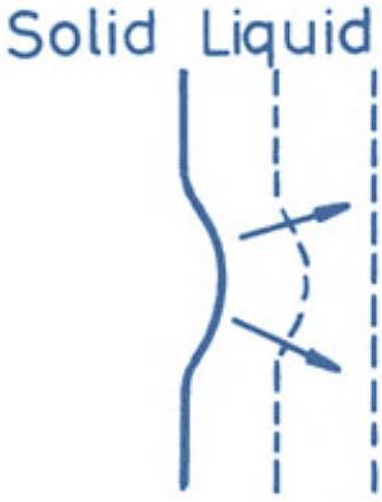
Solidification of pure material: - Gr.



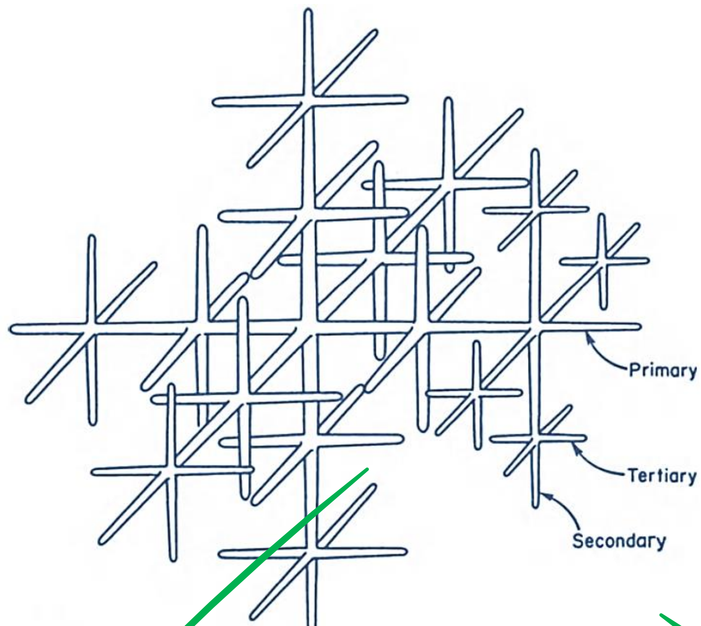
$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t} = \rho L v$$



Solidification of pure material: - Gr.



$$k_S \frac{\partial T_S}{\partial x} - k_l \frac{\partial T_l}{\partial x} = \rho L \frac{\partial x}{\partial t} = \rho L v$$



