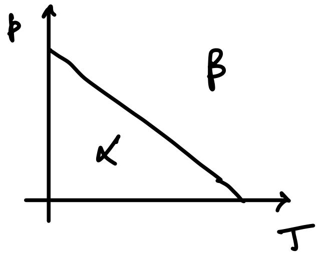
CLAUSIUS - CLAPEYRON:



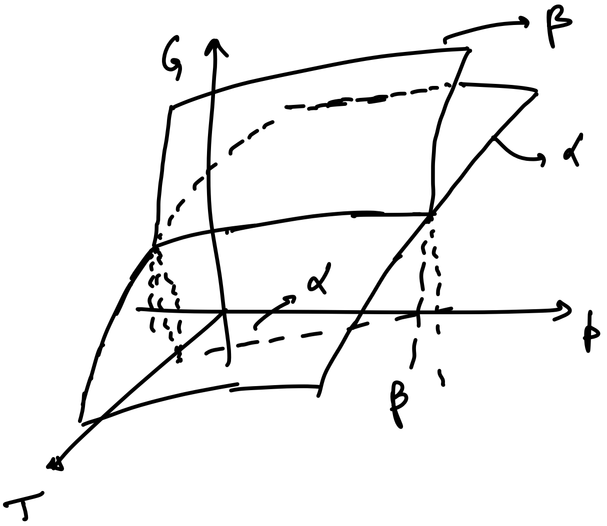
- Can we say anything about the slope of the coexistence lines in a T-p diagram?

Coexistence line defined by:

$$G^{\alpha} = G^{\beta}$$

and $dG^{\alpha} = dG^{\beta}$

Let the transition temperature be denoted as T^*, transition pressure as p^*



$$dG^{\alpha} = dG^{\beta}$$

$$\Rightarrow V^{\alpha} dp^* - S^{\alpha} dT^* = V^{\beta} dp^* - S^{\beta} dT^*$$

$$\underbrace{\left(V^{\beta} - V^{\alpha}\right)}_{\Delta V^{\alpha \to \beta}} dp^* = \underbrace{\left(S^{\beta} - S^{\alpha}\right)}_{\Delta S^{\alpha \to \beta}} dT^*$$

$$\boxed{\frac{dp^*}{dT^*} = \frac{\Delta S^{\alpha \to \beta}}{\Delta V^{\alpha \to \beta}} = \frac{\Delta H^{\alpha \to \beta}}{T \Delta V^{\alpha \to \beta}}}$$

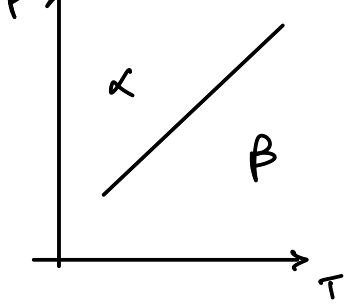
gives the slope of the coexistence line

* Going from a low-temperature phase (α) to a high-temperature phase (β)

$H^{\beta} > H^{\alpha} \Rightarrow \Delta H^{\alpha \to \beta} > 0$

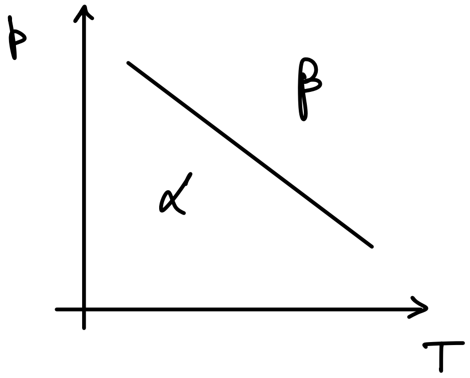
- if $\Delta V^{\alpha \to \beta} > 0$ (expands upon transformation)

$$\frac{dp^*}{dT^*} > 0 \rightsquigarrow$$



- if $\Delta V^{\alpha\to\beta} < 0$

$$\frac{dp^*}{dT^*} < 0$$



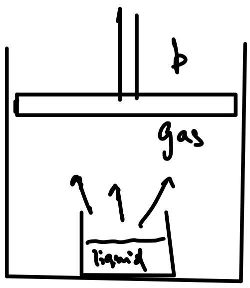
NOTICE: increase pressure ⟶ favor the phase with the smaller volume

