Phase Equilibria and Phase Transitions in Unary Systems

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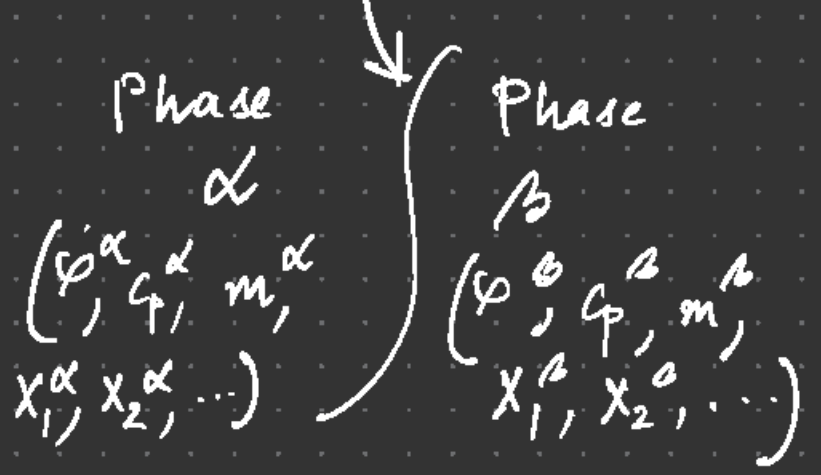
Definition of a phase

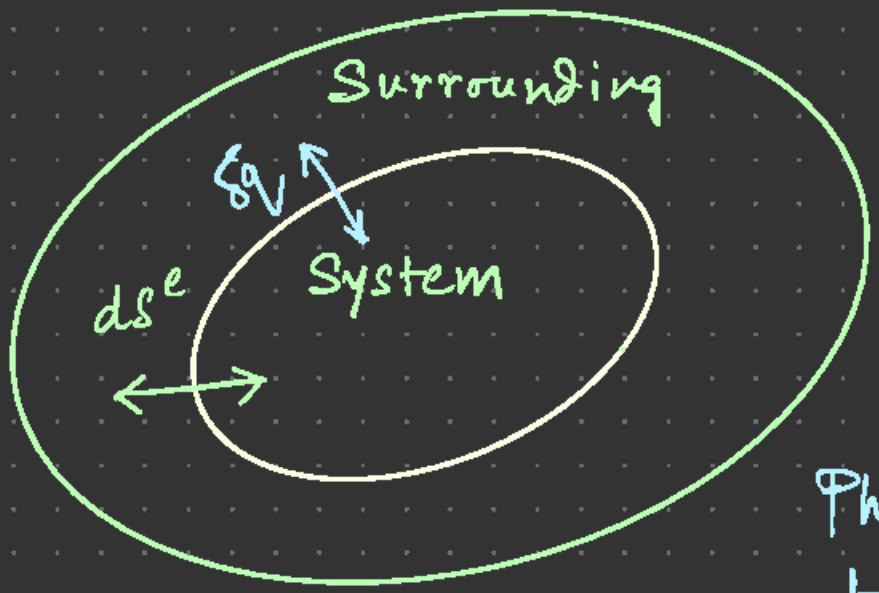
A phase is a portion of matter that is chemically uniform, physically distinct, mechanically separable

phase — a subsystem of a composite system

phase boundary — portion of a thermodynamic system throughout which properties such as density, chemical composition, magnetization, heat capacity are uniform



Phase Equilibrium and Phase transitions



$dS^e \rightarrow$ Entropy transfer
or
entropy exchange
between system
and surrounding

$\alpha \rightleftharpoons \beta$

T_{tr}, P_{tr}

Phase transition
temperature and pressure

Consider an internal process inside a system

Entropy produced inside the system $= dS^{in}$
or
dS^p

$dS^{irr} = 0$ When the process is reversible

First law

$dV^e = dV =$ change in volume of the system

or, volume exchange between system and surroundings

$dN^e = dN =$ change in amount of a component inside the system

or, matter exchange between system and surrounding

$$dU = TdS^e - pdV^e + \mu dN^e$$

$$= TdS - pdV + \mu dN \quad \text{— reversible process}$$

Irreversible or natural or Spontaneous process creates entropy dS^{in}

$$\therefore \quad dS^e = dS - dS^{in}$$

$$dU = TdS - pdV + \mu dN - TdS^{in}$$

Hillert - Phase Diagrams and Phase Transformations - Their Thermodynamic Basis

L. Q. Chen - Thermodynamic Equilibrium and Stability of Materials

$$dU = TdS - pdV + \mu dN - TdS^{in}$$ $TdS^{in} = Dd$

$D \rightarrow$ amount of dissipation of internal energy (driving force for the spontaneous process)

ξ (xeta) $\rightarrow$ Extent of the process (internal process variable or an order parameter)

$\xi = 0$ or ξ_i at the start of process

$= 1$ or ξ_f at the end of process

$\mathcal{D} = 0$ for a reversible process

> 0 for an irreversible or spontaneous process

$$T dS^{in} = \mathcal{D}\, d\xi$$

$$\mathcal{D} = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N}$$

ξ — order parameter in a phase transition process

$\xi = 0$ is the parent phase

$0 < \xi < 1$ is a mixture of parent & product phases

$\xi = 1$ is the product phase

Amount of entropy produced or energy dissipated

$$\Delta S^{ir} = \int_{\text{initial}}^{\text{final}} dS^{ir} = \int_{\xi_i}^{\xi_f} \frac{D}{T} d\xi$$

$$dS^{ir} = \frac{D\, d\xi}{T} = dS \text{ for an irreversible process in an isolated system}$$

Isolated system

$$D = T\left(\frac{\partial S}{\partial \xi}\right)_{U,V,N} = T\left(\frac{\partial S^{ir}}{\partial \xi}\right)_{U,V,N}$$

$D = 0$ for an initially equilibrium state

$D > 0$ for an initial nonequilibrium state

Closed system (constant temperature & pressure)

— System in contact with thermal and mechanical reservoir

$$U(S, V, N) \longrightarrow G(T, P, N)$$

$$dS^{in} = dS - dS^{e}$$

$$= dS - \frac{\delta Q_P}{T}$$

$$= dS - \frac{dH}{T}$$

$$= \frac{TdS - dH}{T}$$

$$dU = \delta Q_P - PdV$$

$$\text{or, } \delta Q_P = dU + PdV$$

$$= dH$$

$$(\because dP = 0)$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dT = 0$$

$$\therefore dG = dH - TdS$$

$$dS^{in} = \frac{TdS - dH}{T} = -\frac{dG}{T} = \frac{D d\xi}{T}$$

$$D = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P,N}$$

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

$$\Delta G = -T\Delta S^{in}$$

$\Delta H^{fusion} = \Delta H^{melting}$

1 atm. = 1·01325 bar

is the amount of heat absorbed during the melting of 1 mole of solid to 1 mole of liquid at 1 bar pressure.

$\Delta H^{crystallization} = -\Delta H^{fusion}$

is the amount of heat released when 1 mole of liquid solidifies or crystallizes to form 1 mole of solid at 1 bar pressure

$0°C$

ice $\rightleftharpoons$ water

1 bar

1 bar = 10^5 Pa

$$dU = TdS - pdV + \mu dN - TdS^{ir}$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

At constant pressure

$$dP = 0$$

$$dH = dU + pdV$$

$$dH = TdS + \mu dN - TdS^{ir}$$

$\rho = \frac{M}{V_m}$

ice $\rightleftharpoons$ Water $\quad \Delta H^{fusion} = 6006$ J/mol

$T^m = 0^\circ C = 273$ K (phase transition temperature)

$M = 18.02$ gm/mol $\quad$ 1 bar = 1.01325 atm.

$\rho^{water} = \frac{18.02 \text{ gm/mol}}{18.02 \text{ cm}^3/\text{mol}}$

$= 1$ gm/cc

$\frac{V_m^{ice}}{V_m^{water}} \begin{matrix} (273\text{K}, 1\text{ bar}) = 19.66 \text{ cm}^3/\text{mol} \\ (273\text{K}, 1\text{ bar}) = 18.02 \text{ cm}^3/\text{mol} \end{matrix}$

Amount of heat released per mole of water solidifying to ice

$\rho^{ice} = \frac{18.02}{19.66}$ gm/cc

$= 0.916$ gm/cm^3

$Q_m = \Delta H^{crystallization} = -\Delta H^{fusion} = -6006$ J

$\Delta H = \Delta U + P\Delta V$

$= Q_p = T\Delta S$

entropy released from system to surrounding

$$\therefore \quad Q_p = -T_m \Delta S^e = -6006 \text{ J/K}$$

$$\Delta S^e = \frac{-6006}{273} \text{ J/K}$$

$$= -22 \text{ J/K}$$

$$\Delta S^{\text{surrounding}} = -\Delta S^e = 22 \text{ J/K}$$

$$\Delta S = \Delta S^{\text{system}} = \Delta S^e = -22 \text{ J/K}$$

$$\Delta S^{in} = \Delta S - \Delta S^e = 0$$

$$\Delta S^{universe} = \Delta S^{tot} = \Delta S^{system} + \Delta S^{surroundings}$$

$$= -22 + 22$$

$$= 0$$

Process is Reversible

$$\Delta H^{cryo}_{water \to ice} = H_{ice} - H_{water}$$

$$h^{water} - h^{ice} \left(273\ K,\ 1\ bar\right) \qquad \Delta H^{fusion}_{ice \to water}$$

$$= -\Delta H^{cryotallization}_{water \to ice}$$

$$= \Delta H^{fusion}_{ice \to water} = 6006\ J$$

$$u^{water} - u^{ice} = ?$$

$$h^{water} - h^{ice} = \left(u^{water} + p V_m^{water}\right) - \left(u^{ice} + p V_m^{ice}\right)$$

$$= \underline{6006\ \text{J}}$$

$$u^{water} - u^{ice} = 6006\ \text{J} + \underline{p}\left(V_m^{ice} - V_m^{water}\right)$$

$$10^5$$

$$= 6006 + 1\,\text{bar} \times 101325\ \text{Pa} \times \left(19.66 - 18.02\right) \times 10^{-6}\ \text{m}^3$$

$$= 6006 + 0.166$$

$$\approx 6006\ \text{J}$$

$S^{water} - S^{ice} = 22\ J/K$ $\quad \Delta S_{ice \to water}$

Consider 298 K (25°C) and 1 bar

1 mole of ice irreversibly (spontaneously) melts to 1 mole of water

Assume enthalpy difference and entropy differences between water and ice same as that at 273 K, 1 bar

$$\Delta S^{melting}(298\ K, 1\ bar) = \Delta S^{melting}(273\ K, 1\ bar)$$
$$= 22\ J/K = \Delta S^{system}$$

When ice melts, heat is absorbed by system from surrounding

$$\Delta S^{\text{surrounding}} = -\frac{Q}{T} = \frac{-6006}{298}$$

$$\approx -20.15 \text{ J/K}$$

Entropy exchange during ice melting to water at 298 K, 1 bar

$$\Delta S^{e} = +20.15 \text{ J/K}$$

$$\Delta S^{\text{total}} = \Delta S^{\text{system}} + \Delta S^{\text{surrounding}}$$

$$= 22.0 - 20.15 = 1.85 \text{ J/K}$$

$$\Delta S^{system} = \Delta S = \Delta S^{e} + \Delta S^{in}$$

$$22 = 20.15 + \Delta S^{in}$$

$$\therefore \Delta S^{in} = 1.85 \text{ J/K}$$

$$\Delta G\left(\begin{matrix}298\text{K}\\1\text{bar}\end{matrix}\right) = -T\Delta S^{in}$$

$$= -298 \times 1.85 \text{ J}$$

$$= -551.3 \text{ J}$$

This is the chemical energy changed to thermal energy

Unary system — Single component system

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$$

Chemical potential of species i

N moles of one component (pure system: pure Fe, Si, Al_2O_3, H_2O)

$$\therefore \frac{G}{N} = G_m \text{ or } \overline{G} = \frac{\Delta G}{\Delta N} = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu$$

Free energy per mole

Chemical potential in a unary system is the same as molar free energy of the system

$$dG = VdP - SdT + \mu dN$$

$\frac{V}{N} = v_m$

$\frac{S}{N} = s_m$

$$d\mu = dG_m = d\left(\frac{G}{N}\right) = v_m dP - s_m dT + \mu \cancel{d(1)}^{0}$$