Phase transformations in metals and alloys

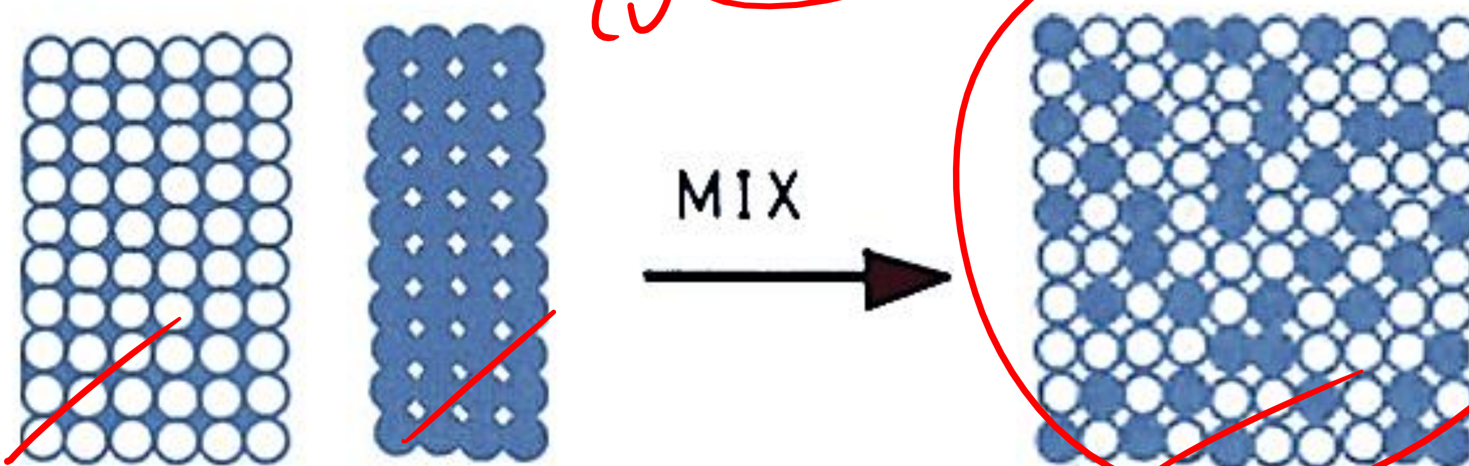
Binary Mixture

Cu $X_A + X_B = 1$

Before mixing

After mixing

Al



X_A mol A

X_B mol B

F.E. $X_A G_A$

F.E. $X_B G_B$

1 mol solid solution

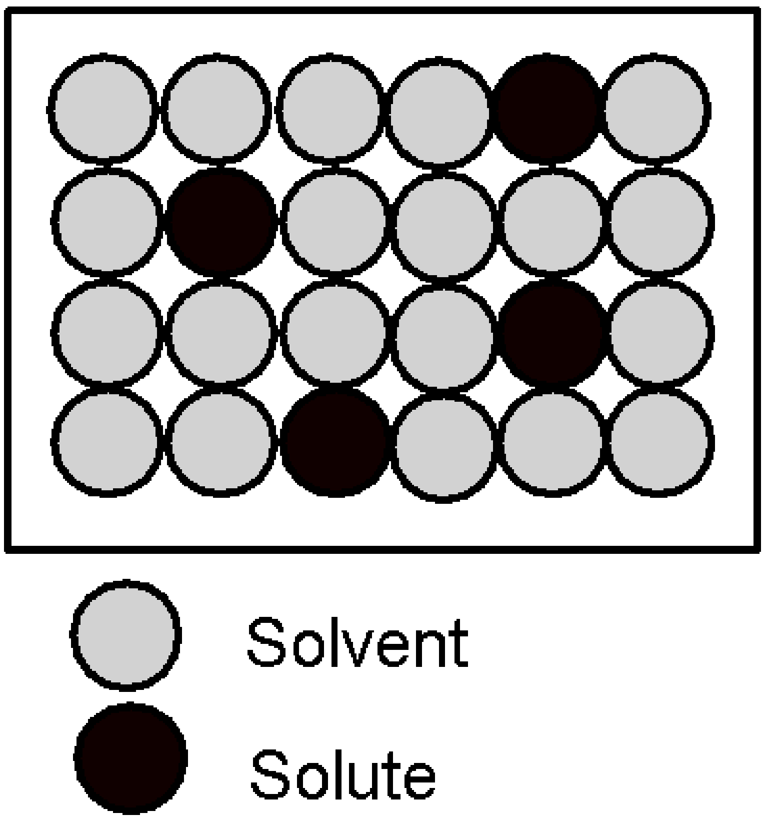
Total free energy =

$$\boxed{G_1 = X_A G_A + X_B G_B}$$

Total free energy =

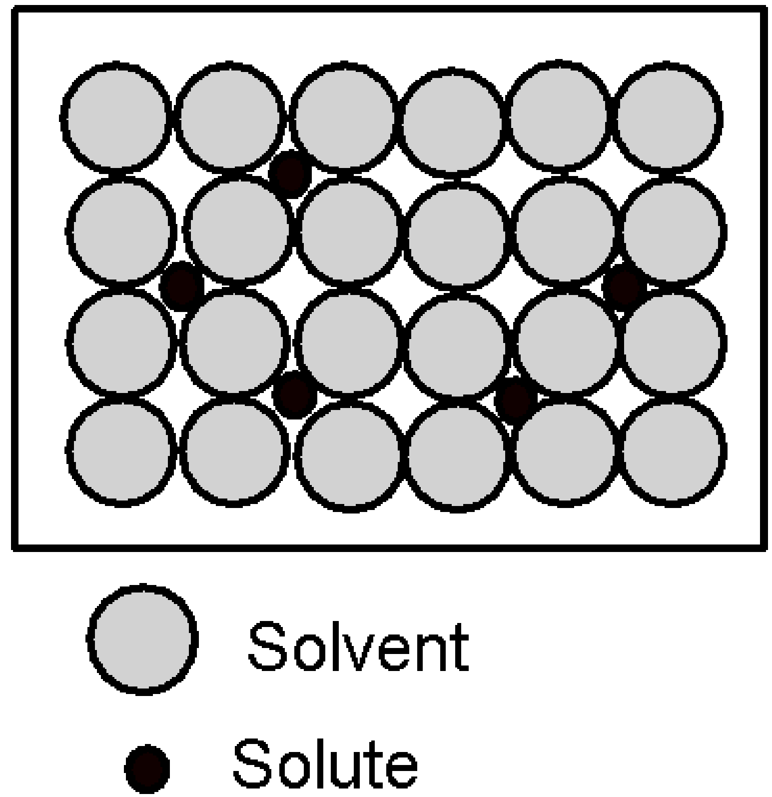
$$G_2 = G_1 + \Delta G_{mix}$$

Solid solution – Multi-component Metals



(a) Substiutional solid solution

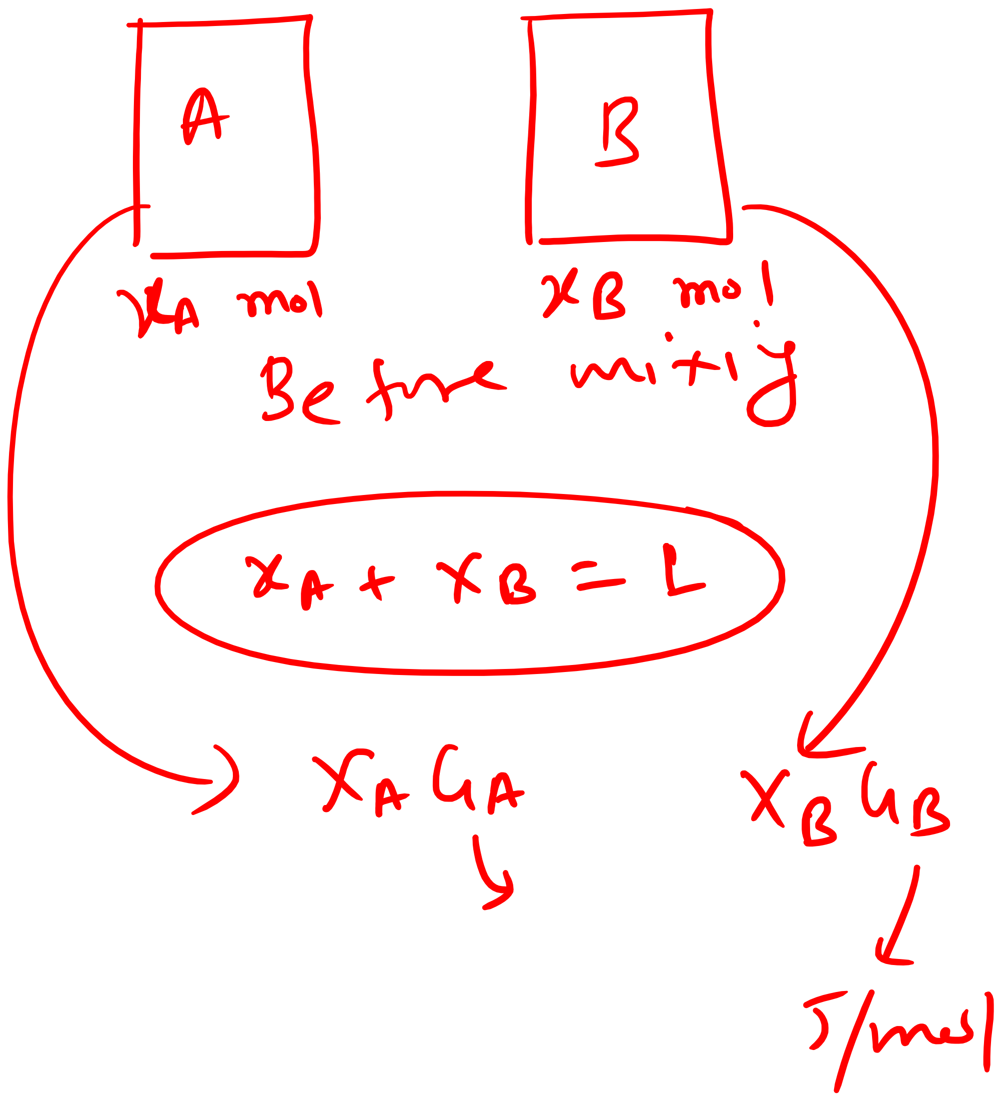
Similar atomic size (same order)
+/- 15%
Eg: Brass, Cu-Ni



(b) Interstitial solid solution

Much smaller
(at least one order of magnitude lower)
Eg: Carbon in Iron (Steel)

Binary mixture



$$G_1 = x_A G_A + x_B G_B$$

Before mixing

Binary mixture

$\boxed{A + B}$

After mixing

$G_2 = G_1 + \Delta G_{mix}$

$\boxed{\Delta G_{mix} = G_2 - G_1}$

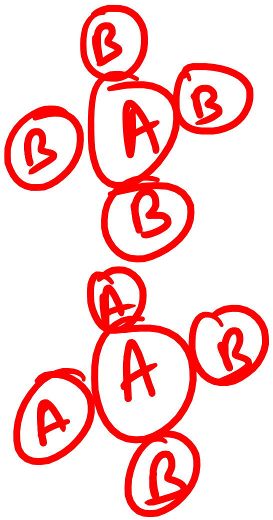
$\boxed{\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}}$

$\Delta H_{mix} = H_2 - H_1$

$\Delta S_{mix} = S_2 - S_1$

$=$

Binary mixture : IDeal soln



$$\Delta H_{mix} = 0$$

$$\Delta G_{mix} = 0 - T\,\Delta S_{mix}$$
$$= -T\,\Delta S_{mix}$$

$$\boxed{S = k \ln w}$$

→ measure the randomness.

Binary mixture

$\ln(100000)!$

$=$

$5!$

$\ln N!$ $\quad N \to \infty$

$= N \ln N$

$\Delta S_{mix} = k \ln \omega$

$\Delta S_{mix} = \cancel{S_{th}}^{\,0} + S_{conf.}$

$N_A = x_a N_a$

$\downarrow$ avogadro no.

