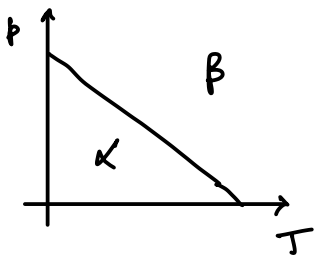


CLAUSIUS - CLAPEYRON:



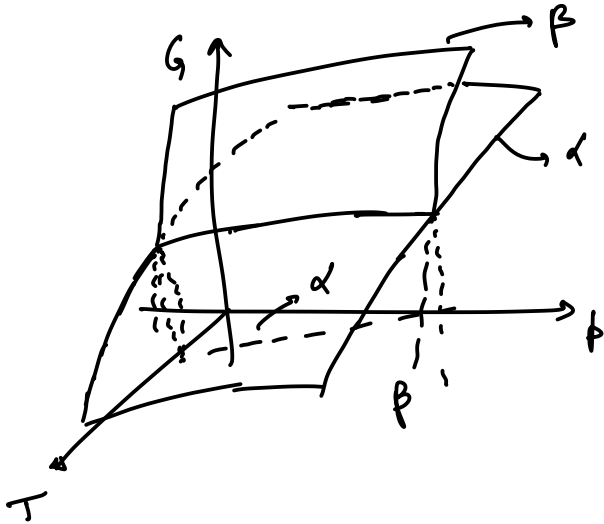
- Can we say anything about the slope of the coexistence lines in a T-p diagram?

Coexistence line defined by:

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

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

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



$$dG^\alpha = dG^\beta$$

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

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

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

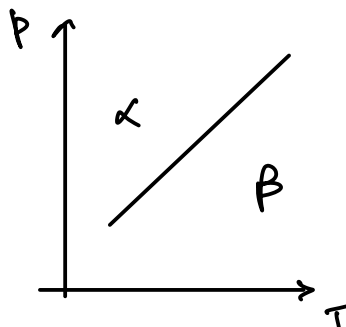
↑ gives the slope of the coexistence line

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

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

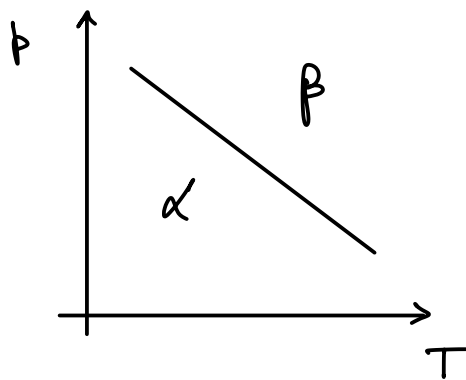
• if $\Delta V^{\alpha \rightarrow \beta} > 0$ (expands upon transformation)

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



• if $\Delta V^{\alpha \rightarrow \beta} < 0$

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



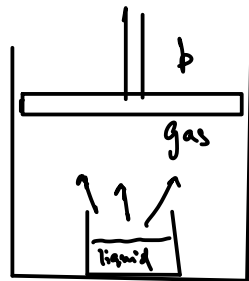
NOTICE: increase pressure \rightarrow favor the phase with the smaller volume

Le Chatelier principle

\hookrightarrow impose a force \rightarrow system favors the state that somewhat undoes that force

* Liquid - gas coexistence line

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



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

$$\begin{aligned} \Delta V^{l \rightarrow g} &\approx V^g \\ &\approx \frac{nRT}{p} > 0 \end{aligned}$$

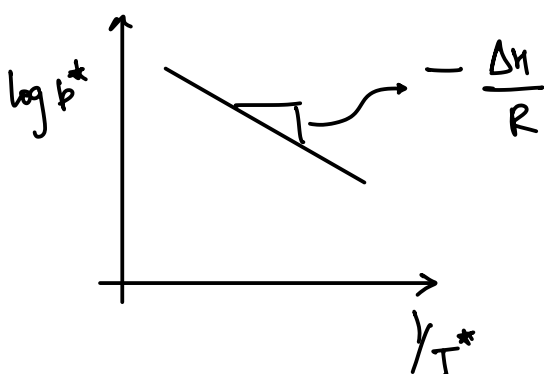
$$\frac{nR dp^*}{p^*} = \frac{\Delta H^{l \rightarrow g}}{T^{*2}} dT^*$$

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

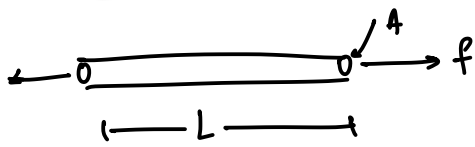
$$nR \log \left(\frac{p^*}{p_0^*} \right) = -\Delta H^{l \rightarrow g} \left(\frac{1}{T^*} - \frac{1}{T_0^*} \right)$$

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

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



* MORE FUN WITH PHASE DIAGRAMS:



at constant T

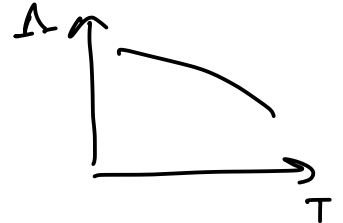
$$dU = TdS + fdL$$

we control f & T

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

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

$$\left[\left(\frac{\partial \underline{\Lambda}}{\partial T} \right)_f = -S \quad \left(\frac{\partial \underline{\Lambda}}{\partial f} \right)_T = -L \right] \underline{\text{EOS}}$$



Response functions:

$$T \left(\frac{\partial S}{\partial T} \right)_f = C_f$$

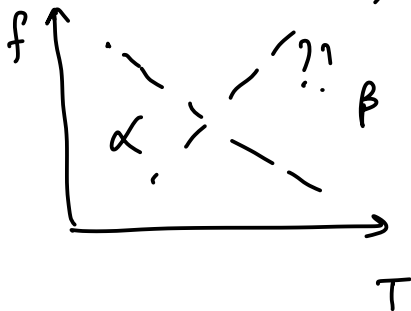
$$\frac{A_0}{L_0} \left(\frac{\partial L}{\partial f} \right)_T = \frac{1}{E} \quad \text{where } \nu = E\varepsilon$$

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

Martensitic phase transformations:



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



2-phase coexistence line is determined by:

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

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

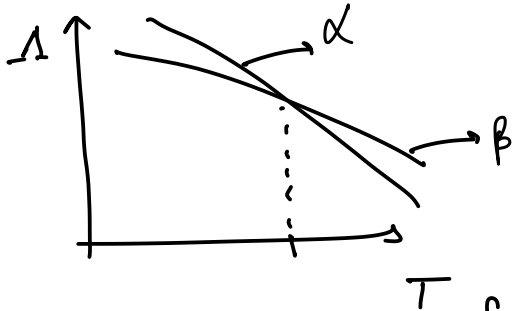
$$-S^\alpha dT^* - L^\alpha df^* = -S^\beta dT^* - L^\beta dT^*$$

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

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

what about S^β, S^α ??

$\Rightarrow \alpha$ is the stable phase at ^{high} temperatures.



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

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