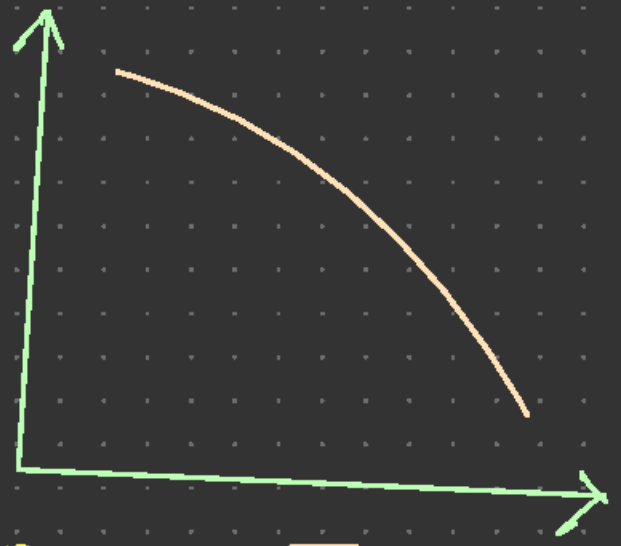
$$d\mu = v_m dp - s_m dT \quad \text{— UNARY}$$

Unary, chemically homogeneous system

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -s_m$$

Slope of $\mu - T$ curve $s_m > 0$

$$\left(\frac{\partial s_m}{\partial T}\right)_p = \frac{c_p}{T}$$

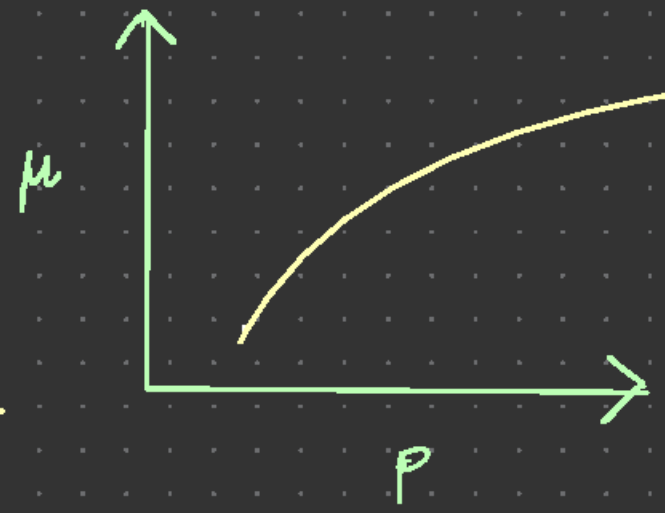


c_p – molar heat capacity

$$\therefore \left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\left(\frac{\partial S_m}{\partial T}\right)_P = -\frac{C_P}{T}$$

Curvature of μ-T curve

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v_m$$



$$\left(\frac{\partial^2 \mu}{\partial p^2}\right)_T = \left(\frac{\partial v_m}{\partial p}\right) = -v_m \beta_T$$

$$\beta_T = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial p}\right)_T$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T = v_m$$

$$= \frac{RT}{p} \quad \text{for ideal gas or perfect gas}$$

$$\int_i^f d\mu = RT \int_i^f \frac{dp}{p} = RT \ln\left(\frac{p_f}{p_i}\right)$$

Driving Force For Phase Transition

$\alpha \rightleftarrows \beta \quad (T_R, P_R)$

Total amount of substance = N

N^α moles of α

N^β moles of β

$N^\alpha + N^\beta = N$

Chemical potentials $\mu^\alpha(T,P) - \alpha$

$\mu^\beta(T,P) - \beta$

$\frac{N^\alpha}{N}$ – fraction of α phase

$$G^{\alpha} = N^{\alpha}\mu^{\alpha}$$
$$G^{\beta} = N^{\beta}\mu^{\beta}$$
} At a given T & P

$$G = G^{\alpha} + G^{\beta} = N^{\alpha}\mu^{\alpha} + N^{\beta}\mu^{\beta}$$

$$dG^{\alpha} = -S^{\alpha} N^{\alpha} dT + v_m^{\alpha} N^{\alpha} dp + \mu^{\alpha} dN^{\alpha}$$
$$dG^{\beta} = -S^{\beta} N^{\beta} dT + v_m^{\beta} N^{\beta} dp + \mu^{\beta} dN^{\beta}$$

Degree or Extent of transition

$$\xi = \frac{N^{\beta}}{N} \quad \text{from } \alpha \text{ to } \beta$$

$$1 - \xi = \frac{N^{\alpha}}{N}$$

At constant T and P

$$dG = \mu^{\alpha} dN^{\alpha} + \mu^{\beta} dN^{\beta}$$

f = mole fraction (or volume fraction of β)

$$G(N, T, P, f)$$

$$= N(1-f)\mu^{\alpha}(T,P) + Nf\mu^{\beta}(T,P)$$

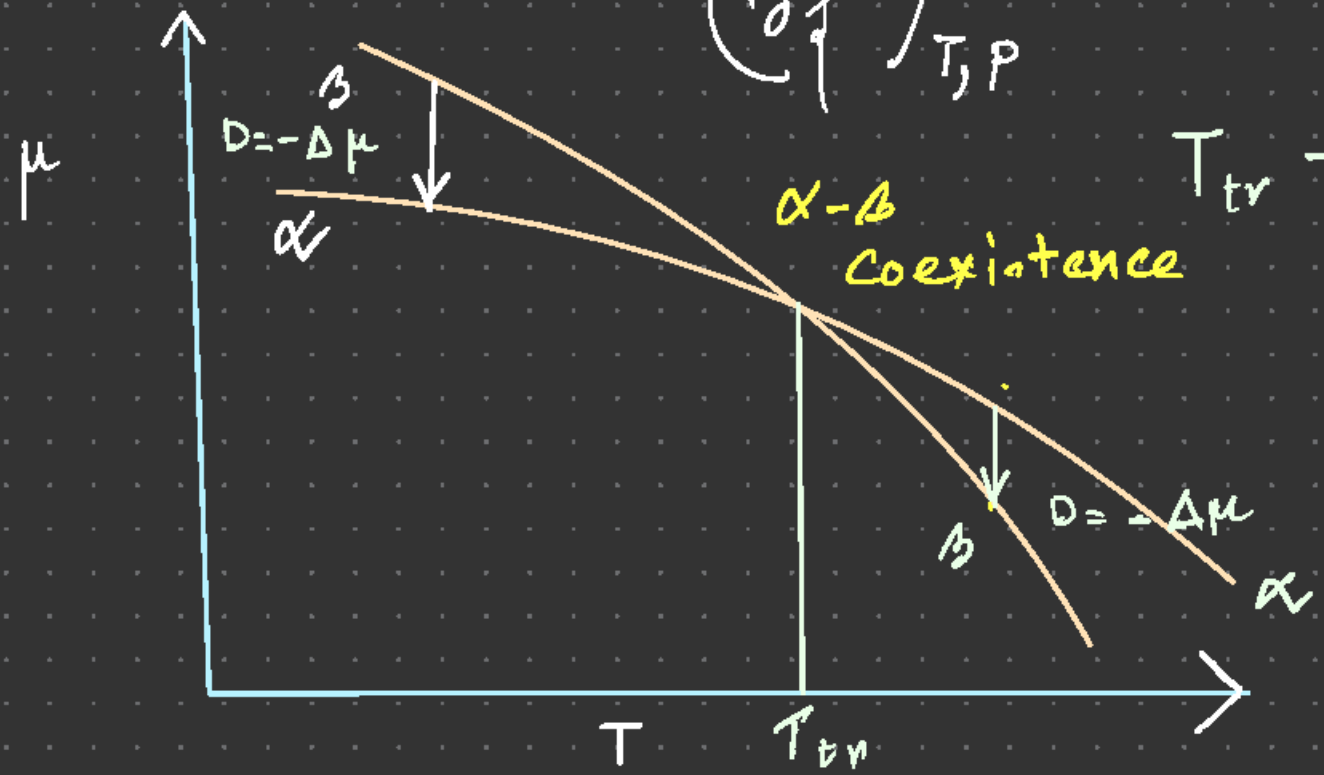
$$= N\mu^{\alpha}(T,P) + Nf\left[\mu^{\beta}(T,P) - \mu^{\alpha}(T,P)\right]$$

$$\mu(T,P,\xi) = \frac{G}{N}(N,T,P,\xi) = \mu^{\alpha}(T,P) + \xi\,\Delta\mu(T,P)$$

where $\Delta\mu = \mu^{\beta} - \mu^{\alpha}$

$$d\mu(T,P) = \Delta\mu(T,P)\,d\xi$$

$$D = -\left(\frac{\partial\mu}{\partial\xi}\right)_{T,P} = -\Delta\mu$$



T_{tr} – Equilibrium transformation temperature

If $T > T_{tr}$, $\mu^\beta < \mu^\alpha$, $\Delta\mu = \mu^\beta - \mu^\alpha < 0$,

$$D = -\Delta\mu > 0$$

α phase is thermodynamically unstable and transforms to β phase

If $T < T_{tr}$, $\mu^\beta > \mu^\alpha$, $\Delta\mu = \mu^\beta - \mu^\alpha > 0$

$$D = -\Delta\mu < 0$$

α phase is thermodynamically stable and does not transition to β spontaneously

If $T = T_{tr}$, $\mu^\beta = \mu^\alpha$, $\Delta\mu = 0$, $D = 0$

$\alpha \rightleftarrows \beta$, α and β are in equilibrium

$$\Delta s^{ir} = \frac{D}{T} = \frac{\mu^{\alpha} - \mu^{\alpha}}{T} = -\frac{\Delta\mu}{T}$$

$$\Delta s^{ir} = 0 \quad \text{at} \quad T = T^{tr}$$

$$\frac{d\xi}{dt} \propto \frac{D}{T} \quad \text{(in a linear kinetic theory)}$$

$$\frac{ds^{ir}}{v_m\, dt} = \frac{D}{T}\frac{d\xi}{v_m\, dt} \qquad \left(\frac{d\mu}{v_m dt} = -D\frac{d\xi}{v_m dt}\right)$$

rate of molar entropy production

rate of phase transition

Driving force as a function of temperature T and pressure P

$\alpha \rightleftharpoons \beta$

$$d\mu^{\alpha} = -s^{\alpha} dT + v_m^{\alpha} dP \longrightarrow (1)$$

$$d\mu^{\beta} = -s^{\beta} dT + v_m^{\beta} dP \longrightarrow (2)$$

(2) − (1)

$$d\left(\mu^{\beta} - \mu^{\alpha}\right) = -\left(s^{\beta} - s^{\alpha}\right) dT + \left(v_m^{\beta} - v_m^{\alpha}\right) dP$$

$$d\Delta\mu = -\Delta s\, dT + \Delta v_m\, dP$$

$$\Delta\mu(T,P) = -\int_{T_{tr},\,p_0}^{T,\,p_0} \Delta s(T,P)\,dT + \int_{T,\,p_0}^{T,\,P\ \text{bar}} \Delta v_m(T,P)\,dP$$

$\Delta\bar{G}$ ΔG_m

$G_m^{\beta} - G_m^{\alpha}$

At equilibrium $\Delta\mu(T,P) = 0$

Assume that for a phase transition, ΔC_p is constant

β^T and α are zero

$$\Delta s(T,P) = \Delta s^0(T_{tr}, p_0) + \Delta C_p \ln\frac{T}{T_{tr}}$$

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_p}{T}$$

$$\Delta v_m(T, p) = \Delta v_m(T, p_0) = \Delta v_m^\circ(T_{tr}, p_0)$$

Δs° — change in molar entropy at T_{tr} and p_0 bar

Δv_m° — change in molar volume at T_{tr} and p_0 bar

$$\Delta\mu = -\int_{T_{tr}, p_0}^{T_{tr}, p_0} \left[\Delta s^\circ + \Delta C_p \ln\frac{T}{T_{tr}}\right] dT + \Delta v_m^\circ (p - p_0)$$

$$\Delta\mu(T,p) = \left(\Delta C_p - \Delta S^\circ\right)\left(T - T_{tr}\right) - \Delta C_p T \ln T/T_{tr} + \Delta V_m^\circ \left(p - p_0\right)$$

$$\alpha \rightleftharpoons \beta$$

$$\Delta T = T - T_{tr}$$

$$\Delta p = p - p_0$$

$$\Delta\mu = \left[\Delta C_p - \Delta S^\circ\right]\Delta T - \Delta C_p T \ln\left(1 + \frac{\Delta T}{T_{tr}}\right) + \Delta V_m^\circ \Delta p$$