$N_B = x_B N_a$

$$\boxed{\omega_{conf} = \frac{(N_A + N_B)!}{(N_A)!\,(N_B)!}}$$

Binary mixture

$$\Delta S_{mix} = k \ln \frac{(N_A + N_B)!}{N_A!\, N_B!}$$

$N_A = x_A N_a$

$N_B = x_B N_a$

$$= k \ln \frac{(x_A N_a + x_B N_a)!}{(x_a N_a)!\,(x_B N_a)!}$$

$$= k \{ \ln (x_a N_a + x_B N_a)! - \ln (x_a N_a)! - \ln (x_B N_a)! \}$$

$\ln N! = N \ln N$

$x_a + x_B = 1$

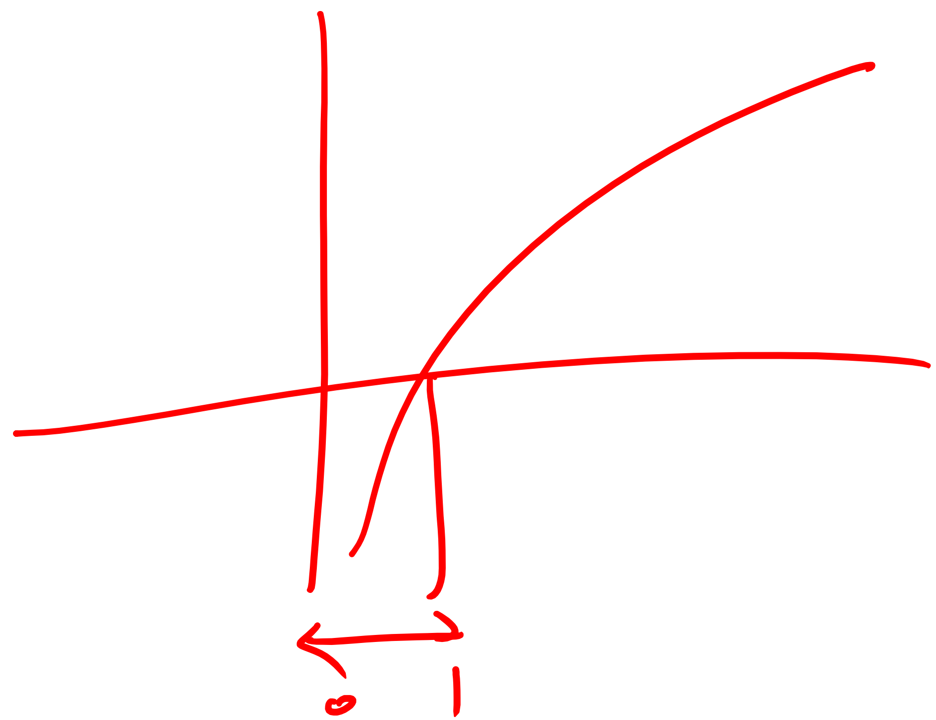
Binary mixture

$$\Delta S_{mix} = -\underbrace{N_a k} \{ x_A \ln x_A + x_B \ln x_B \}$$

$$= -R \{ x_A \ln x_A + x_B \ln x_B \}$$

$$x_A + x_B = 1$$

$$0 < x_A \text{ or } x_B < 1$$



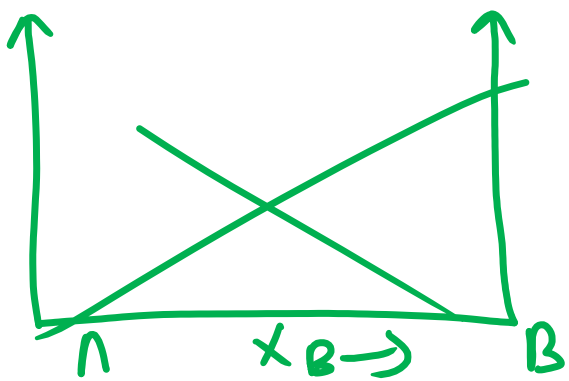
Binary mixture

$$\Delta h_{mix} = -T\Delta S_{mix}$$

$$= -R(-T)\{x_A \ln x_A + x_B \ln x_B\}$$

$$= RT\{x_A \ln x_A + x_B \ln x_B\}$$

$$\boxed{G_1 = x_A G_A + G_B x_B} \quad \boxed{G_2 = G_1 + \Delta h_{mix}}$$



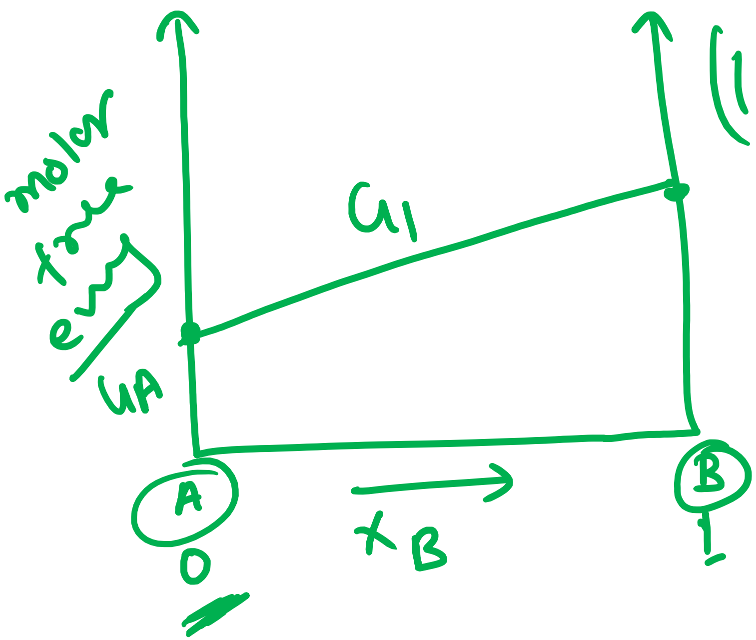
Binary mixture

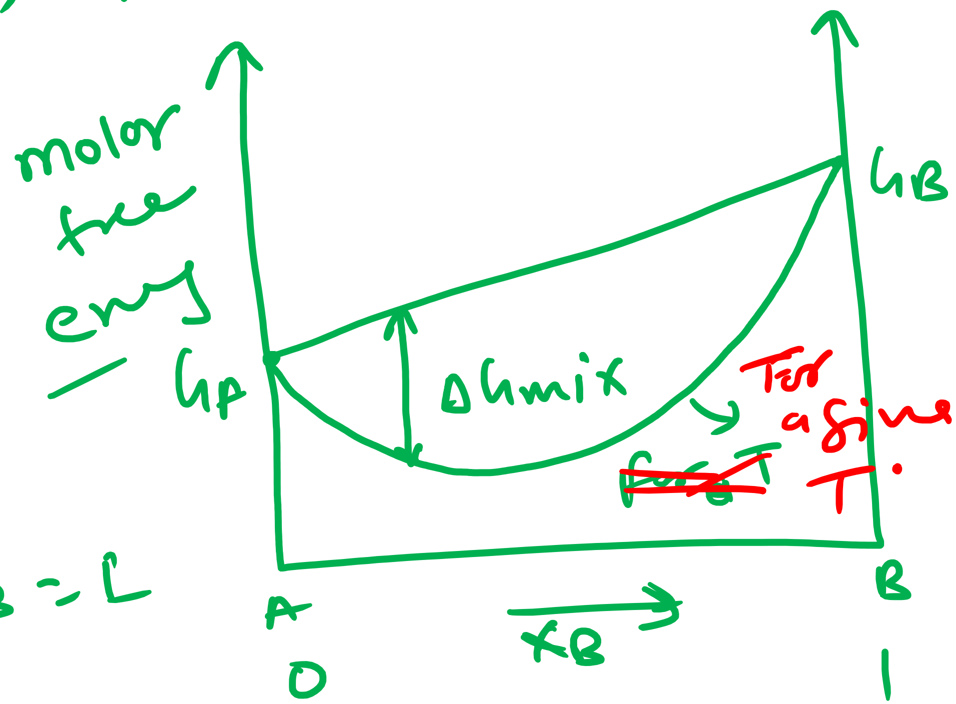
$RT\{(1-x_B)\ln x_A + x_B \ln x_B\}$ $\quad -T\Delta S_{mix}$

