

$$(\Delta A)_{T,V,n} \geq 0, \quad (\delta A)_{T,V,n} = 0, \quad (\delta^2 A)_{T,V,n} \geq 0 \quad \left| \begin{array}{l} dE = TdS - pdV + \mu dn \\ dA = -SdT - pdV + \mu dn \end{array} \right.$$

$$\text{Suppose } \begin{cases} \delta V = 0 = \delta V^{(1)} + \delta V^{(2)} \\ \delta n^{(1)} = \delta n^{(2)} = 0 \end{cases}$$

$$(\delta^2 A)_{T,n} = \left(\frac{\partial^2 A}{\partial V^2} \right)^{(1)} (\delta V)^2 + \left(\frac{\partial^2 A}{\partial V^2} \right)^{(2)} (\delta V^{(2)})^2$$

$$= \left[\left(\frac{\partial^2 A}{\partial V^2} \right)^{(1)} + \left(\frac{\partial^2 A}{\partial V^2} \right)^{(2)} \right] (\delta V^{(1)})^2$$

$$= \left[\left(-\frac{\partial p}{\partial V} \right)_{T,n}^{(1)} + \left(-\frac{\partial p}{\partial V} \right)_{T,n}^{(2)} \right] [\delta V^{(1)}]^2$$

$$\Rightarrow -\left(\frac{\partial p}{\partial V} \right)_{T,n} \geq 0$$

(increase pressure →
< volume at const T)

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,n} = \text{isothermal compressibility} \quad K_T \geq 0$$

$$K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S,n} = \text{adiabatic compressibility} \quad K_S \geq 0$$

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V} \right)_{T,n} \left[\left(\frac{\partial V}{\partial T} \right)_{p,n} \right]^2$$

$$C_p - C_V = \frac{T}{VK_T} \left[\left(\frac{\partial V}{\partial T} \right)_{p,n} \right]^2$$

$$\Rightarrow C_p > C_V$$

If $(\delta^2 A)_{T,V,n} = 0$ subject to

$$\left\{ \begin{array}{l} \left(\frac{\partial p}{\partial v} \right)_T = 0 \\ \delta n^{(1)} = \delta n^{(2)} = 0 \\ -\delta V^{(1)} = \delta V^{(2)} \end{array} \right.$$

$$\begin{array}{l} \Rightarrow (\delta^3 A)_{T,V,n} \geq 0 \\ \Rightarrow \left(\frac{\partial^2 p}{\partial v^2} \right)_T = 0 \end{array} \left. \begin{array}{l} \text{several} \\ \text{steps} \end{array} \right| 0 \leq (\delta V^{(1)})^3 \left[\left(\frac{\partial^3 A}{\partial V^3} \right)_{T,n}^{(1)} - \left(\frac{\partial^3 A}{\partial V^3} \right)_{T,n}^2 \right]$$

Let Φ = Energy or a Legendre transform of E
 which is a function of X_1, \dots, X_r extensive variables
 I_{r+1}, \dots, I_n intensive variables

$$d\Phi = \sum_{i=1}^r I_i dX_i - \sum_{j=r+1}^n X_j dI_j$$

$$0 \leq \left(\frac{\partial I_i}{\partial X_i} \right)_{x_1, x_{i-1}, x_{i+1}, \dots, x_r, I_{r+1}, \dots, I_n}$$



stability criteria

$$-\left(\frac{\partial p}{\partial V} \right)_S, \left(\frac{\partial \mu_i}{\partial n_i} \right)_{T, V, n_j}, C_p$$

are all ≥ 0

Phase Equilibria

v phases in equilibrium

$$\mu_i^{(\alpha)} = \mu_i^{(\gamma)}, \quad \mu_i^{(\alpha)} = \text{mole fraction of } i \text{ in phase } \alpha$$

$$1 \leq \alpha < \gamma \leq v, \quad 1 \leq i \leq r \quad \left| \quad \text{i.e., for all phases and components} \right.$$