Let $\frac{T}{T_{tr}} = Z$

$$Z = \frac{T}{T_{tr}}$$

$$dZ = \frac{1}{T_{tr}}\, dT$$

$$\ln T/T_R \; dT = T_{tr} \int_{T_{tr}}^{T} \ln Z \; dZ$$

$$= T_{tr}\left[Z \ln Z - Z\right]_{T_{tr}}^{T}$$

$$= T \ln\left(\frac{T}{T_{tr}}\right) - T + T_{tr}$$

$$\Delta s^\circ = \frac{\Delta h^\circ}{T_{tr}}$$

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\Delta G_m = 0 \quad \text{and} \quad T = T_{tr}$$

$$\therefore \Delta H_m = T_{tr}\,\Delta S_m$$

$$\Delta C_p \Delta T - \Delta C_p T \frac{\Delta T}{T_{tr}}$$

$$\Delta C_p \Delta T \left(1 - \frac{T}{T_{tr}}\right) = -\frac{\Delta C_p (\Delta T)^2}{T_{tr}}$$

$$\therefore \Delta\mu = -\left[\frac{\Delta h^\circ + \Delta C_p \Delta T}{T_{tr}}\right] \Delta T + \Delta v_m^\circ \Delta p$$

Order of a Phase Transition

$\alpha \rightleftarrows \beta$

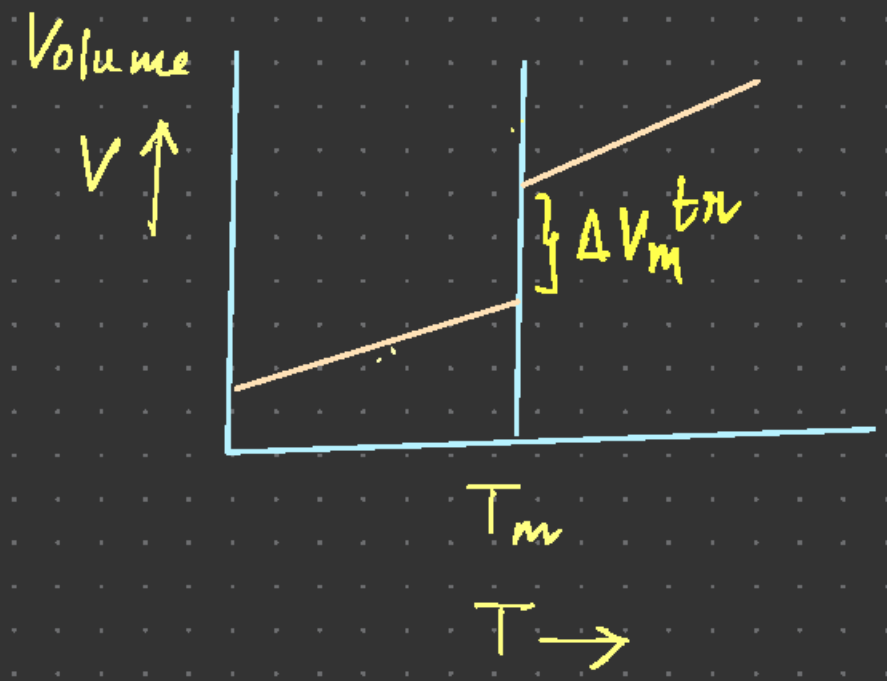
$$\left(\frac{\partial \mu^{\beta}}{\partial p}\right)_T - \left(\frac{\partial \mu^{\alpha}}{\partial p}\right)_T = V_m^{\beta} - V_m^{\alpha} = \Delta V_m^{tr}$$

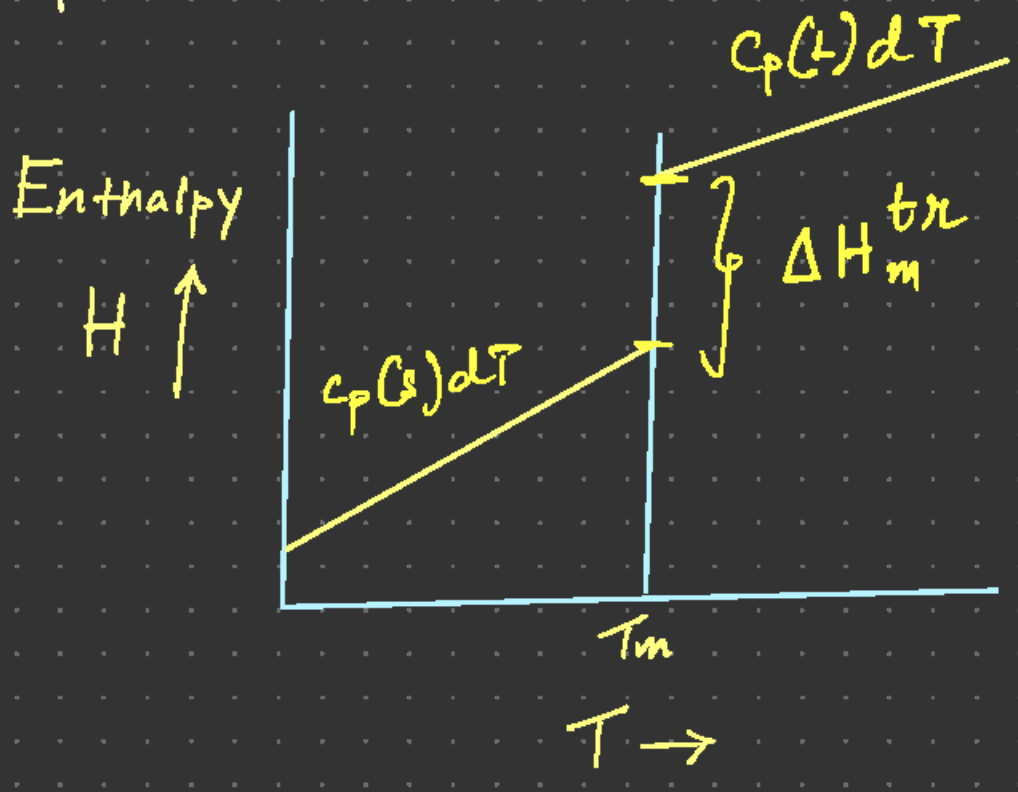
$$\left(\frac{\partial \mu^{\beta}}{\partial T}\right)_p - \left(\frac{\partial \mu^{\alpha}}{\partial T}\right)_p = -S_m^{\beta} + S_m^{\alpha} = \Delta S_m^{tr} = \frac{\Delta H_m^{tr}}{T_{tr}}$$

$\left.\begin{array}{l} \Delta V_m^{tr} \neq 0 \\ \Delta H_m^{tr} \neq 0 \end{array}\right\}$ melting, vaporization, solidification

First Order Transition

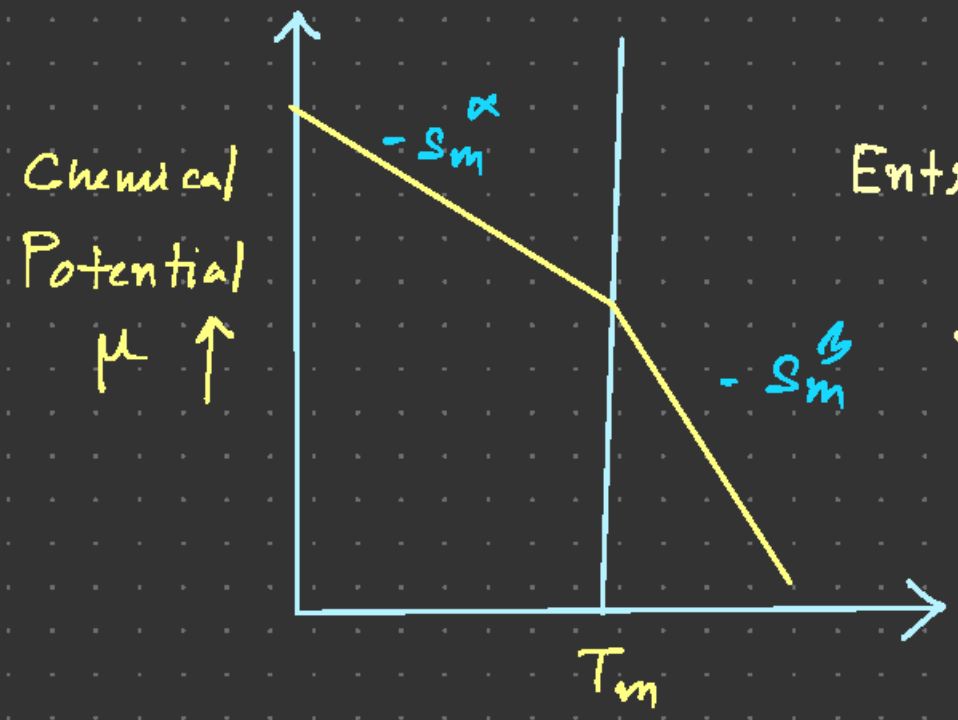
First derivative of chemical potential μ with respect to temperature is discontinuous