Le Chatelier principle

↳ impose a force ⟶ system favors the state that somewhat undoes that force

★ Liquid - gas coexistence line

$$\frac{dp^*}{dT^*} = \frac{\Delta H^{l\to g}}{T^* \Delta V^{l\to g}}$$



$V^g \gg V^l$ for fixed # of moles

$$\Delta V^{l\to g} \approx V^g \approx \frac{nRT}{p} > 0$$

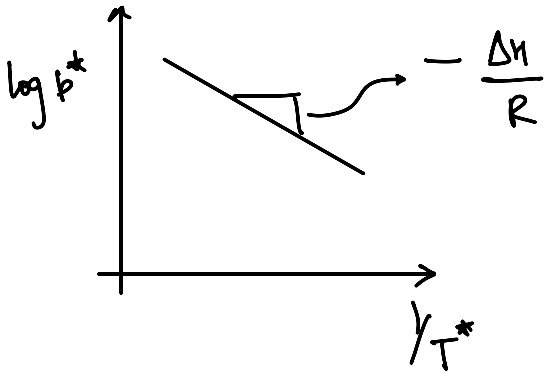
$$nR\frac{dp^*}{p^*} = \frac{\Delta H^{l\to g}}{T^{*2}}\, dT^*$$

Assume $\Delta H^{l\to g}$ is independent of T & p

$$nR\log\left(\frac{p^*}{p^*_0}\right) = -\Delta H^{l\to g}\left(\frac{1}{T^*} - \frac{1}{T^*_0}\right)$$

$$\boxed{p^* = C\exp\left(-\frac{\Delta \bar{H}^{l\to g}}{RT^*}\right)}$$

where $\Delta\bar{H} = \frac{\Delta H}{n}$



✱ MORE FUN WITH PHASE DIAGRAMS:

at constant T

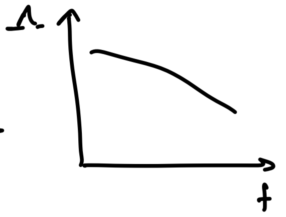
$$dU = TdS + f\,dL$$

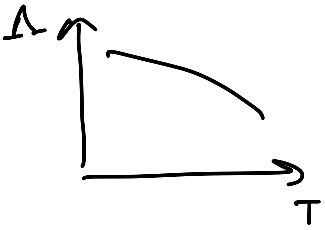
we control f & T

$$\underline{\Lambda} = U - TS - fL$$

$$\underline{\boxed{d\underline{\Lambda} = -SdT - Ldf}}$$

$$\left.\begin{aligned}\left(\frac{\partial \Lambda}{\partial T}\right)_f = -S \qquad \left(\frac{\partial \Lambda}{\partial f}\right)_T = -L\end{aligned}\right] \;\underline{\underline{\text{EOS}}}$$



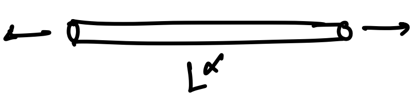


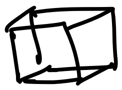
Response functions:

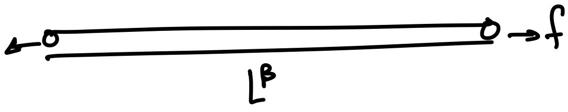
$$T\left(\frac{\partial S}{\partial T}\right)_f = C_f \qquad \frac{A_o}{L_o}\left(\frac{\partial L}{\partial f}\right)_T = \frac{1}{E} \quad \text{where } \sigma = E\varepsilon$$

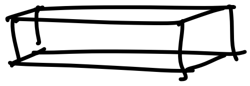
$$\frac{1}{L}\left(\frac{\partial L}{\partial T}\right) = \beta_L$$

Martensitic phase transformations:

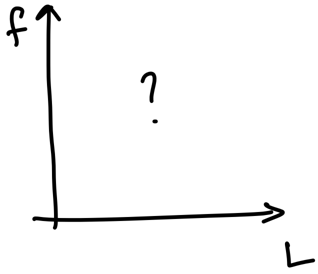








$L^\beta > L^\alpha$; α is the stable phase at low temperature



2-phase coexistence line is determined by:

$$\underline{\Lambda}^\alpha = \underline{\Lambda}^\beta$$

$$d\underline{\Lambda}^\alpha = d\underline{\Lambda}^\beta$$

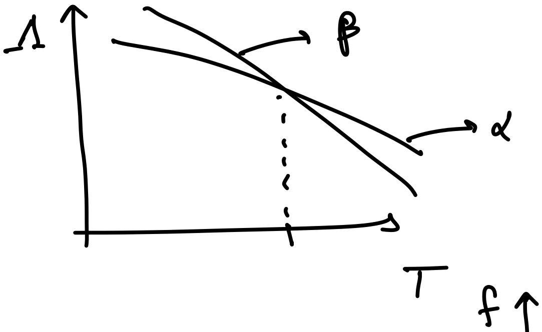
$$-S^\alpha dT^* - L^\alpha df^* = -S^\beta dT^* - L^\beta dT^*$$

$$\Rightarrow \boxed{\frac{df^*}{dT^*} = -\frac{(S^\beta - S^\alpha)}{(L^\beta - L^\alpha)}}$$