degrees of freedom =

$$f = \underbrace{2 + v(r-1)} - \underbrace{r(v-1)}$$

$$f = 2 + r - v$$

$r(v-1)$ equations that couple

$2 + v(r-1)$ intensive variables

T, p

Gibbs phase rule

- 1 phase, one species

$$f = 2 \rightarrow \text{e.g., } T, p$$

- 2 phases, one species

$$f = 1 \text{ (line)} \Rightarrow \text{e.g., } T, p \text{ not indep.}$$

- 3 phases, one species

$$f = 0 \text{ (point)}$$

- 1 phase, two species

$$f = 3, \text{ e.g., } T, p, x_1, x_2$$

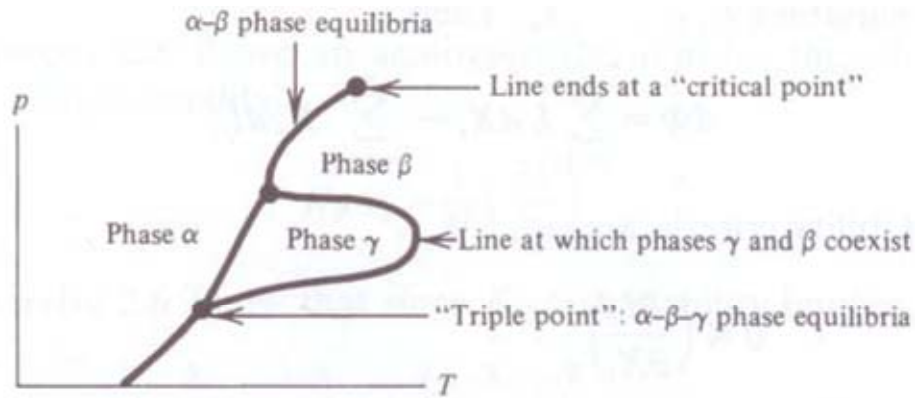
- impossible for > 3 phases for a one-component system

consider a one-component system with 3 possible phases

α, β, γ

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

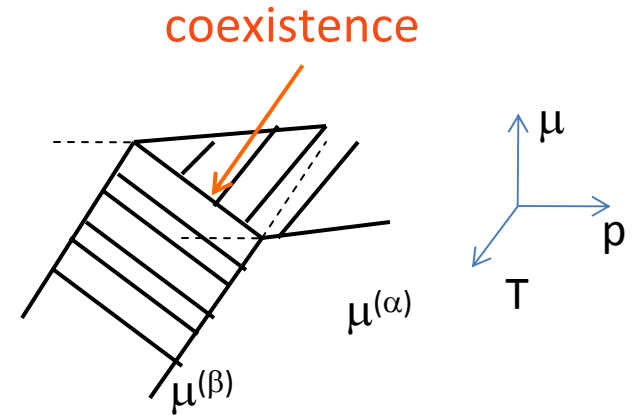
stable phase has lowest Gibbs free energy



$$\left(\frac{\partial \mu}{\partial p}\right)_T = v \quad \left(\frac{\partial \mu}{\partial T}\right)_p = -s \quad \text{for phase change}$$

if surfaces join smoothly, then
 v and s are continuous \Rightarrow 2nd (or higher)
 order phase transition

if v and s discontinuous \Rightarrow 1st order
 phase transition



for one-component system
 2nd - order transition can
 only happen at critical
 point

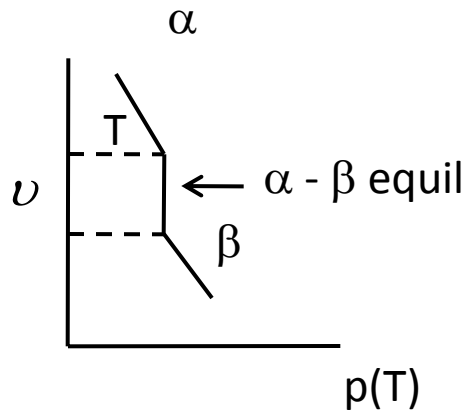
$p - T$ coexistence line obeys a diff. eq.