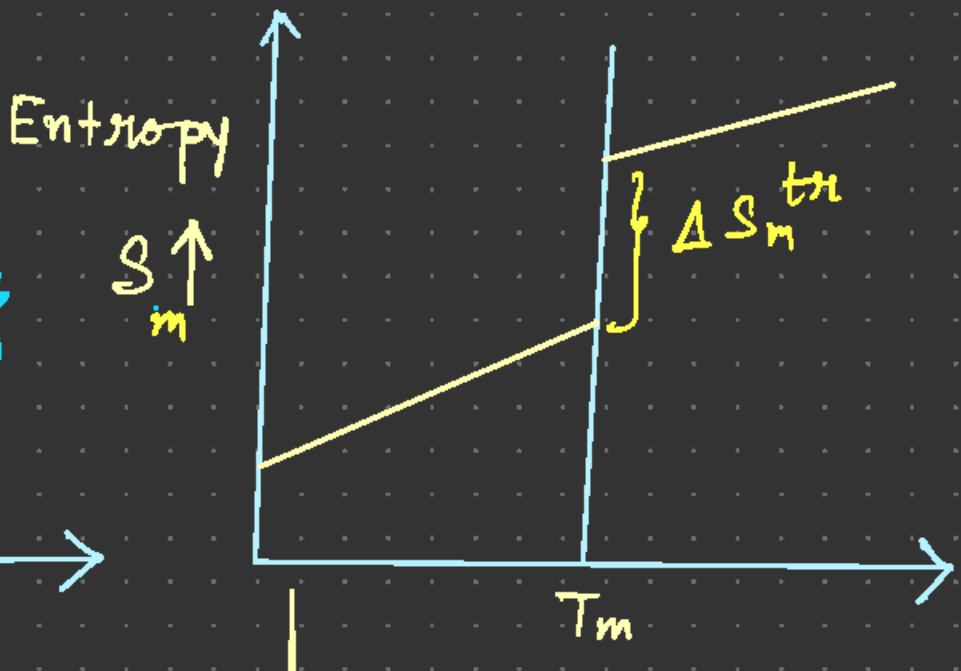


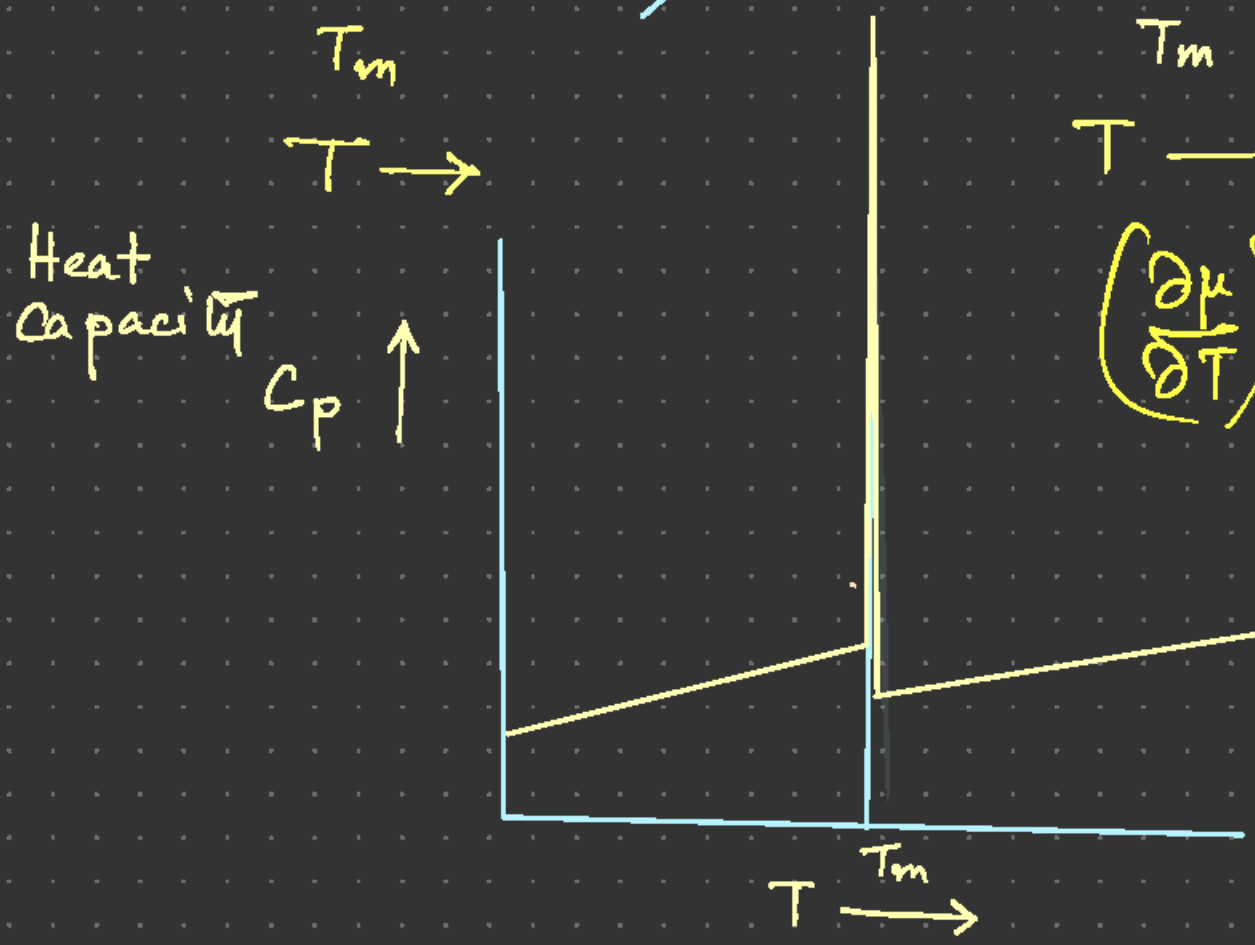


T_m – melting point/freezing point

Example – melting, solidification, vaporization





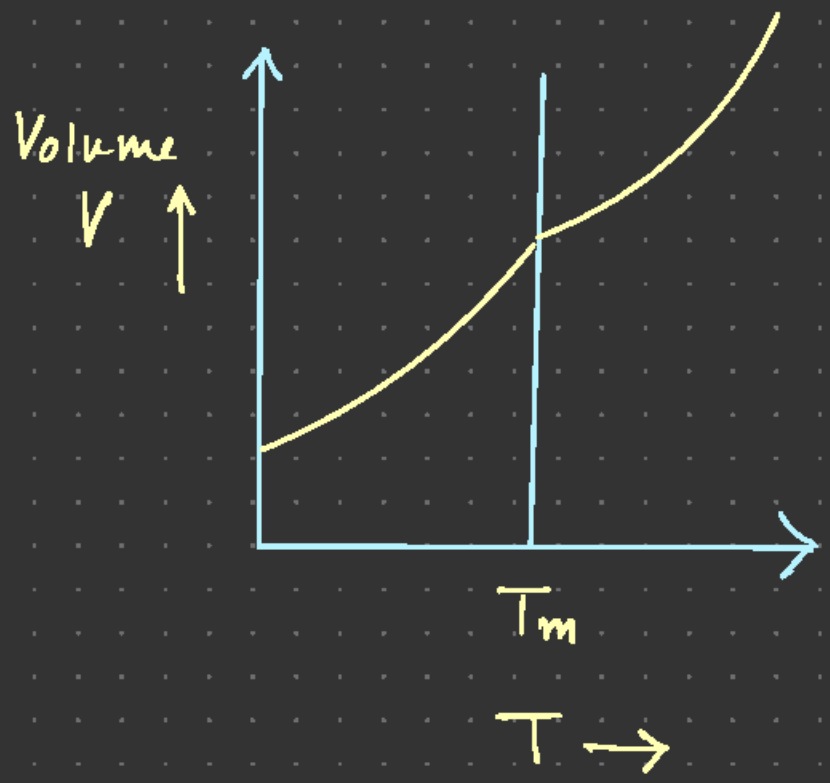


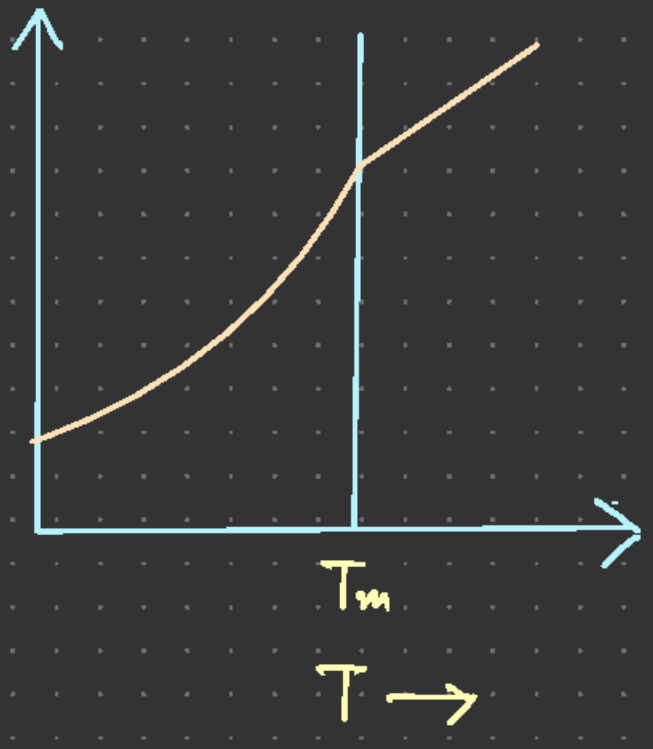
$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

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

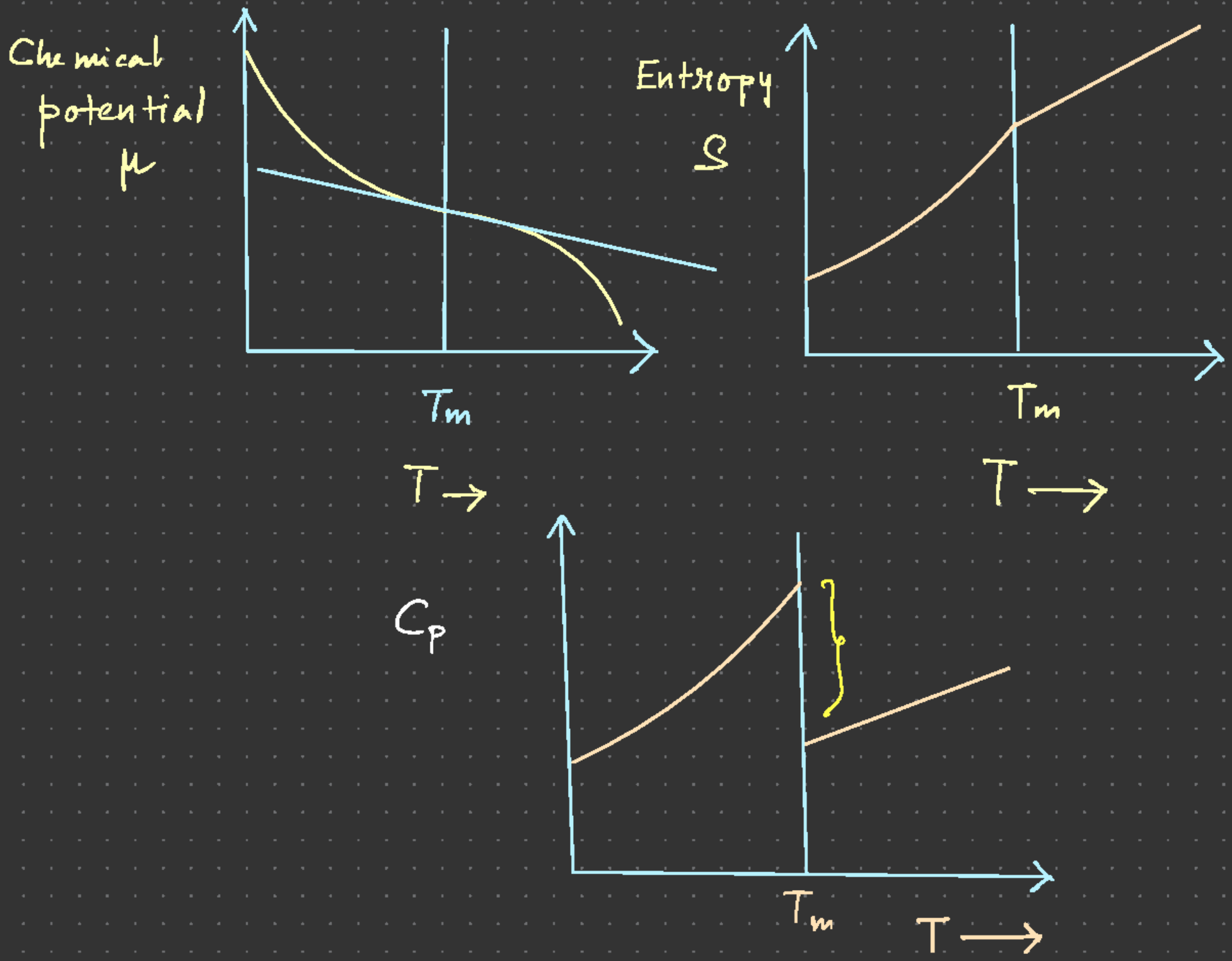
$$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_p = -\frac{C_p}{T}$$