$L^\beta > L^\alpha \longrightarrow$ given

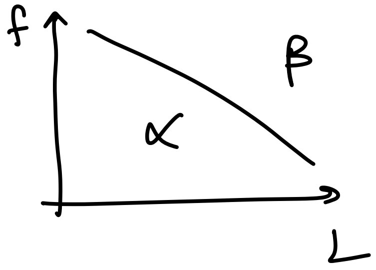
what about S^β, S^α ??

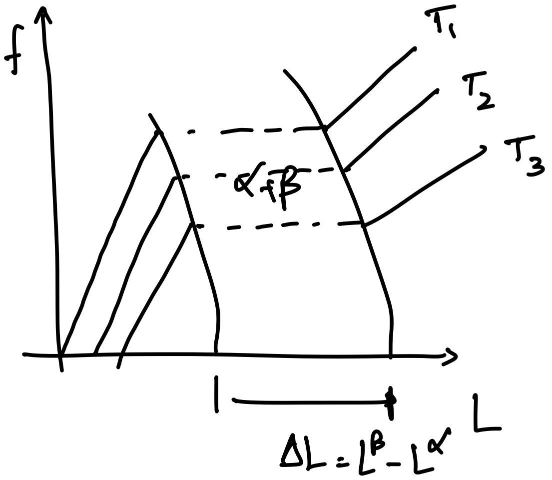
$\Longrightarrow \alpha$ is the stable phase at low temperatures.



$\Rightarrow S^\beta > S^\alpha$

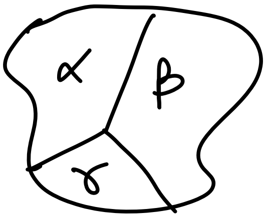
$$\frac{df^*}{dT^*} < 0$$





* MULTI-PHASE SYSTEMS:

Objective: describe multi-phase systems with multiple chemical elements.



① Compute properties of each phase as a function of composition

② " " " total system as a function of composition.

③ How do I compute eq^m in multi-phase systems?

- The system has c components (different species)
- $N_1, N_2, \ldots, N_c \longrightarrow$ # of mole of each component

FUNDAMENTAL EQUATION OF THERMO:

$U(S, x_i, N_i)$:

$$dU = TdS + \sum Y_i dx_i + \sum_{i=1}^{c} \mu_i dN_i$$

$$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{T, x_i, N_{j\neq i}} \longleftarrow \text{definition of the chemical potential}$$

* Review of some eqns. we derived before

- EULER: $U = TS - pV + \sum_i \mu_i N_i$

other potentials:

$H(S, p, N_i)$ = enthalpy $= U + pV = TS + \sum \mu_i N_i$

$F(T, V, N_i)$ = Helmholtz free energy $= U - TS = -pV + \sum_i \mu_i N_i$

$G(T, p, N_i) = U - TS + pV = \sum_i \mu_i N_i$

- GIBBS-DUHEM:

$$\underset{\uparrow}{S\,dT} - \underset{\uparrow}{V\,dp} + \sum_i N_i \underset{\nearrow}{d\mu_i} = 0$$

all intensive

$$G = U - TS + pV$$

$$dG = V\,dp - S\,dT + \sum_{i=1}^{c} \mu_i\, dN_i$$

EoS (for the multicomponent free energy) $\longrightarrow$ $N_c + 2$ equations of state

new eos: $\left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \mu_i \longrightarrow \mu_i\left(T, p, \{N_j\}\right)$ $\longrightarrow$ all mole numbers!