$\Delta G_{mix} = RT\{x_A \ln x_A + x_B \ln x_B\} =$

$G_1 = x_A G_A + x_B G_B$, $\quad \boxed{G_2 = G_1 + \Delta G_{mix}}$

$(1-x_B)\,G_A + x_B G_B$

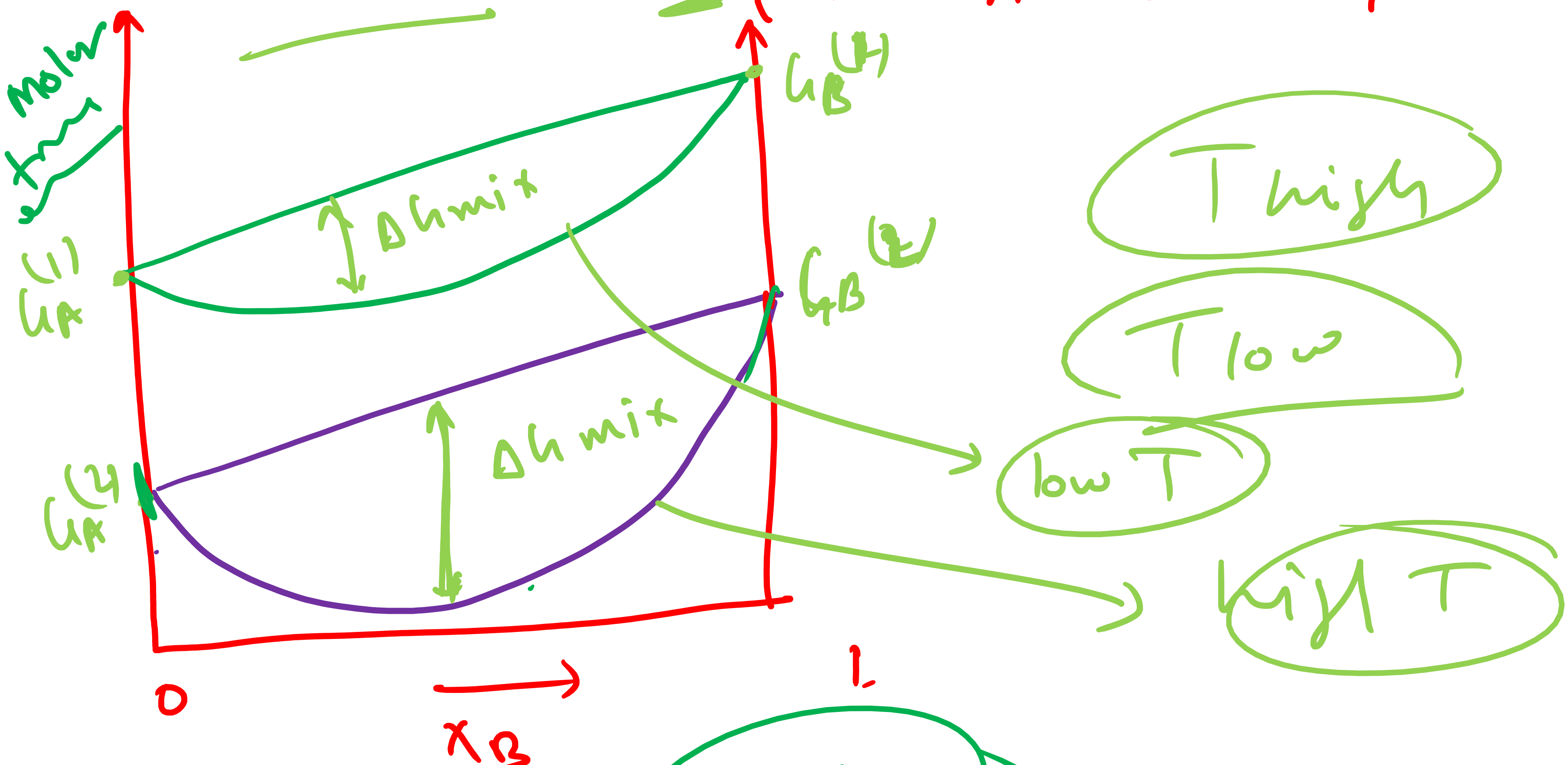




$x_A + x_B = 1$

Binary mixture

$$\Delta G_{mix} = RT\{x_A \ln x_A + x_B \ln x_B\}$$



$$\frac{\partial G}{\partial x}$$

Binary mixture

$$\mu = \frac{\partial G}{\partial x}$$

10 % A
90 % B

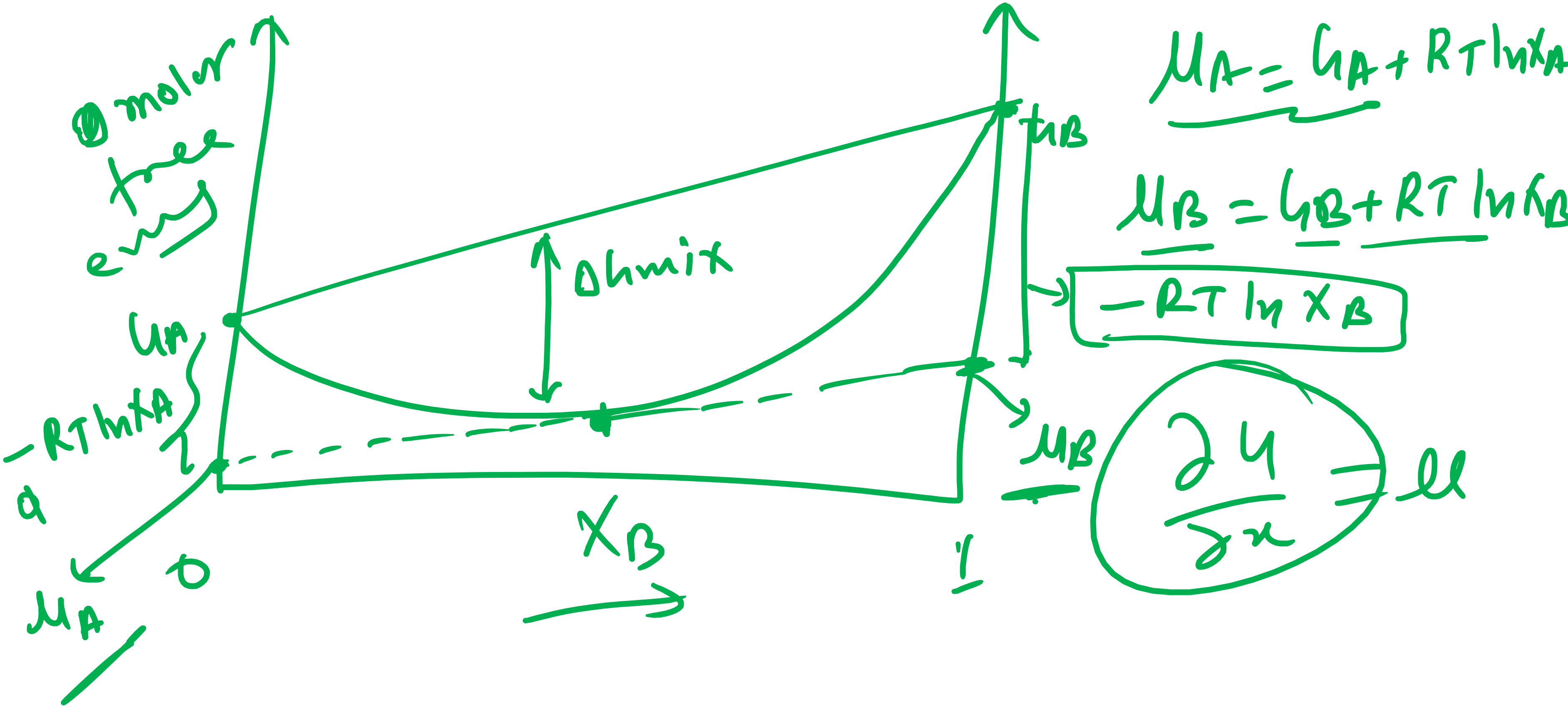
10.001 % A
89.999 % B

$$\boxed{G = \mu_A x_A + \mu_B x_B}$$

$$G_2 = G_2 + \Delta G_{mix} = x_A G_A + x_B G_B + RT\{x_A \ln x_A + x_B \ln x_B\}$$

$$\mu_A = G_A + RT \ln x_A \quad \Big| \quad \mu_B = G_B + RT \ln x_B$$

Binary mixture



Binary mixture : Regular Soln

$$\Delta H_{mix} = \Omega X_A X_B$$

A–A

B–B

A–B

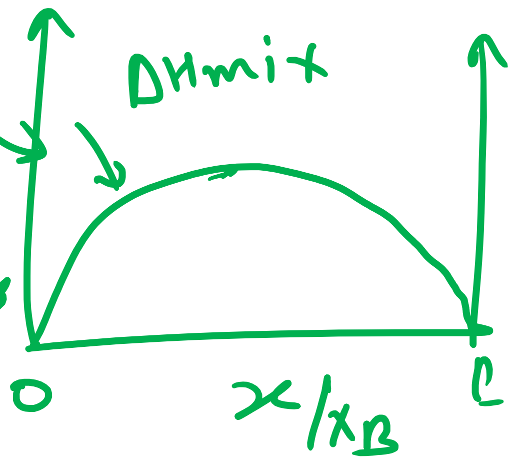
A B

$$\Omega = N_a \varepsilon_0 Z$$

$$\boxed{\varepsilon_0 = \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}}$$