SECOND ORDER PHASE TRANSITION





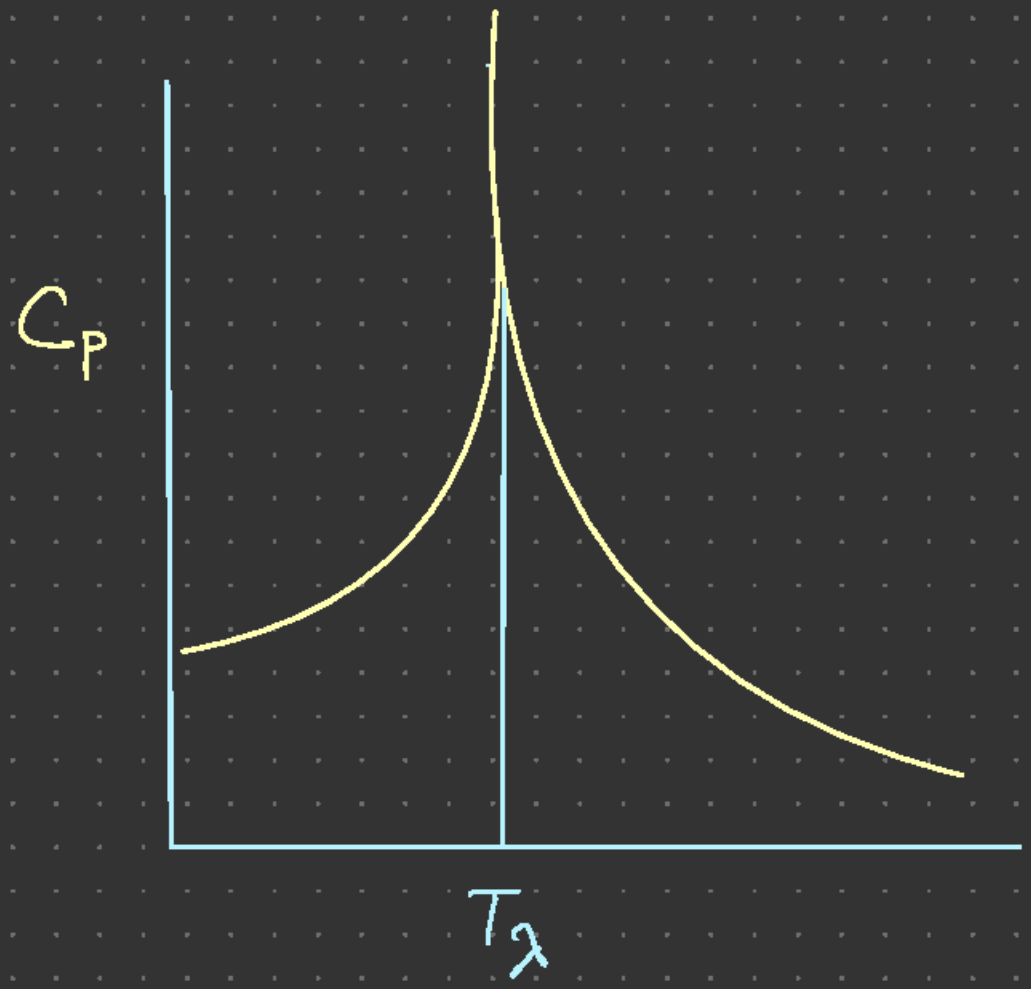
Conducting - superconducting transition


Chemical potential
μ
Tm
T →
Entropy
S
Tm
T →
Cp
Tm
T →

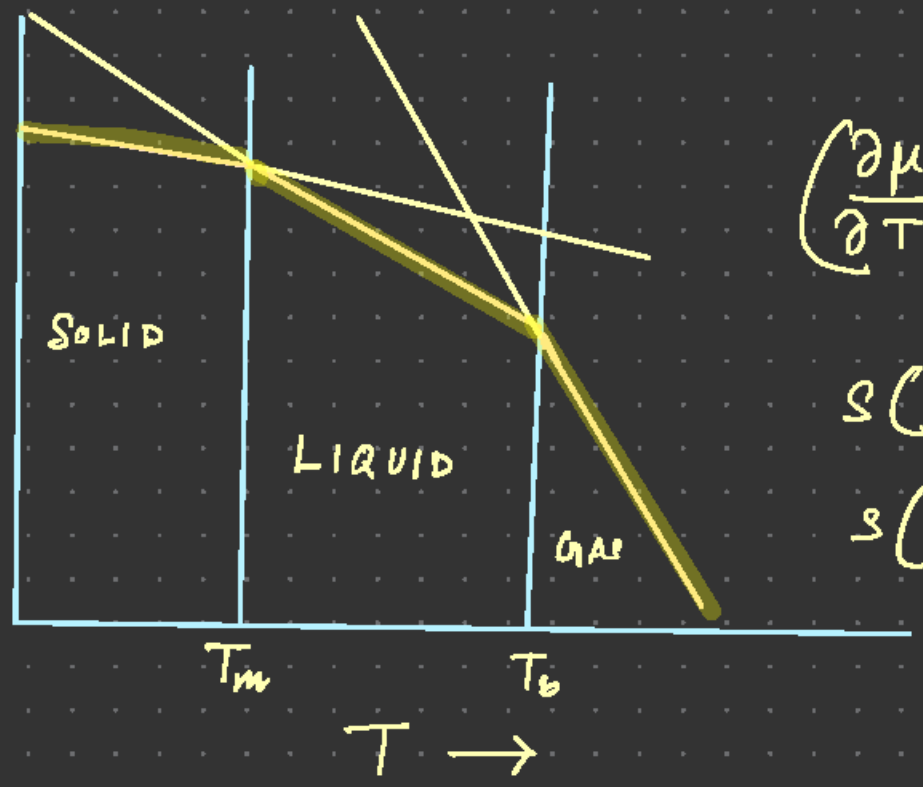
λ-transition

Example

Cubic – tetragonal transition



Chemical potential μ



$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S \text{ or } -S_m$$

$S(gas) > S(liquid)$

$S(liquid) > S(solid)$

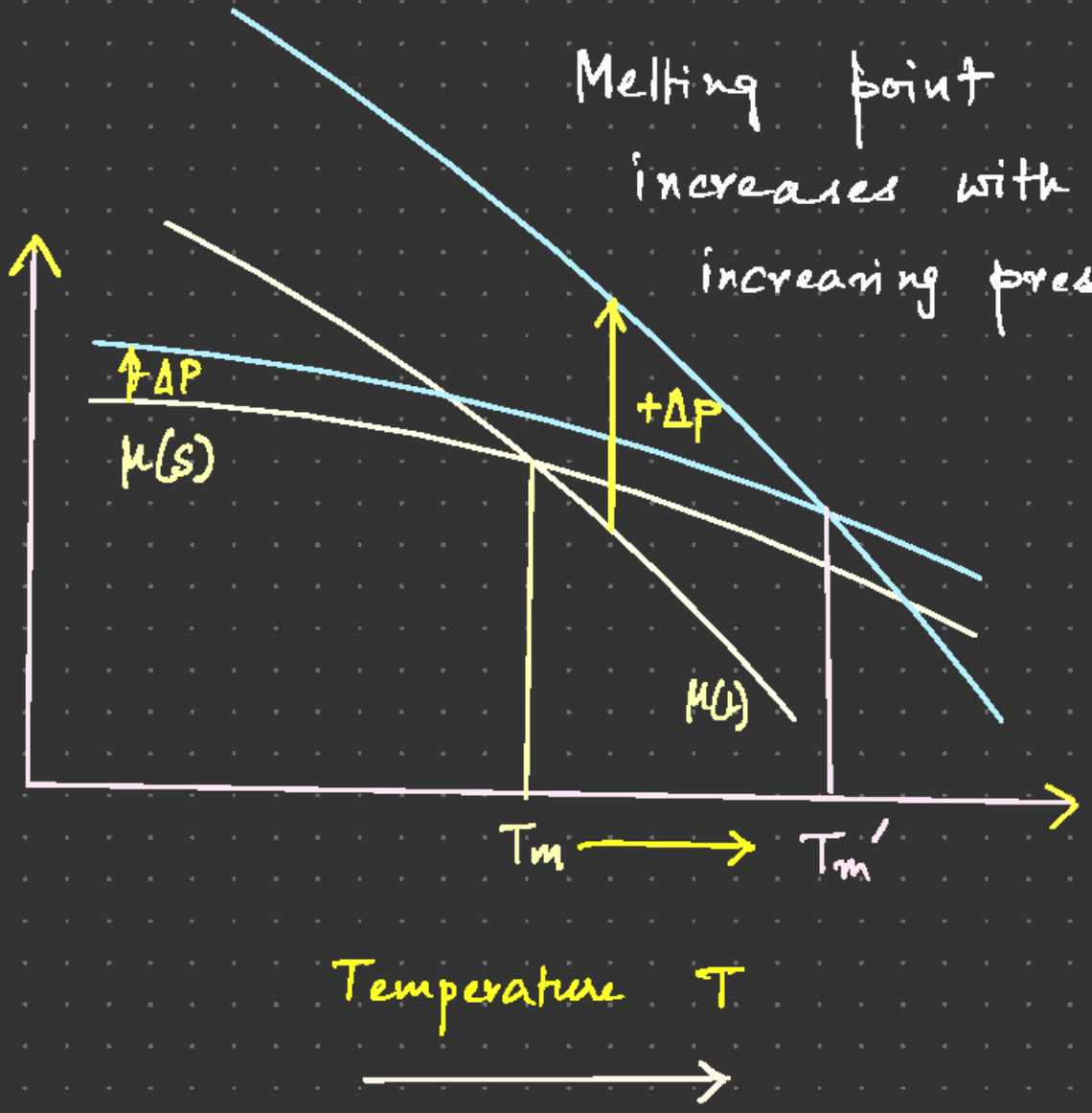
S or S_m - entropy per mole

Melting as a function of applid pressure

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m$$

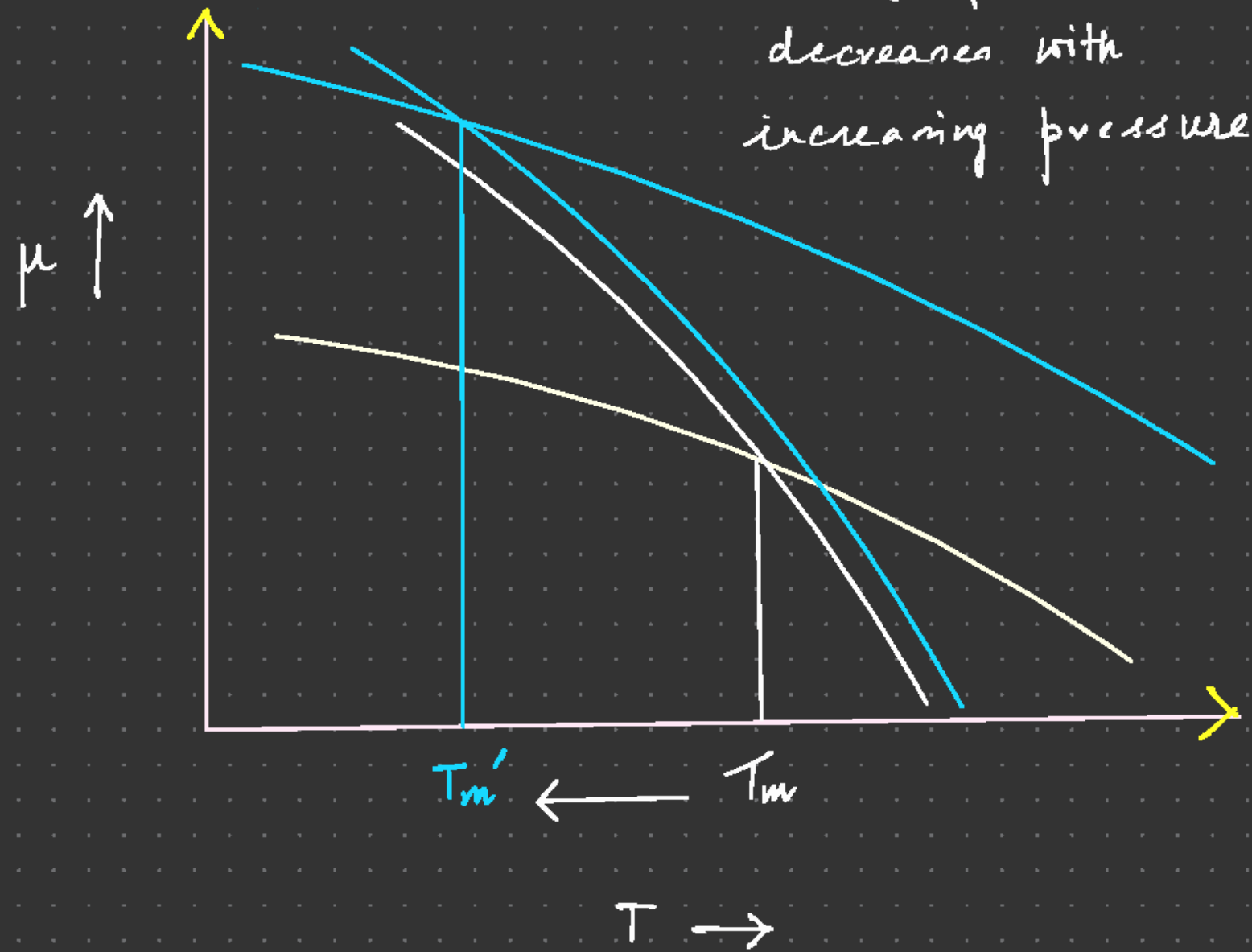
$V_m > 0$ $\quad \mu \uparrow$

$V_m(l) > V_m(s)$



$V_m(s) > V_m(l)$

Melting point decreases with increasing pressure



ρ (ice) = 0.917 g/cm^3 Temperature = 0°C

ρ (water) = 0.999 g/cm^3 pressure: 1 bar → 2 bar

$\Delta p = 2 - 1$

$= 1$ bar

$= 10^5$ Pa

$M = 18.02$ g/mol

$= 18.02 \times 10^{-3}$ kg/mol

$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$

$V_m = \frac{M}{\rho}$

or, $\Delta \mu = V_m \Delta p$

$$\Delta \mu \text{ (ice)} = \frac{18.02 \times 10^{-3} \times 1 \times 10^5}{917}$$

$= 1.97$ J/mol

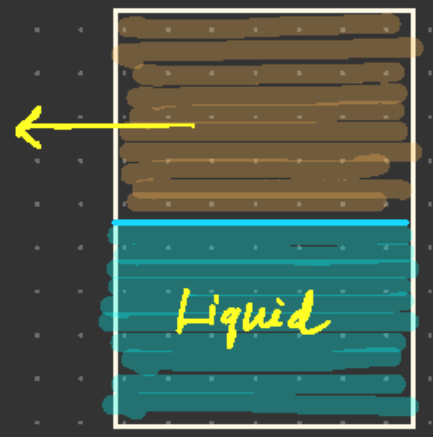
$$\Delta \mu \text{ (water)} = \frac{18.02 \times 10^{-3} \times 1 \times 10^5}{999}$$

$= 1.8$ J/mol

Applied pressure on vapour pressure of a liquid

Assumption

- Dissolution of pressurizing gas in liquid is ignored
- Gas Solvation or attraction of liquid molecules by gas phase molecules in ignored