Hessian:

$$\begin{array}{c|cc:c} & T & p & N_i \\ \hline T & -C_p/T & \alpha V & \partial^2 G/\partial N_i \partial T \\ p & \alpha V & -V\kappa & \partial^2 G/\partial N_i \partial p \\ \hdashline N_i & & & \partial^2 G/\partial N_i^2 \end{array}$$

$$\partial^2 G/\partial N_i \partial T \longrightarrow = -\frac{\partial S}{\partial N_i} = -\overline{S}_i \longrightarrow \text{PARTIAL MOLAR ENTROPY of } i$$

$$\partial^2 G/\partial N_i \partial p \longrightarrow \frac{\partial V}{\partial N_i} = \overline{V}_i \longrightarrow \text{PARTIAL MOLAR VOLUME of } i$$

$$\partial^2 G/\partial N_i^2 \longrightarrow \left(\frac{\partial \mu}{\partial N_i}\right) = \chi_{ii}$$

In general: A $\underbrace{\text{partial molar quantity}}$:

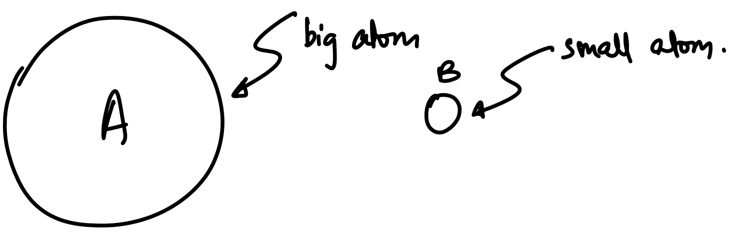
$$\left(\frac{\partial X}{\partial N_i}\right)_{N_{j\neq i}, T, p} = \overline{X}_i$$

New Maxwell relations:

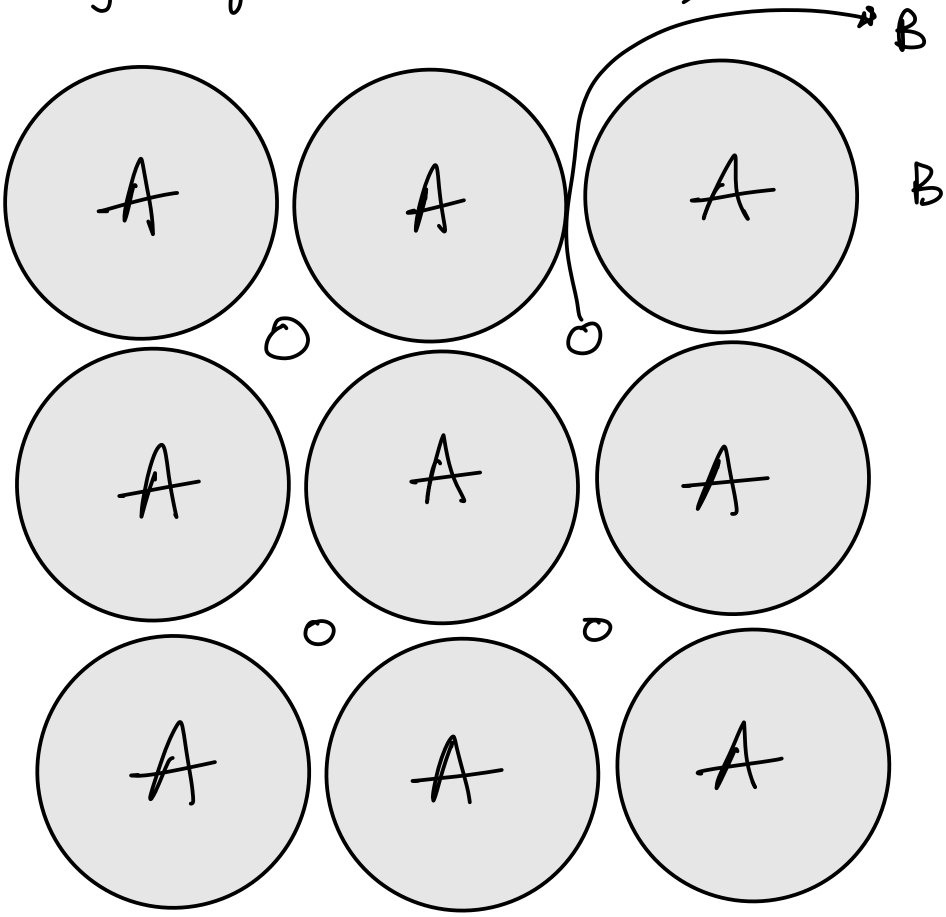
$$\overline{V}_i = \left(\frac{\partial V}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial p}\right)_{N_i, T}$$

$$\overline{S}_i = \left(\frac{\partial S}{\partial N_i}\right) = -\left(\frac{\partial \mu_i}{\partial T}\right)_{N_i, p}$$

(eg)