Binary mixture

$$\Delta H_{mix} = \Omega X_A X_B$$



$\Omega > 0$

$\Omega < 0$

$\Omega (X_A X_B)$

$\Omega X_B (1 - X_B)$

$\Omega (x - x^2)$

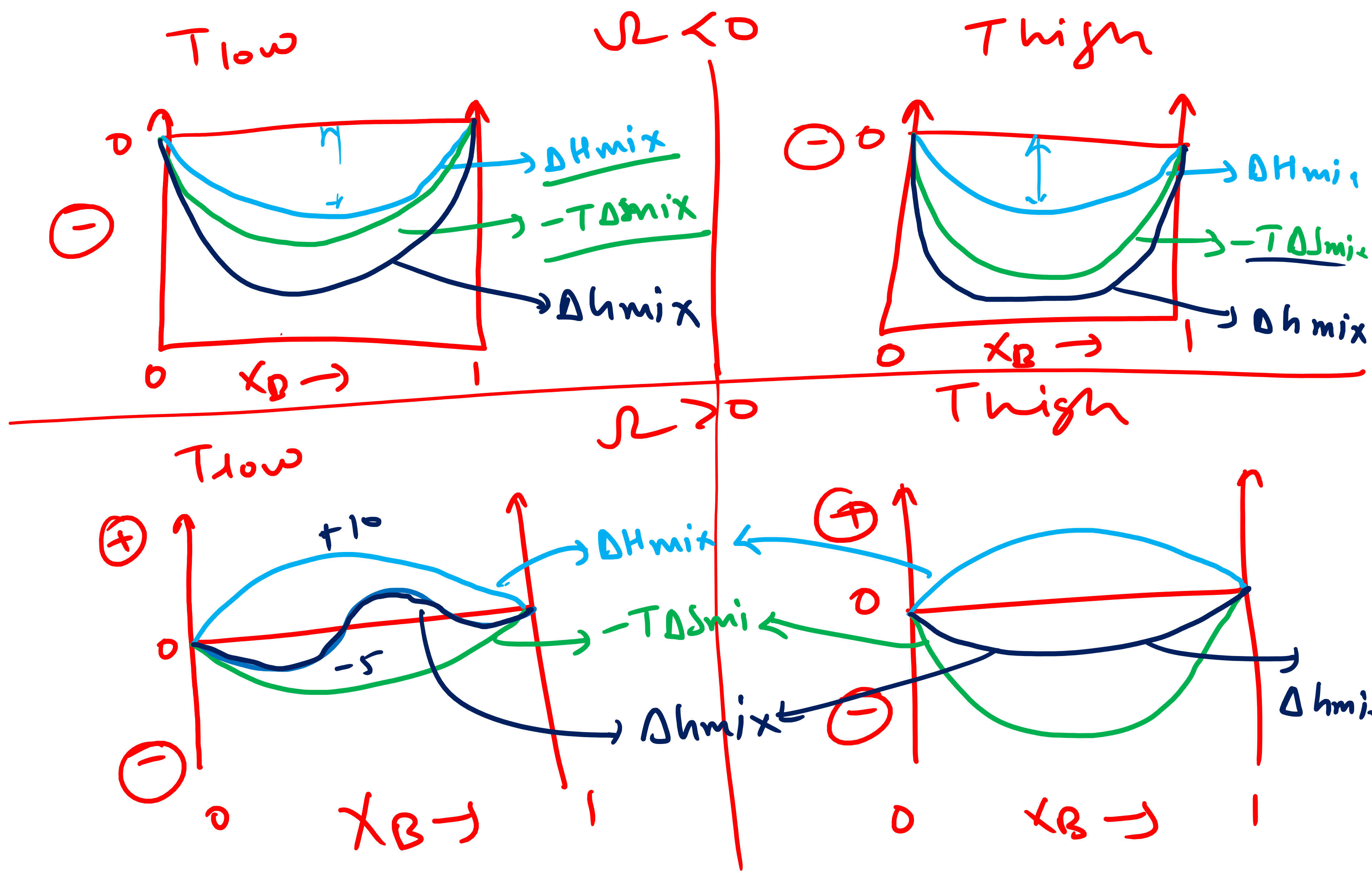
$$\varepsilon_{AB} = \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2}$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

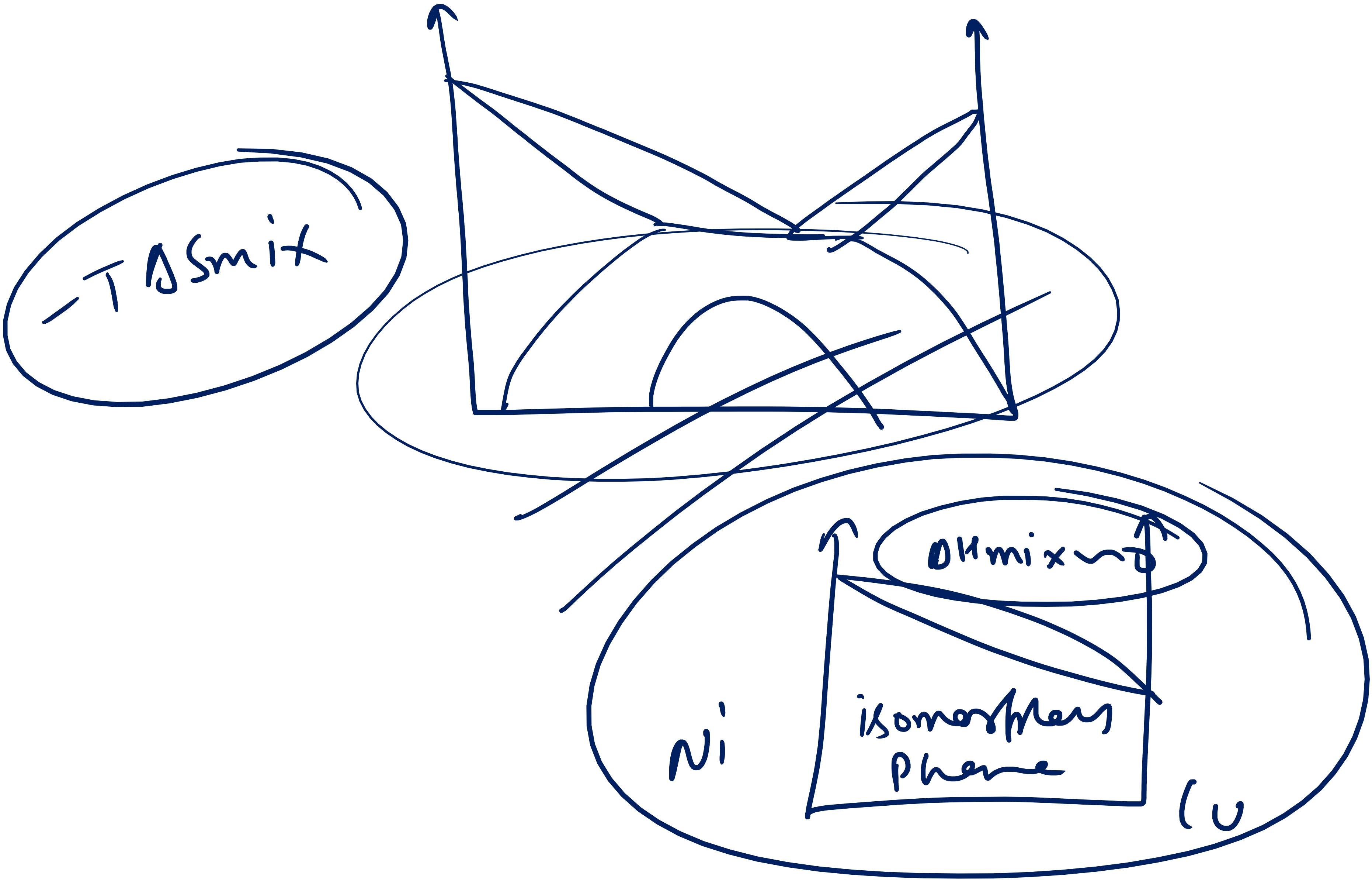
$$= \Omega X_A X_B + TR\{X_A \ln X_A + X_B \ln X_B\}$$

Binary mixture

$\Delta h_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Omega X_A X_B + RT\{X_A \ln X_A + X_B \ln X_B\}$