Vapour pressure in absence of pressurizing gas - p^i

Applied pressure ΔP

At liquid - vapor equilibrium

$$\mu(l) = \mu(g)$$

or, $$d\mu(l) = d\mu(g)$$

$$d\mu(l) = V_m(l)\, dP$$

$$d\mu(g) = V_m(g)\, dP$$

Assume the vapor to be an ideal gas

$$V_m(g) = \frac{RT}{P}$$

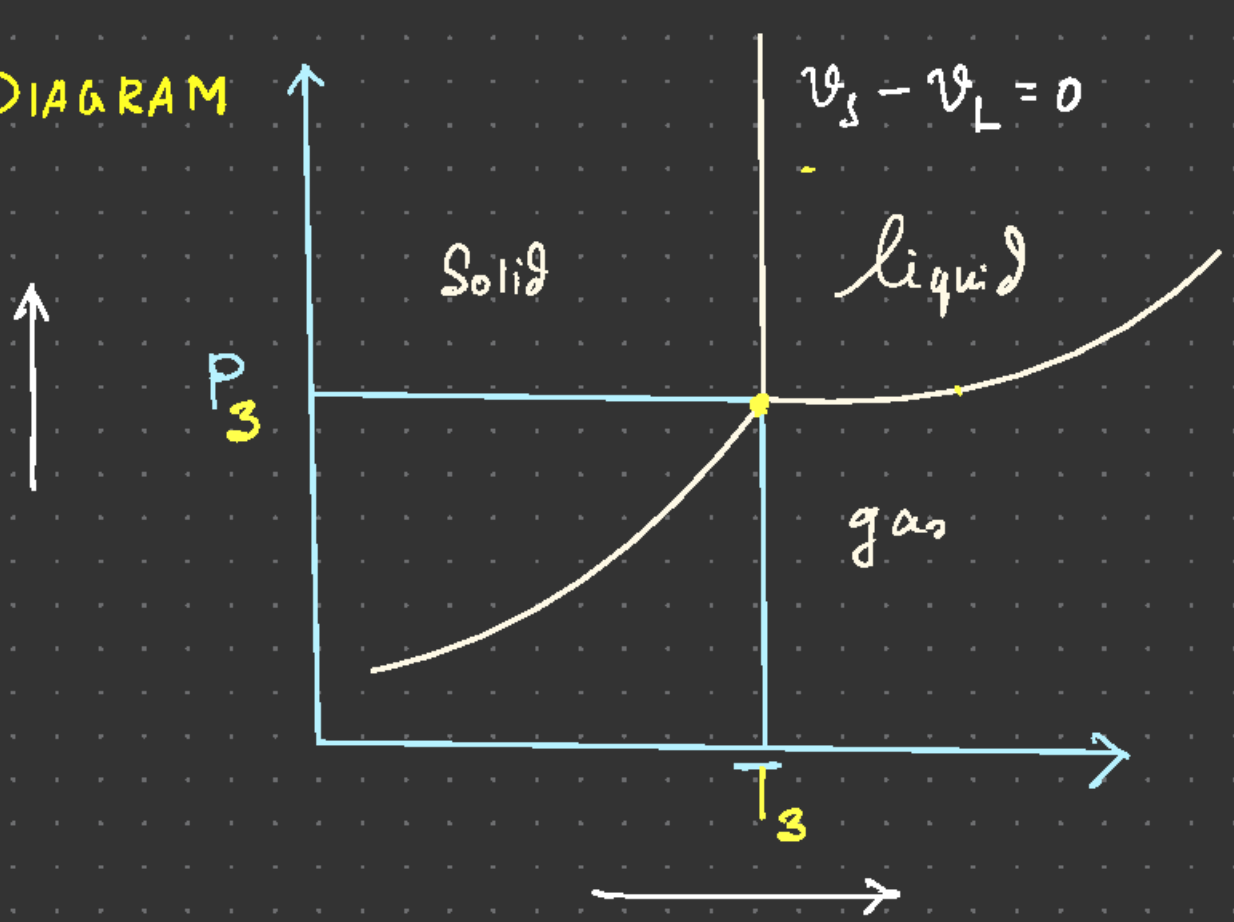
$$d\mu(g) = \frac{RT}{P}\,dP = d\mu(l) = V_m(l)\,dP$$

$$RT\int_{p^i}^{p}\frac{dP}{P} = V_m(l)\int_{p^i}^{p^i+\Delta P} dP$$

$$\ln\left(p/p^i\right) = \frac{V_m(l)}{RT}\,\Delta P$$

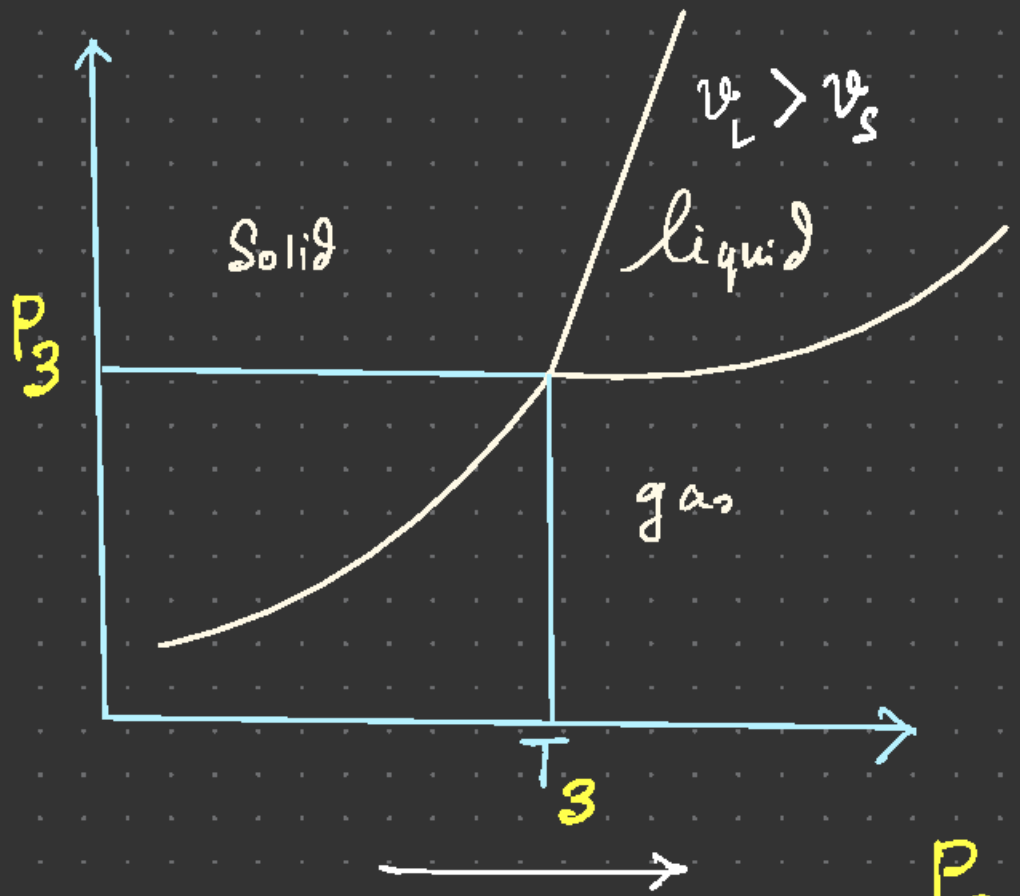
$$p = p^i\, e^{\frac{V_m(l)\Delta P}{RT}}$$

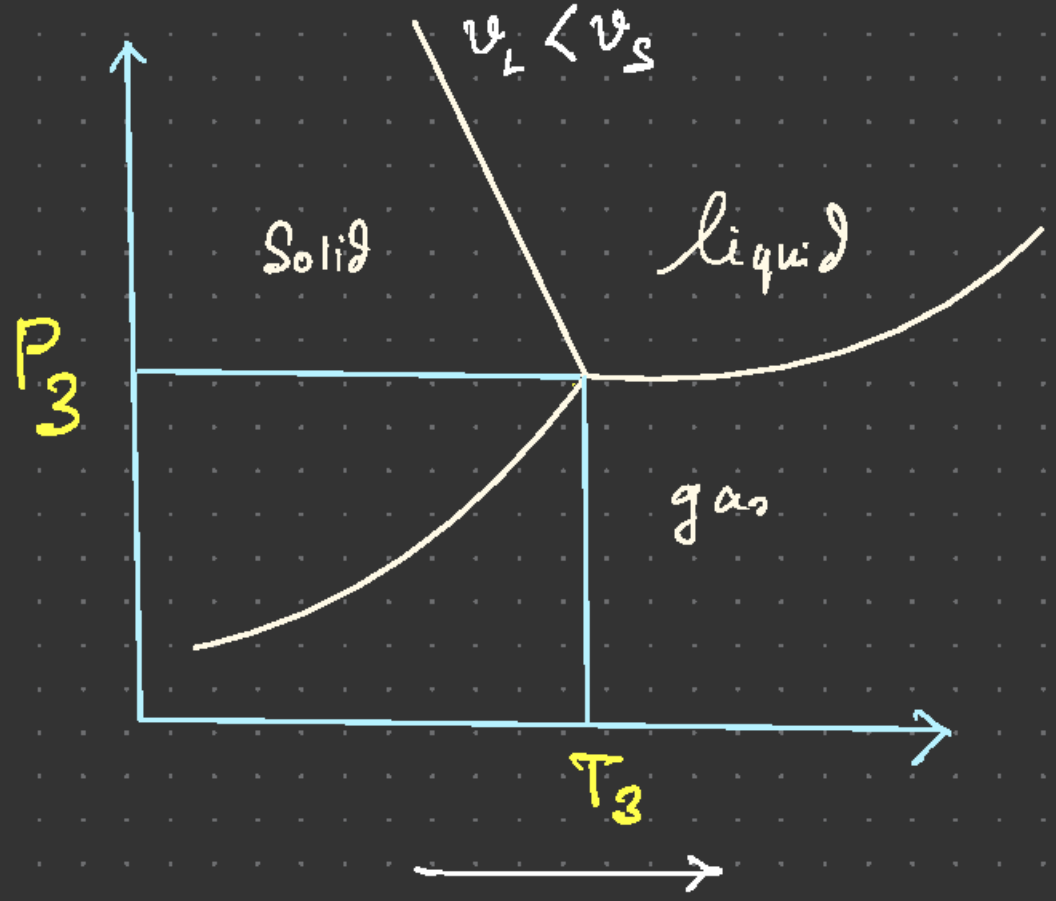
PHASE DIAGRAM

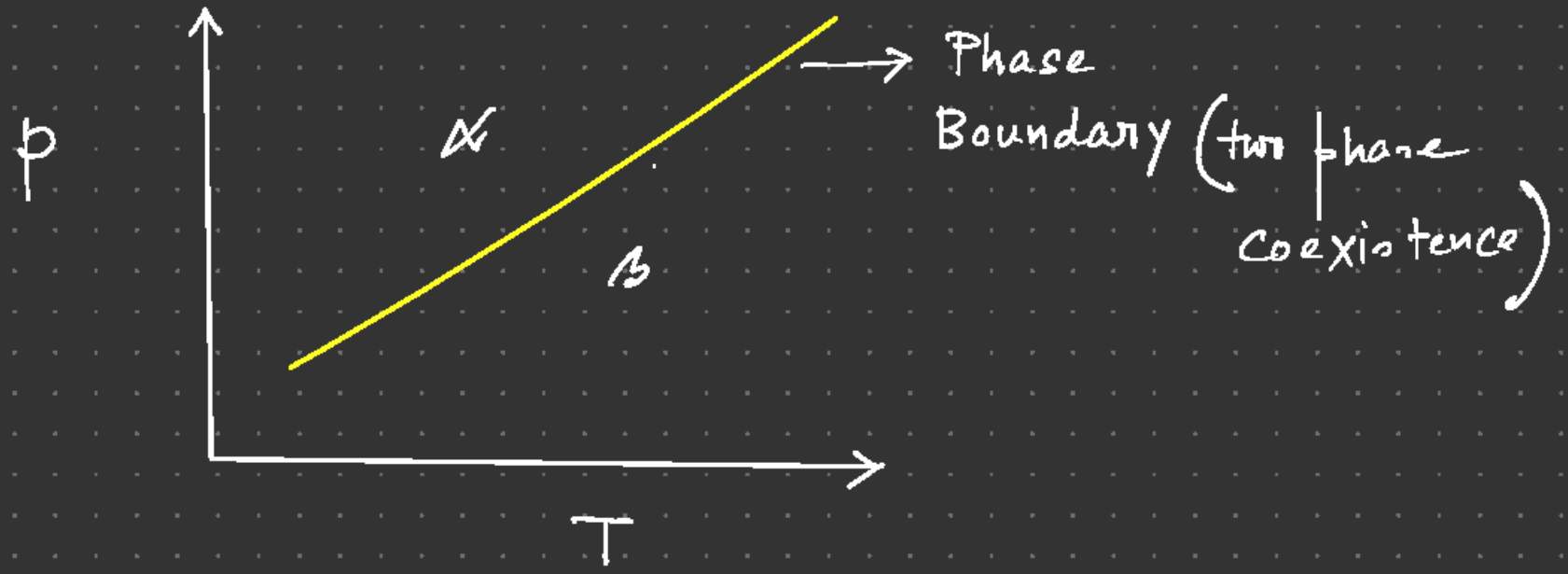


P–T diagram

T_3, P_3 — Triple point


$v_L > v_s$
Solid
liquid
P_3
gas
T_3


$v_L < v_s$
Solid
liquid
P_3
gas
T_3



At the phase boundary

$$\mu^{\alpha}(p,T) = \mu^{\beta}(p,T)$$

GIBBS PHASE RULE

No. of Components = 1

$$\left.\begin{aligned} x - y + 2z &= 7 \\ x + y + z &= 3 \\ x - 3y + 5z &= 4 \end{aligned}\right\}$$