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

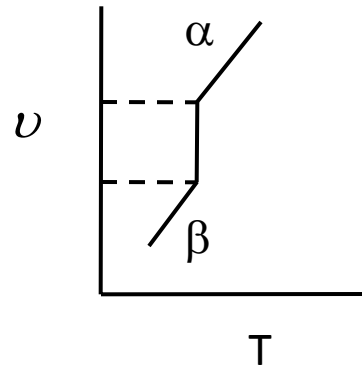
$$d\mu = -s dT + \nu dp$$

$$-s^{(\alpha)} dT + \nu^{(\alpha)} dp = -s^{(\beta)} dT + \nu^{(\beta)} dp \Rightarrow \boxed{\frac{dp}{dT} = \frac{\Delta s(T)}{\Delta \nu(T)}}$$

Clausius -Clapeyron Equation
(not applicable to 2nd-order
transitions)



isotherm



isobar

v, T not conjugate variables \Rightarrow need not be monotonic function of T

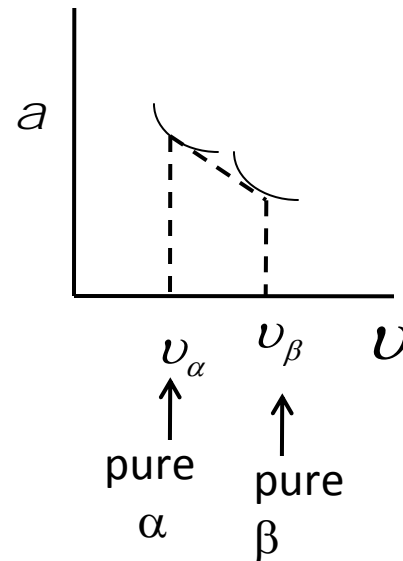
for 1st order phase transitions

$$dA = -s dT - p dV + \mu dn$$

$$a = A/n, \quad v = V/n$$

plot a vs v at const. T

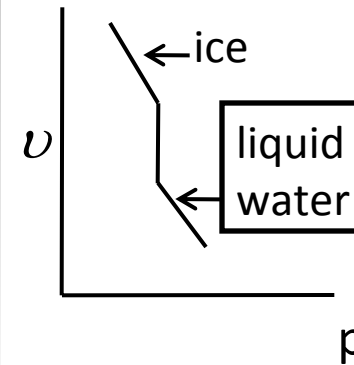
$$\left(\frac{\partial a}{\partial v} \right)_T = -p$$



$p = 1 \text{ atm}$

$T \approx 0^\circ \text{C}$

ice has larger density than water (less dense \rightarrow floats)



at equilibrium: $p^{(\alpha)}(T, v^{(\alpha)}) = p^{(\beta)}(T, v^{(\beta)})$

Which means the slope
of α at $v^{(\alpha)}$ = slope
of α at $v^{(\beta)}$

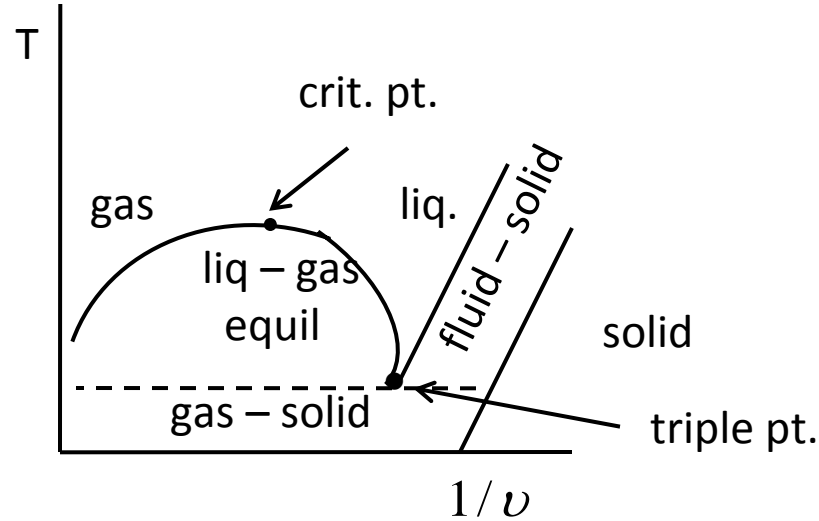
$$a(T, v^{(\alpha)}) - a(T, v^{(\beta)}) \\ = -p(T) [v^{(\alpha)} - v^{(\beta)}]$$