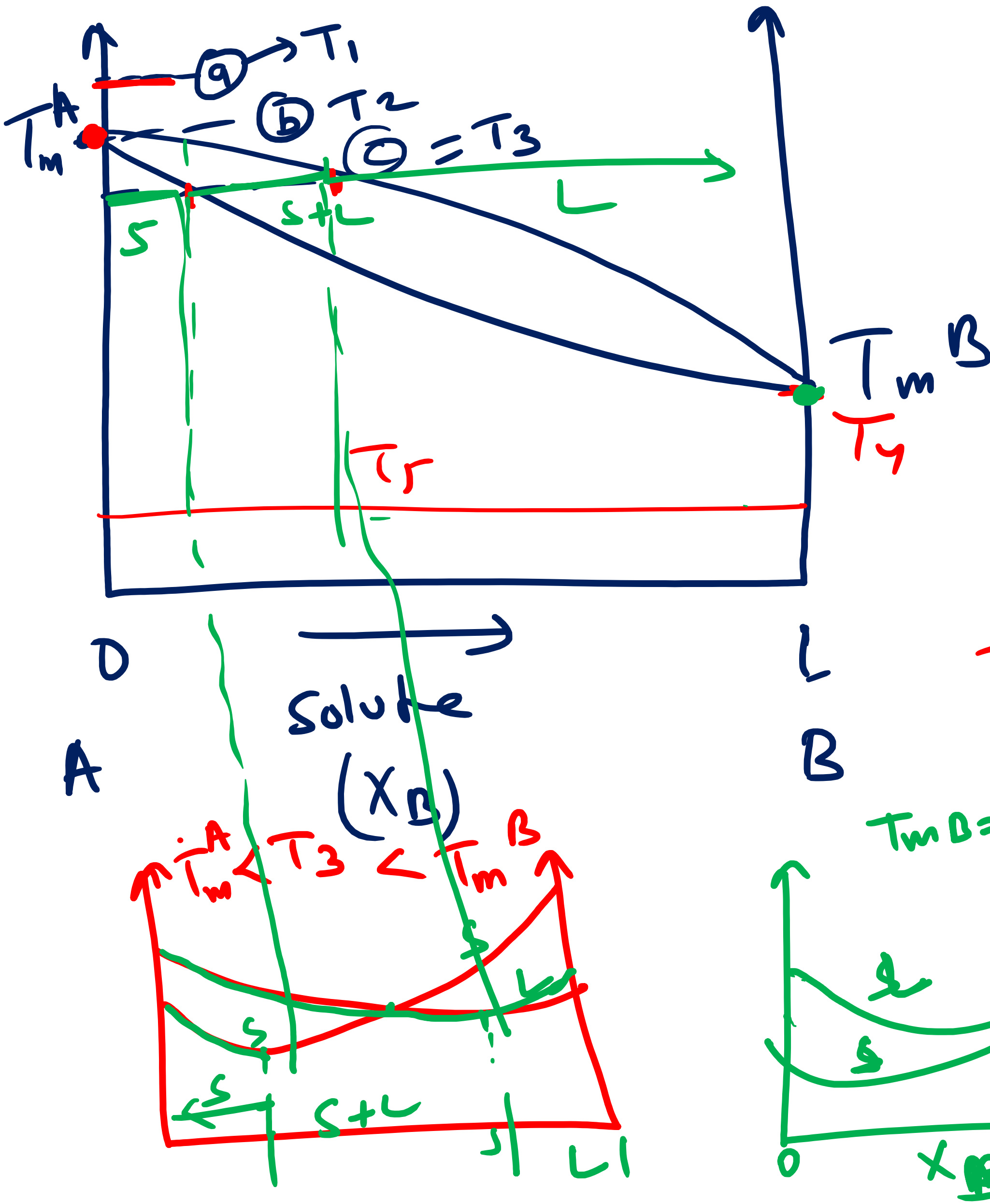
Binary mixture

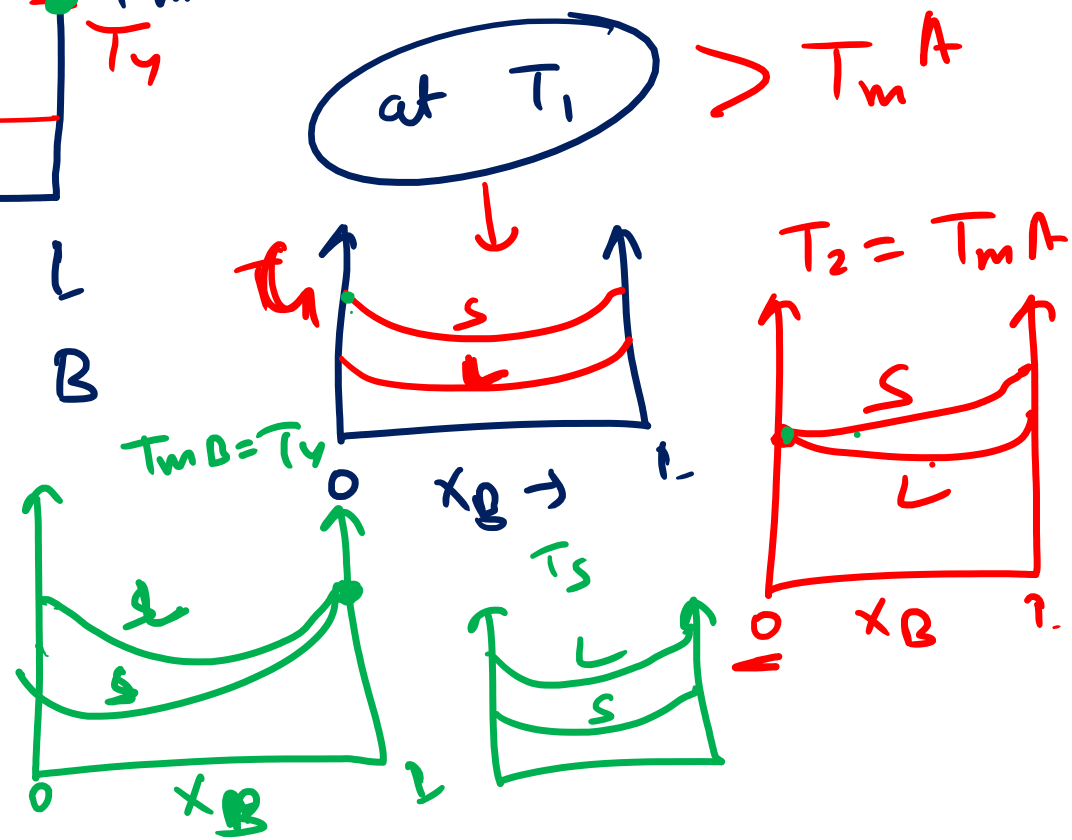


Binary mixture

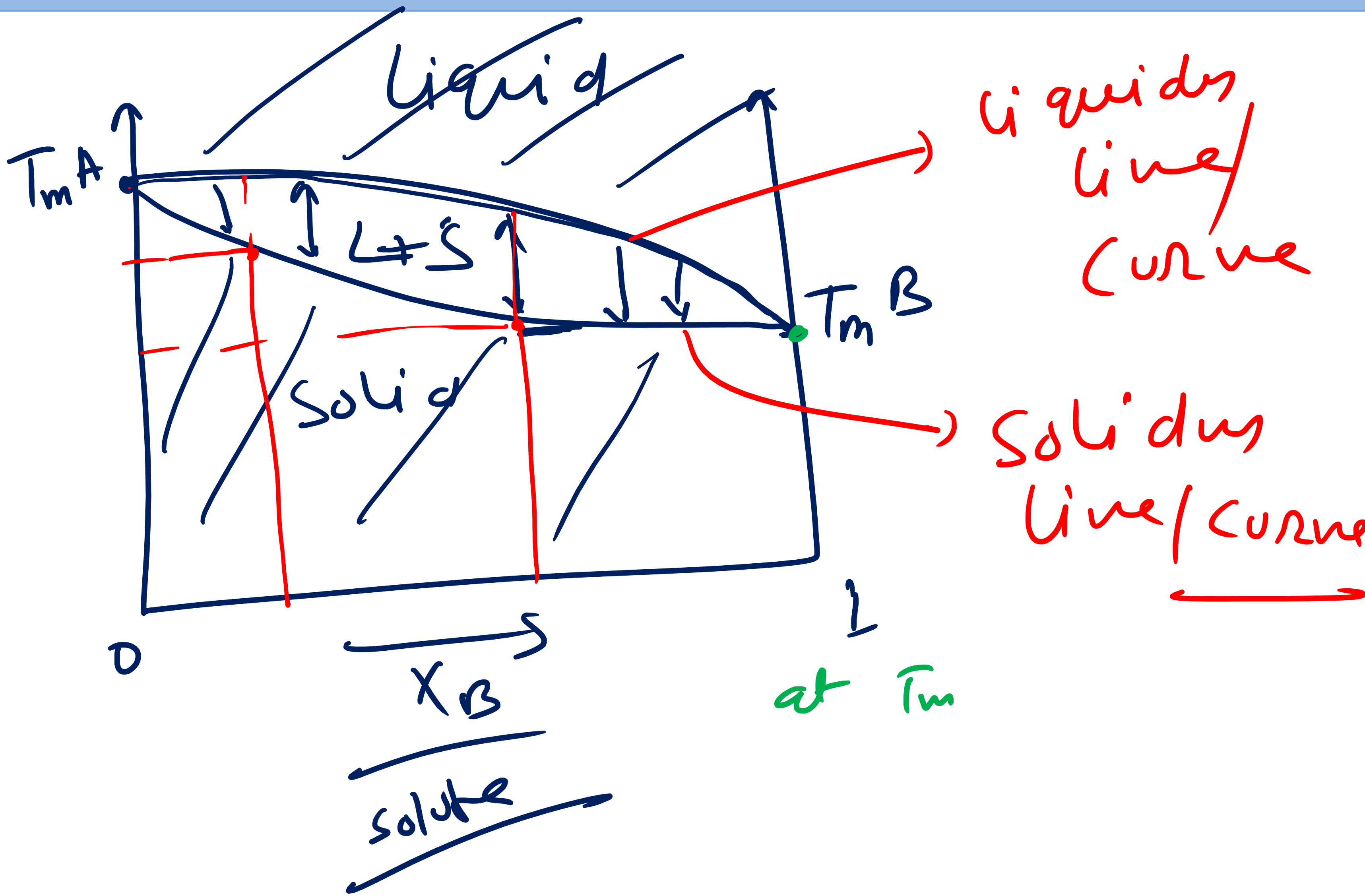
T_m^A = melting point of A

T_m^B = " " of B

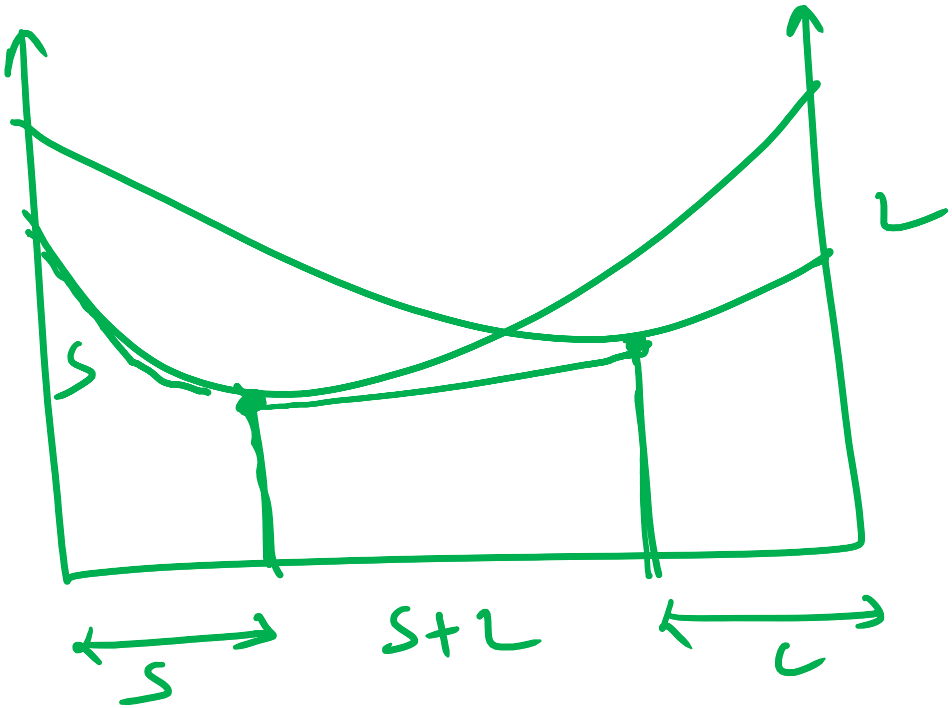




Binary mixture