3 eqn, 3 unknowns or variables x, y, z

Unique Solution

DF = 0 $\quad f = 3 - 3 = 0$

Degrees of freedom (f) = f = No. of variables (m) − No of equations (n)

$= m - n$

$$\left.\begin{aligned} x - y + 2z &= 7 \\ x + y - z &= 2 \end{aligned}\right\} \quad f = m - n$$

$= 3 - 2 = 1$

Infinite Solutions

$x+y=3$

$3x+2y=4$

$x-y=-1$

$x+7y=11$

No solution

$f = m - n$

$= 2 - 4$

$= -2$

Multicomponent, multiphase system with C components and P phases

1 component, two phases

Equations

$$T^{\alpha} = T^{\beta}$$
$$P^{\alpha} = P^{\beta}$$
$$\mu^{\alpha} = \mu^{\beta}$$

Variables

T^{α}, T^{β}
P^{α}, P^{β}

$$f = 4 - 3 = 1$$

2 components, two phases

Equations	Variables
$\mu_1^\alpha = \mu_1^\beta$	x_2^α, x_2^β
$\mu_2^\alpha = \mu_2^\beta$	T^α, T^β
$p^\alpha = p^\beta$	p^α, p^β
$T^\alpha = T^\beta$	

$f = 6 - 4 = 2$

$x_1^\alpha + x_2^\alpha = 1$

$x_1^\beta + x_2^\beta = 1$

$x_2^{\alpha,e}(\alpha/\beta)$

$x_2^{\beta,e}(\beta/\alpha)$

1 component, three phases

Equations	Variables
$\mu^\alpha = \mu^\beta = \mu^\gamma$	$p^\alpha, p^\beta, p^\gamma$
$p^\alpha = p^\beta = p^\gamma$	$T^\alpha, T^\beta, T^\gamma$
$T^\alpha = T^\beta = T^\gamma$	

$f = 6 - 6 = 0$

$$2 \begin{cases} T^\alpha = T^\beta = T^\gamma = \dots = T^p \xrightarrow{\text{Each row}} p-1 \text{ equations} \\ P^\alpha = P^\beta = P^\gamma = \dots = P^p \end{cases}$$

$$+ \quad c \text{ Components} \begin{cases} \mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots = \mu_1^p \\ \mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \dots = \mu_2^p \\ \vdots \\ \mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \dots = \mu_c^p \end{cases}$$

Number of equations

$$n = (p-1)(c+2)$$

p phases

c Components

$$x_1^\alpha + x_2^\alpha + \dots + x_c^\alpha = 1$$

Variables

$$T^\alpha, T^\beta, \dots, T^p$$

$$P^\alpha, P^\beta, \dots, P^p$$

$$x_2^\alpha, x_3^\alpha, \dots, x_c^\alpha$$

$$x_2^\beta, x_3^\beta, \dots, x_c^\beta$$

Phase α : $T^{\alpha}, P^{\alpha}, x_2^{\alpha}, x_3^{\alpha}, \ldots, x_C^{\alpha}$

Phase β : $T^{\beta}, P^{\beta}, x_2^{\beta}, x_3^{\beta}, \ldots, x_C^{\beta}$

$\vdots$

Phase p : $T^{p}, P^{p}, x_2^{p}, x_3^{p}, \ldots, x_C^{p}$

For each phase, no. of Variables

$= 2 + C - 1 = C + 1$

Variables $m = p(C+1)$

∴ Degrees of freedom

$f = 1 - 1 + 2$

$f = 1 - 2 + 2$

$= 1$

$f = 1 - 3 + 2$

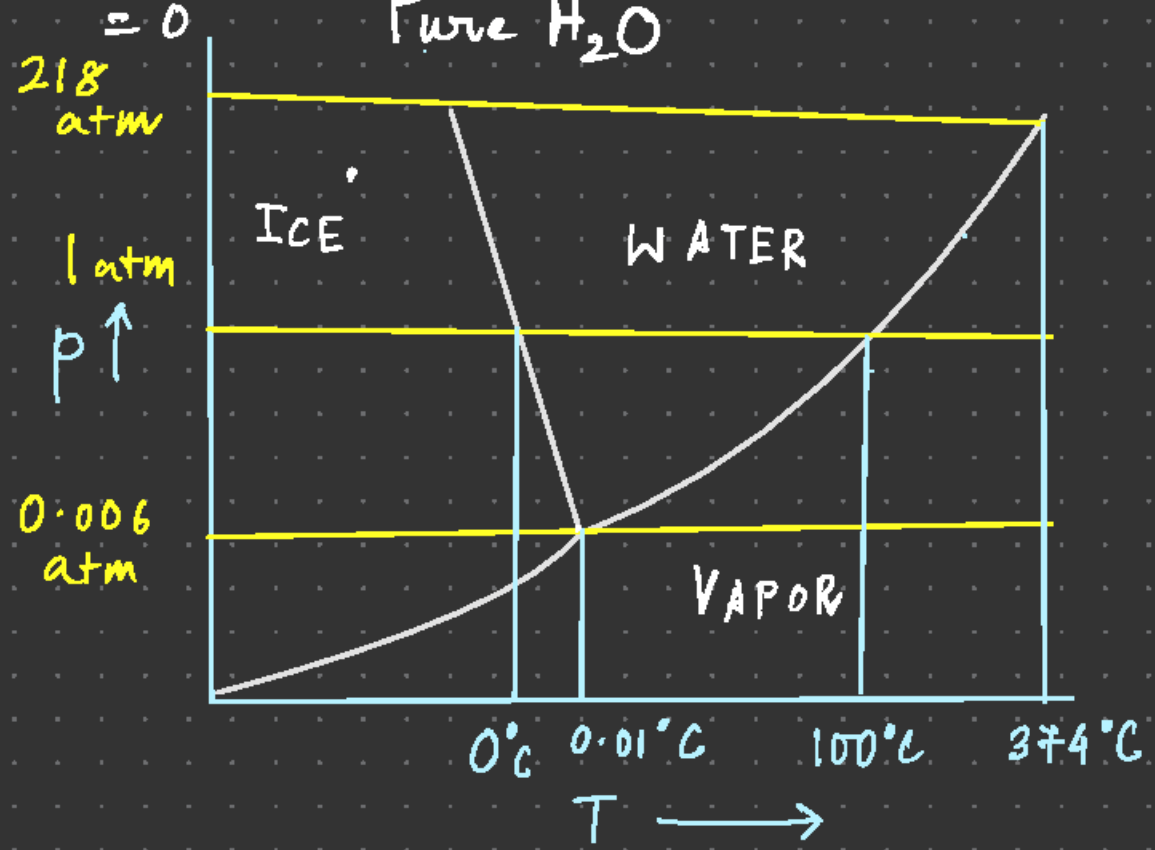
$= 0$

$f = m - n$

$= p(c+1) - (p-1)(c+2)$

$= pc + p - pc - 2p + c + 2$

$= c - p + 2$



Single phase region — Area

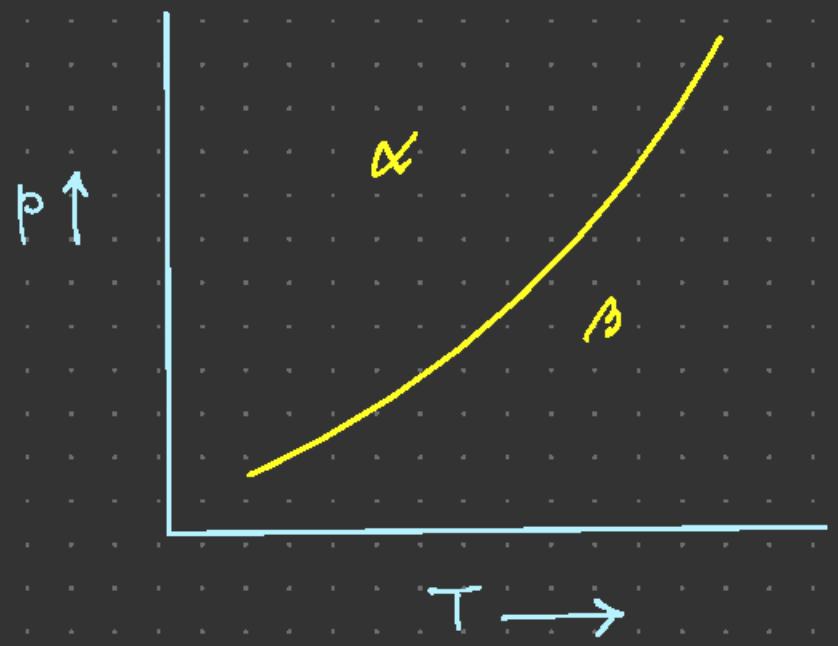
Phase boundary — Line

Triple point — Point

What is the slope of a phase boundary?

$$G^\alpha = G^\beta$$

$$\mu^\alpha(p,T) = \mu^\beta(p,T)$$



$$d\mu^\alpha = -s^\alpha dT^\alpha + V_m^\alpha dp^\alpha$$

$$d\mu^\beta = -s^\beta dT^\beta + V_m^\beta dp^\beta$$

$$d\mu^\alpha = d\mu^\beta$$

$$-s^\alpha dT^\alpha + V_m^\alpha dp^\alpha = -s^\beta dT^\beta + V_m^\beta dp^\beta$$

$$p^\alpha = p^\beta = p$$

$$T^\alpha = T^\beta = T$$

$$\left(V_m^\beta - V_m^\alpha\right) dp = \left(s^\beta - s^\alpha\right) dT$$

$$\left(V_m^{\beta} - V_m^{\alpha}\right) dp = \left(S^{\beta} - S^{\alpha}\right) dT$$

$$\Delta V_m^{\alpha \to \beta} dp = \Delta S^{\alpha \to \beta} \, dT$$

$$\frac{dp}{dT} = \frac{\Delta S^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}}$$

Clausius Clapeyron Equation

Solid–Liquid boundary

$T_m \rightarrow$ Melting or freezing point

$$\alpha\,(\text{SOLID}) \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftarrows}} \beta\,(\text{LIQUID})$$

$$\mu^{\alpha} = \mu^{\beta} \quad (G^{\alpha} = G^{\beta})$$

$$H^{\alpha} - TS^{\alpha} = H^{\beta} - TS^{\beta}$$

$$\text{or,} \quad H^{\beta} - H^{\alpha} = T(S^{\beta} - S^{\alpha})$$

$$\text{or,} \quad \Delta H^{\alpha \rightarrow \beta} = T \Delta S^{\alpha \rightarrow \beta}$$

$$T = T_{tr} = T_m$$

Clausius Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta S^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}} = \frac{\Delta H^{\alpha \to \beta}}{T \; \Delta V_m^{\alpha \to \beta}}$$

Let T_m° be melting temperature at pressure p°

T_m " " " " " p

If $\Delta H^{\alpha \to \beta}$ and $\Delta V_m^{\alpha \to \beta}$ do not vary with T,

$$\int_{p^\circ}^{p} dp = \frac{\Delta H^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}} \int_{T_m^\circ}^{T_m} \frac{dT}{T}$$

$$p = p^{\circ} + \frac{\Delta H^{\alpha \to \beta}}{\Delta V_m^{\alpha \to \beta}} \ln\left(\frac{T_m}{T_m^{\circ}}\right)$$

If $T_m - T_m^{\circ}$ is small,

$$\ln\left(T_m / T_m^{\circ}\right) = \ln\left(1 + \frac{T_m - T_m^{\circ}}{T_m^{\circ}}\right) \approx \frac{T_m - T_m^{\circ}}{T_m^{\circ}}$$

$$\approx \frac{\Delta T_m}{T_m^{\circ}}$$

$$p = p^{\circ} + \frac{\Delta H^{\alpha \to \beta}}{T_m^{\circ} \Delta V_m^{\alpha \to \beta}} \Delta T_m$$