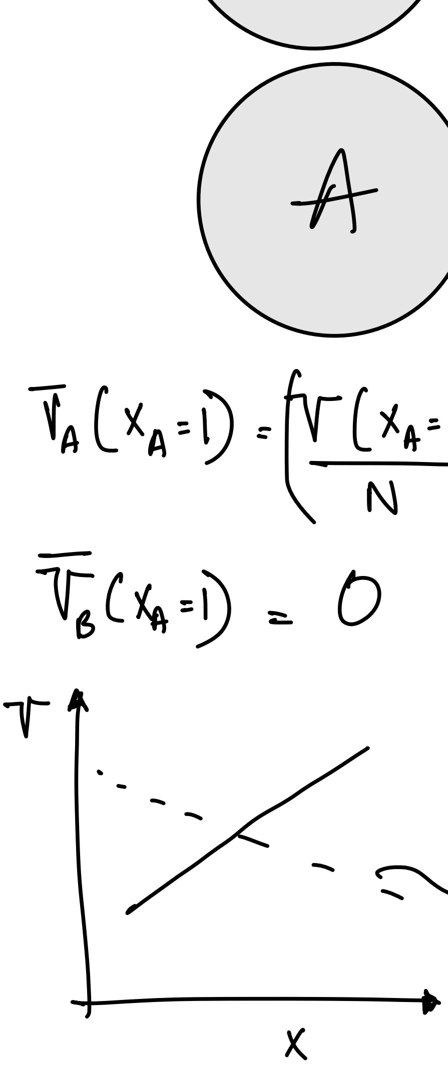
A is usually arranged (in the solid state) in a "pattern".



B fits in "interstitial" sites.

$$\bar{V}_A(x_A=1) = \left(\frac{V(x_A=1)}{N}\right)$$ ← volume per atom of pure A

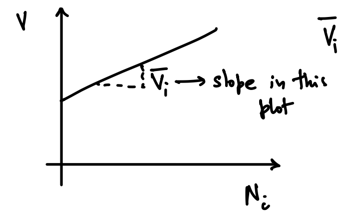
$$\bar{V}_B(x_A=1) = 0$$



(eg) $H_2O + MgSO_4$

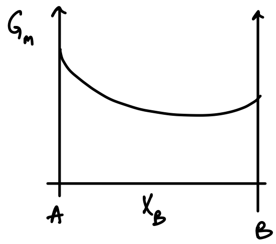
⊚ Li in Li_xNiO_2

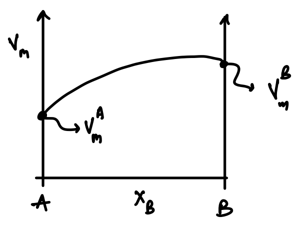
* GRAPHICAL REPRESENTATION of $\bar{Z}_i$



$\bar{V}_i = \frac{\partial V}{\partial N_i}$

In most applications we plot molar quantities $\left(\frac{Z}{N}\right)$





* DEFINITIONS:

total number of atoms

$$N = N_1 + N_2 + \cdots + N_c$$

* molar quantity: So far we have avoided normalizing extensive variables

$$X_m \rightsquigarrow \text{(eg)}\quad G_m = \frac{G}{N}$$

$$H_m = \frac{H}{N}$$

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

NOTE: Sometimes these quantities are also written as

$\bar{G}, \bar{H}, \bar{V}$

$\hookrightarrow$ not to be confused with partial molar quantities

* What is the chemical potential @ const. T,p?

$$\left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} = \mu_i \rightsquigarrow$$

change in Gibbs free energy when I add a small amount of element i

N is NOT constant!

what we usually want is to compute the effects of changing compositions.

Say we have a binary: n_A, n_B, p, T

$$dG = Vdp - SdT + \mu_A dN_A + \mu_B dN_B$$

$$n_A + n_B = n_{tot} \Rightarrow n_B = n_{tot} - n_A$$

$$\Rightarrow dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_{tot} - \mu_B dn_A$$

$$dG = Vdp - SdT + (\mu_A - \mu_B)dn_A + \mu_B dn_{tot}$$

$$\left(\frac{\partial G}{\partial n_A}\right)_{p,T,\underset{\overset{\uparrow}{\text{Constant}}}{n_{tot}}} = \mu_A - \mu_B$$

$$\Rightarrow \left(\frac{\partial \left(G/n_{tot}\right)}{\partial \left(n_A/n_{tot}\right)}\right)_{p,T,n_{tot}} = \left(\frac{\partial G_m}{\partial x_A}\right)_{p,T,n_{tot}} = \mu_A - \mu_B$$

$$\boxed{(\mu_A - \mu_B) \longrightarrow \text{Molar Gibbs energy change when we change the composition}}$$