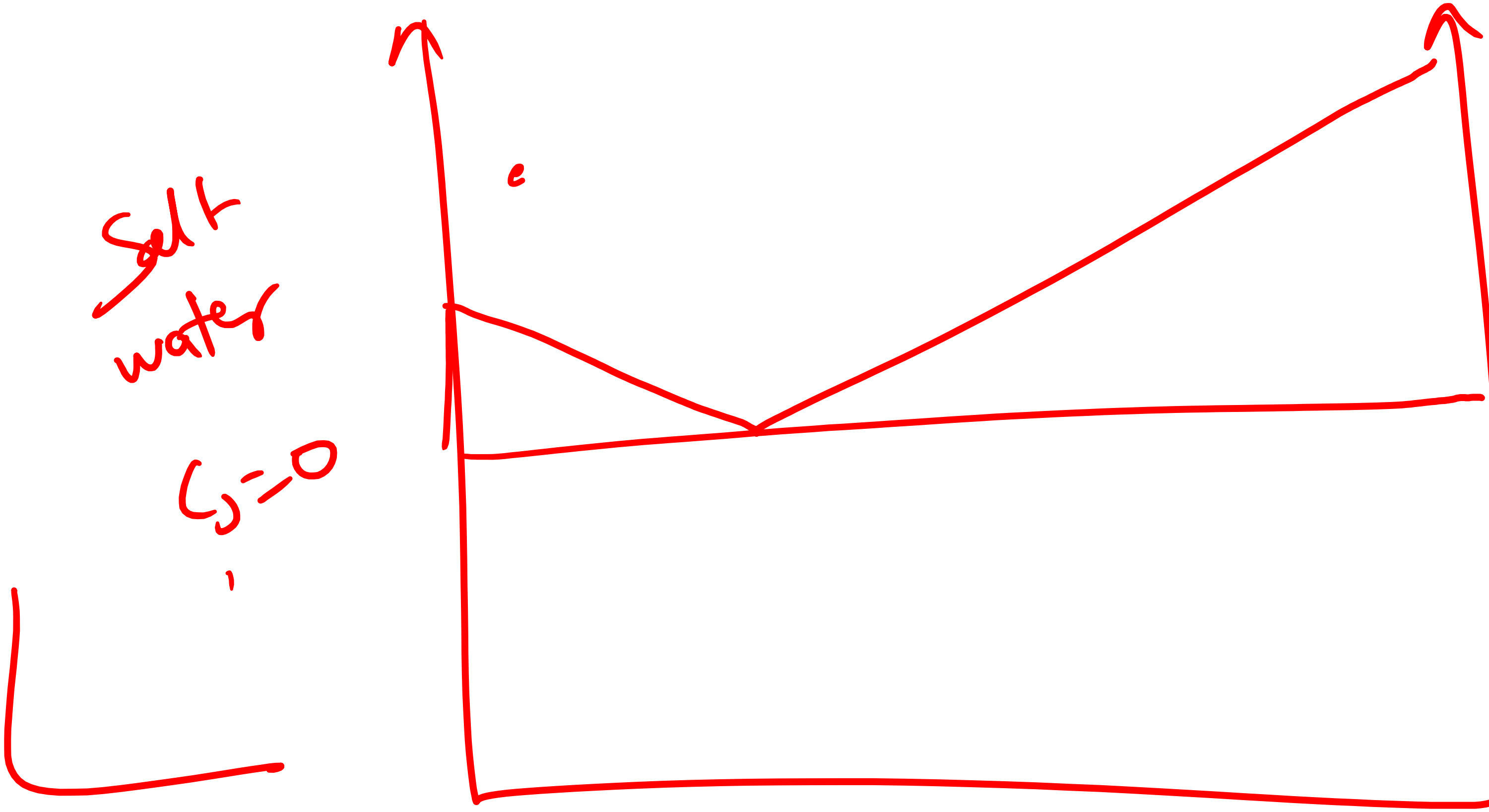


Binary mixture

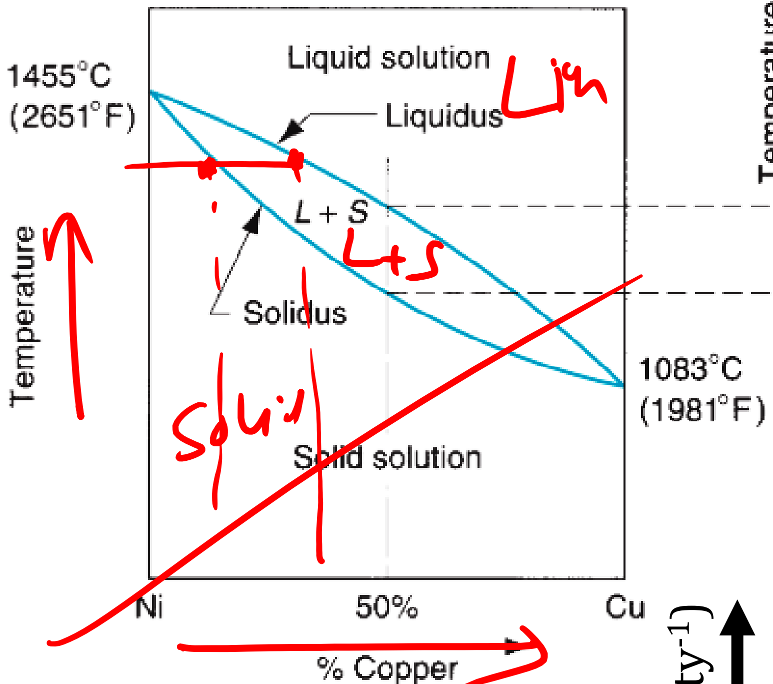


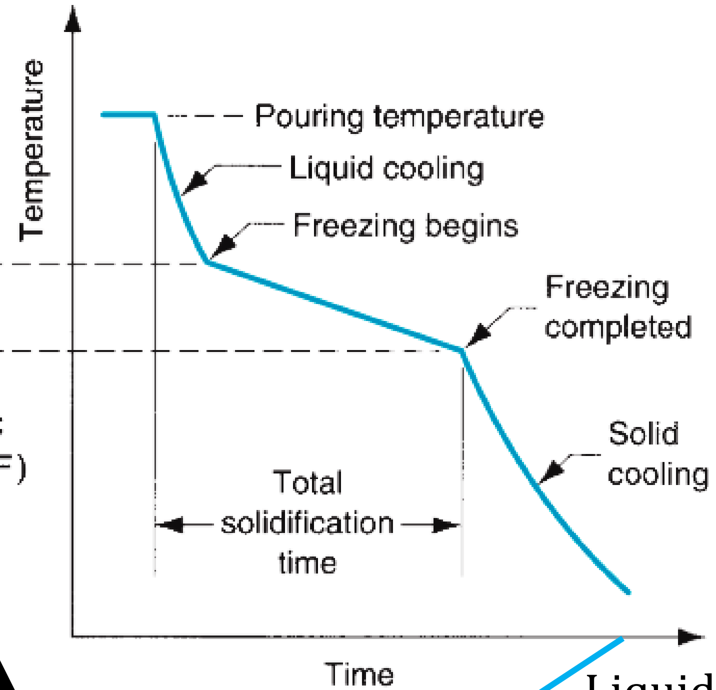
Binary mixture

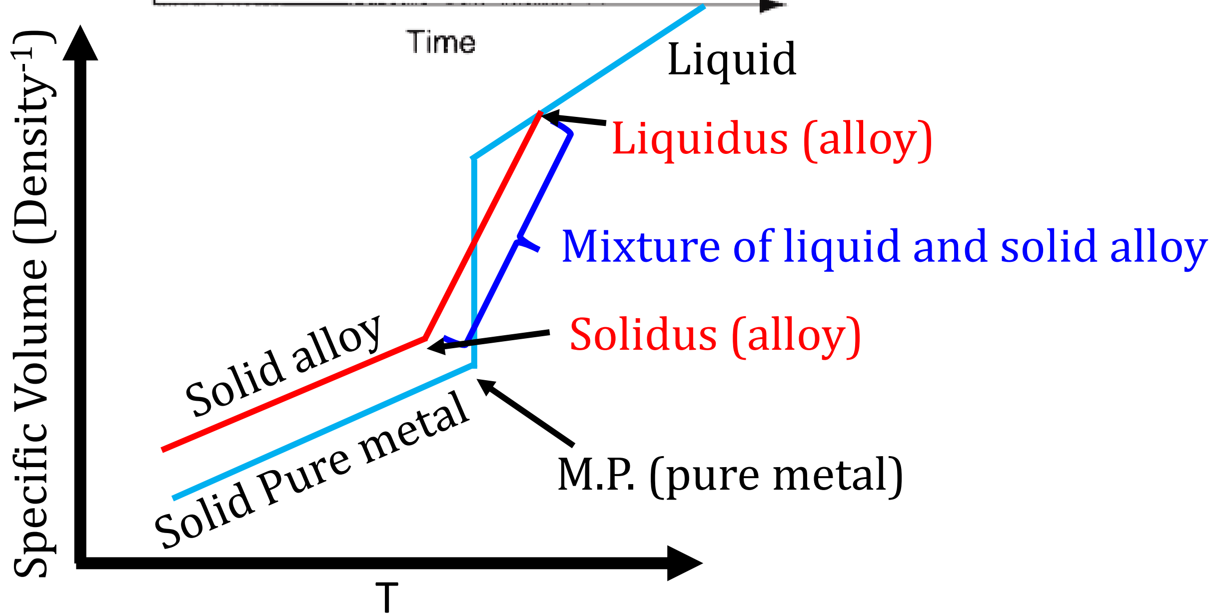
Binary mixture



Binary alloy: Isomorphous phase diagram



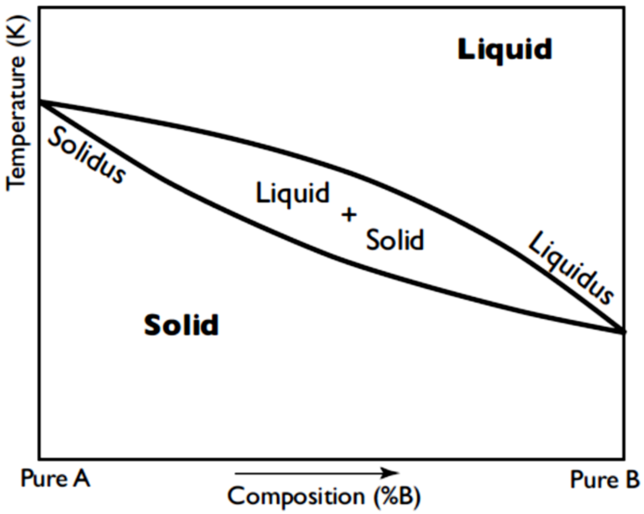