$$(a + pv)^{(\alpha)} = (a + pv)^{(\beta)} \quad \mu^{(\alpha)} = \mu^{(\beta)}$$

$$\frac{a - a^{(\alpha)}}{v - v^{(\alpha)}} = \frac{a^{(\beta)} - a}{v^{(\beta)} - v}$$

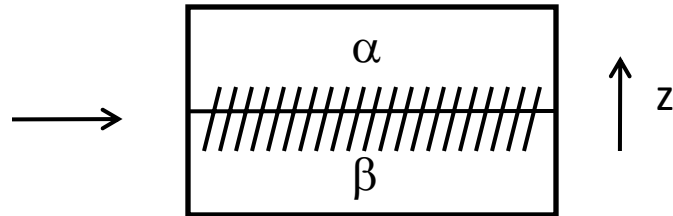
$$\frac{A}{n} = \frac{a^{(\beta)}(v - v^{(\alpha)})}{v^{(\beta)} - v^{(\alpha)}} + \frac{a^{(\alpha)}(v^{(\beta)} - v)}{v^{(\beta)} - v^{(\alpha)}}$$

Phase diagram for Argon



Plane Interfaces

dividing surface
(area σ)



$$E = E^{(\alpha)} + E^{(\beta)} + E^{(s)}$$

$E^{(s)}$ = energy of interface

$$\text{let } \gamma = \left(\frac{\partial E}{\partial \sigma} \right)_{S, v, n} = \geq 0$$

$$dE = TdS - pdV + \mu dn + \gamma d\sigma$$

← surface tension (intensive quantity)

$$dE = TdS - pdV + \mu dn + \gamma d\sigma$$

$$E \propto N$$

$$\gamma\sigma \propto N^{2/3}$$

So would not expect surface tension contribution to be important for bulk properties

$$n^{(\alpha)} = \int_{z_d}^{\infty} dz \rho_d(z)$$

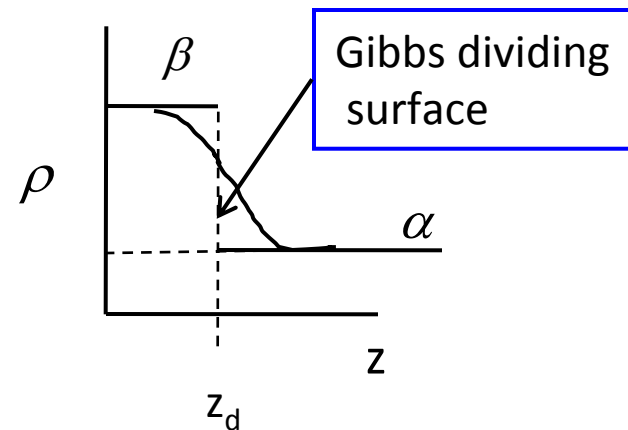
$$n^{(\beta)} = \int_{-\infty}^{z_d} dz \rho_d(z)$$

$$n^{(s)} = \int_{-\infty}^{\infty} dz [\rho - \rho_d] \quad \leftarrow \text{choose } z_d \text{ s.t.}$$

$$n^s(z_d) = 0$$

$$dE^{(s)} = TdS^{(s)} + \gamma d\sigma$$

$$\text{at } z_d \quad E^{(s)} = TS^{(s)} + \gamma\sigma \rightarrow \gamma = \frac{E^{(s)} - TS^{(s)}}{\sigma}$$



a real interface varies smoothly rather than abruptly