Liquid - Vapor boundary

$$\alpha\,(\text{LIQUID}) \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \beta\,(\text{Vapor})$$

$$V_m^{\beta}(\text{gas}) \gg V_m^{\alpha}(\text{liquid})$$

$$\therefore \Delta V_m^{vap} = V_m^{\beta}$$

$$\frac{dP}{dT} = \frac{\Delta H^{vap}}{T\,\Delta V_m^{vap}}$$

Let the vapor phase β be an ideal gas

$$V_m^{\beta} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H^{vap}}{T\,(RT/P)}$$

$$\frac{dp}{p} = \frac{\Delta H^{vap}}{RT^2} dT$$

$$d \ln p = \frac{\Delta H^{vap}}{R} \frac{dT}{T^2}$$

$T = T^\circ \qquad p = p^\circ$ (vapor pressure)

$T = T \qquad p = p$

$$\int_{p^\circ}^{p} d \ln p = \frac{\Delta H^{vap}}{R} \int_{T^\circ}^{T} \frac{dT}{T^2}$$

$$\ln\left(\frac{p}{p^\circ}\right) = -\frac{\Delta H^{vap}}{R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right)$$

$$p = p_0 e^{-\chi} = p_0 \exp(-\chi)$$

$$\frac{p}{p_0} = \exp\left[-\frac{\Delta H^{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

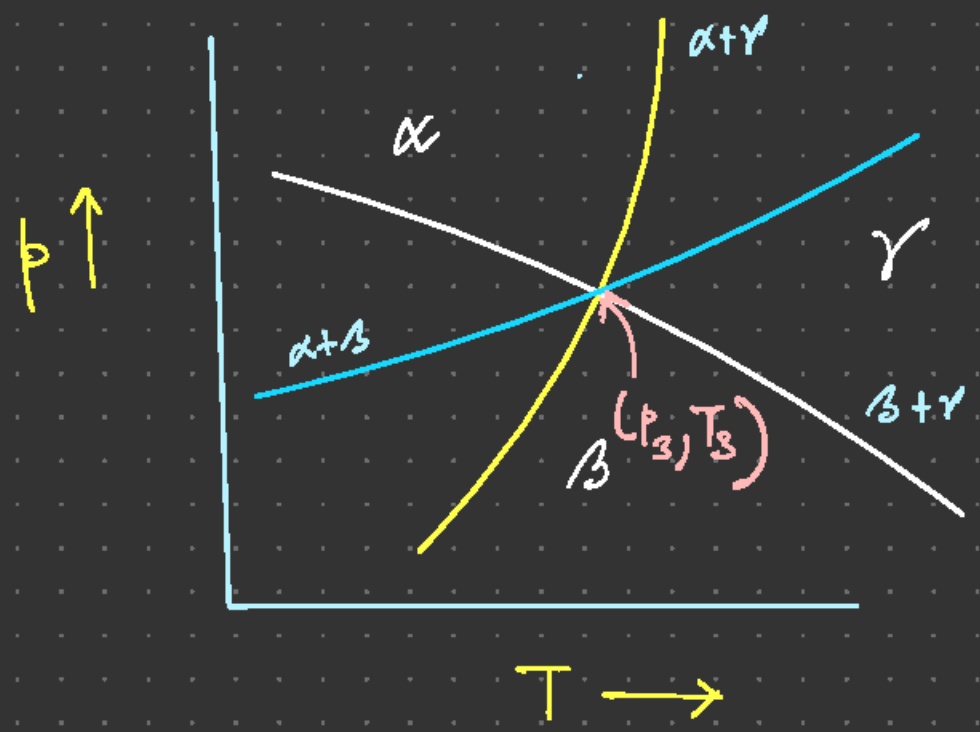
$$\therefore \quad \chi = \frac{\Delta H^{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)$$

Solid - Vapor boundary

$$\alpha(\text{solid}) \underset{\text{deposition}}{\overset{\text{sublimation}}{\rightleftharpoons}} \beta(\text{vapor})$$

$$\ln\left(\frac{P_s}{P_s^0}\right) = -\frac{\Delta H^{subl}}{R_v}\left(\frac{1}{T_s} - \frac{1}{T_s^0}\right)$$

Triple Point



α (Solid)
β (Liquid)
γ (gas)

$$\Delta V^{\alpha \to \gamma} = V^{\gamma} - V^{\alpha}$$

$$= V^{\gamma} - V^{\beta} + V^{\beta} - V^{\alpha}$$

$$= \Delta V^{\beta \to \gamma} + \Delta V^{\alpha \to \beta}$$

Solid — vapor equilibrium

$$p^s = A^s \exp\left(-\Delta H^{\alpha\to\gamma}/RT\right)$$

Liquid - vapor equilibrium

$$p^v = A^v \exp\left(-\Delta H^{\beta\to\gamma}/RT\right)$$

Triple point (p_3, T_3)

$$p_3 = A^s \exp\left(-\Delta H^{\alpha\to\gamma}/RT_3\right)$$

$$p_3 = A^v \exp\left(-\Delta H^{\beta\to\gamma}/RT_3\right)$$

$$\therefore \quad A^{s} \exp\left(-\Delta H^{\alpha \to \gamma} / RT_3\right)$$

$$= A^{v} \exp\left(-\Delta H^{\beta \to \gamma} / RT_3\right)$$

$$\ln A^{s} - \frac{\Delta H^{\alpha \to \gamma}}{RT_3} = \ln A^{v} - \frac{\Delta H^{\beta \to \gamma}}{RT_3}$$

$$RT_3 \ln\left(\frac{A^{s}}{A^{v}}\right) = \Delta H^{\alpha \to \gamma} - \Delta H^{\beta \to \gamma}$$

$$T_3 = \frac{\Delta H^{\alpha \to \gamma} - \Delta H^{\beta \to \gamma}}{R \ln\left(A^{s}/A^{v}\right)}$$

$$\Delta H^{d} = \Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}$$

$$\ln p_3 = \ln A^{s} - \frac{\Delta H^{\alpha\to\gamma}}{RT_3}$$

$$= \ln A^{s} - \frac{\Delta H^{\alpha\to\gamma} \ln\left(A_s/A_v\right)}{\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}}$$

$$\Delta H_d \ln p_3 = \Delta H^{\alpha\to\gamma} \ln A^{s} - \Delta H^{\beta\to\gamma} \ln A^{s}$$

$$- \Delta H^{\alpha\to\gamma} \ln A^{s} + \Delta H^{\alpha\to\gamma} \ln A_v$$

$$\Delta H_d \ln p_3 = \Delta H^{\alpha\to\gamma} \ln A_v - \Delta H^{\beta\to\gamma} \ln A_v$$

$$- \Delta H^{\beta\to\gamma} \ln A_s + \Delta H^{\beta\to\gamma} \ln A_v$$

$$\Delta H_d \ln p_3 = -\Delta H^{\alpha\to\gamma} \ln A_s + \Delta H^{\alpha\to\gamma} \ln A_v$$

$$(-\Delta H^{\beta\to\gamma}) \qquad (\Delta H^{\alpha\to\gamma})$$

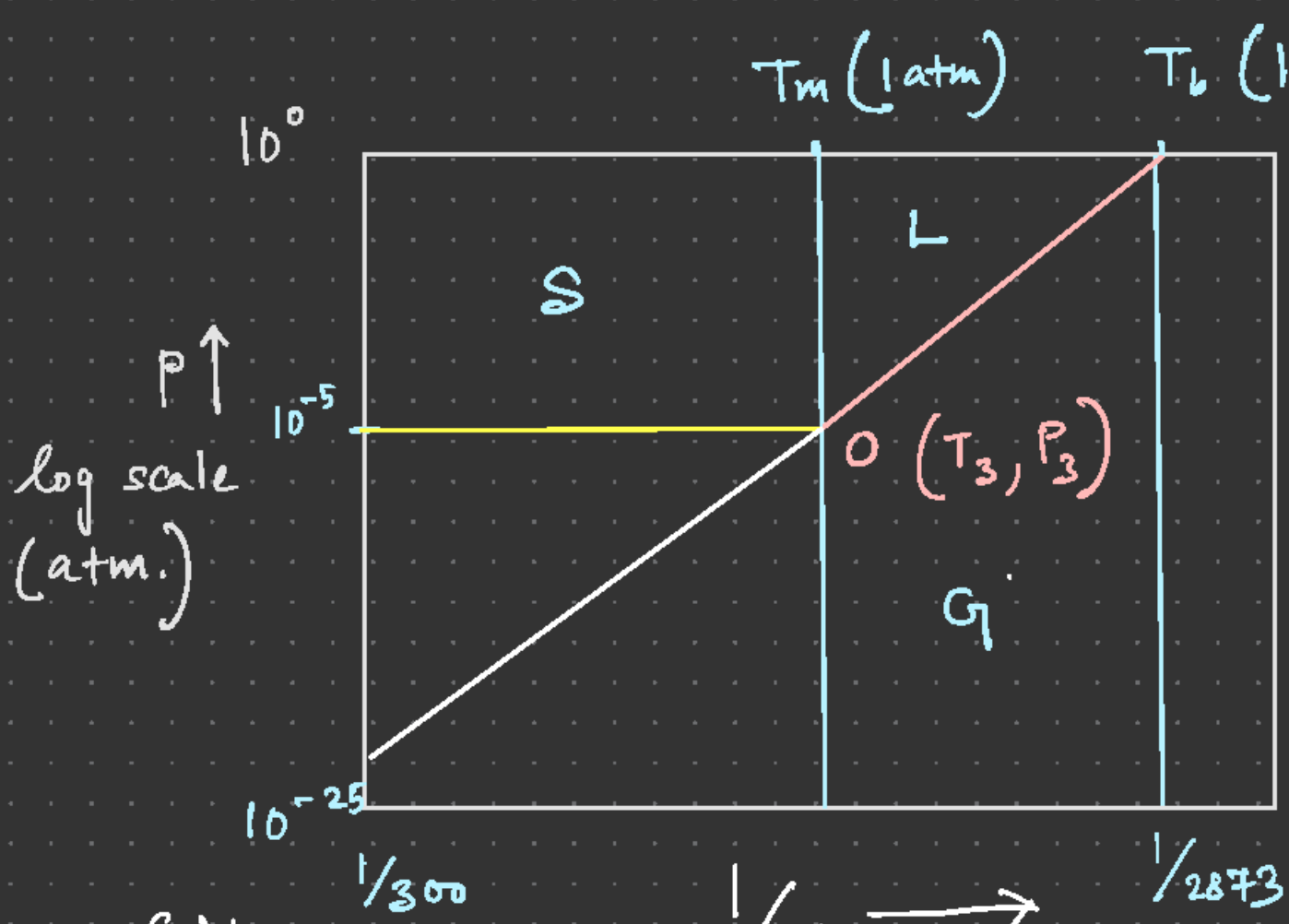
$$= \ln A_s + \ln A_v$$

$$\ln p_3^{\left(\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}\right)} = \ln\left(A_S^{-\Delta H^{\beta\to\gamma}} A_V^{\Delta H^{\alpha\to\gamma}}\right)$$

$$\left(p_3\right)^{\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}} = \left(A_S\right)^{-\Delta H^{\beta\to\gamma}} \left(A_V\right)^{\Delta H^{\alpha\to\gamma}}$$

$$p_3 = \left(A_S\right)^{\left(\frac{\Delta H^{\beta\to\gamma}}{\Delta H^{\beta\to\gamma} - \Delta H^{\alpha\to\gamma}}\right)} \left(A_V\right)^{\left(\frac{\Delta H^{\alpha\to\gamma}}{\Delta H^{\alpha\to\gamma} - \Delta H^{\beta\to\gamma}}\right)}$$

$$\Delta H^{\alpha \to \gamma} = \Delta H^{\alpha \to \beta} + \Delta H^{\beta \to \gamma}$$



$$\Delta H_{Si}^{S \to L} = 50.2 \text{ kJ/mol}$$

$$\Delta H_{Si}^{L \to V} = 386 \text{ kJ/mol}$$

($P = 1$ atm, $T = 2873$ K)

$$\therefore A^V = P^V e^{\Delta H_{Si}^{L \to V}/RT}$$

$$= 1.04 \times 10^7 \text{ atm}$$

$T_m = 1685$ K (1 atm)

$T_3 = 1685$ K

$$P_V = 1.04 \times 10^7 \, e^{-\frac{386000}{8.314T}}$$

$$\therefore \quad P_3 = 1.04 \times 10^7 \, e^{-386000/8.314 \times 1685}$$

$$= 1.13 \times 10^{-5} \text{ atm.}$$

$$\Delta H_{Si}^{S \to V} = \Delta H_{Si}^{S \to L} + \Delta H_{Si}^{L \to V}$$

$$= 50.2 + 386$$

$$= 436.2 \text{ kJ/mol}$$

$$A_S = P_3 \exp\left(\frac{436200}{8.314 \times 1685}\right) \approx 3.8 \times 10^8 \text{ atm}$$

$$P^S = 3.8 \times 10^8 \, e^{-436200/RT}$$