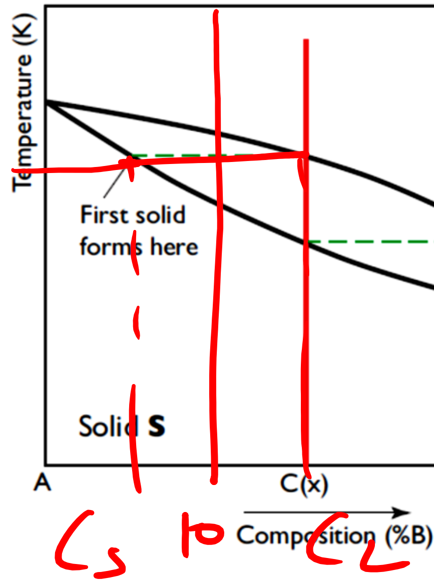


Gibbs Phase Rule:

$F = C\text{-}P+2$

Binary alloy: Isomorphous phase diagram



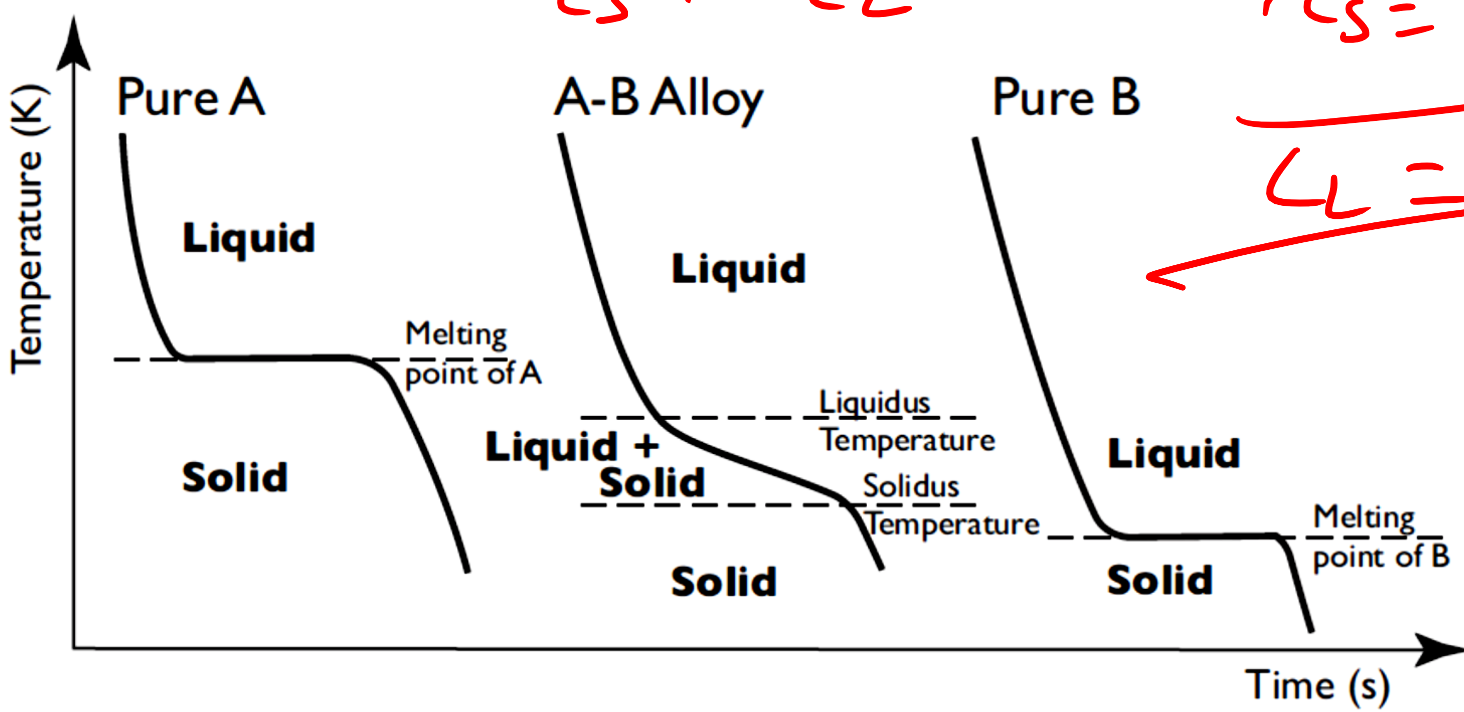


$C_s << C_L$

$C_0 = 10\%$

$C_s = 3\%$

$C_L = 14\%$



Binary eutectic phase diagram