* The phases and phase diagram of water:

Water is commonly known to have 3 PHASES

- Solid
- Liquid
- Gas

Let $\alpha \rightarrow$ denote one of these phases of water

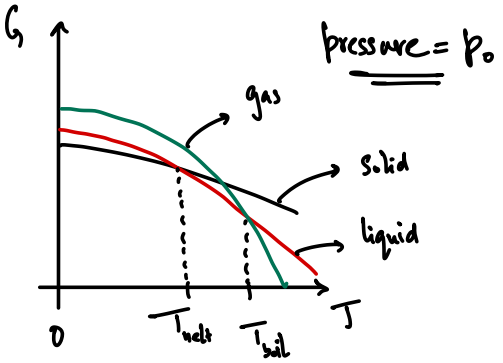
$G^\alpha = U^\alpha - TS^\alpha + pV^\alpha \longrightarrow$ we control $T$ & $p$

$$\boxed{G^\alpha = H^\alpha - TS^\alpha}$$

Notice @ $T=0$

$G^\alpha = H^\alpha$

Usually $\left[ \begin{array}{l} S^{gas} > S^{liquid} > S^{solid} \\ H^{gas}(T=0) > H^{liquid}(T=0) > H^{solid}(T=0) \end{array} \right]$




Recall for eq$^m$: $dG \leq 0$ @ $G$ (the characteristic potential) is minimized

$\Rightarrow$ At any given temperature the phase with the lowest Gibbs free energy is the eq$^m$ phase

$T < T_{melt} \longrightarrow$ solid

$T_{melt} < T < T_{boil} \longrightarrow$ liquid

$T_{boil} < T \longrightarrow$ gas

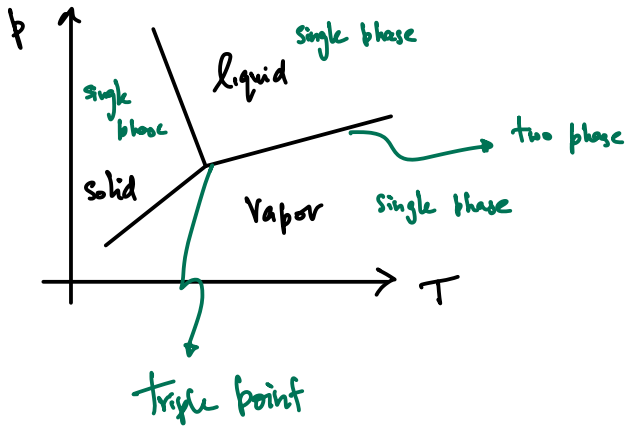
At $T = T_{melt}$

$$\left(G^{solid} = G^{liquid}\right) < G^{gas}$$

At $T = T_{boil}$

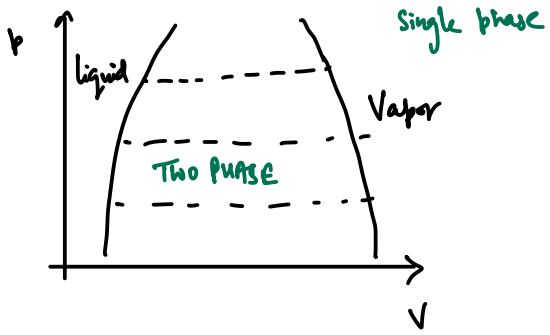
$$\left(G^{liquid} = G^{gas}\right) < G^{solid}$$

Repeat the exercise at many different pressures: → collect $T_{melt}$, $T_{boil}$ at each pressure




→ phase diagram of 2 intensive variables

p-V phase diagram of water:




→ phase diagram of an intensive v/s an extensive variable.

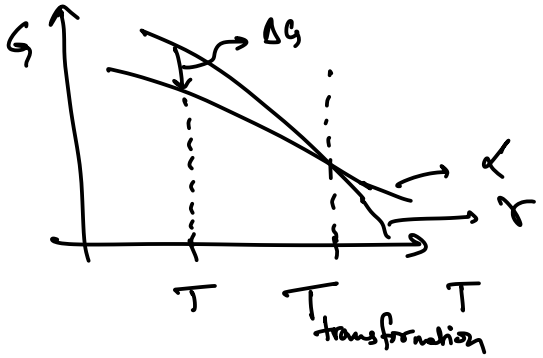
* NOTE: Real transformations rarely happen exactly at $T = T_{transformation}$

@ $T = T_{transformation}$

$\Delta G = 0$ (no driving force)

↳ equivalent to $\Delta S^{universe} = 0$

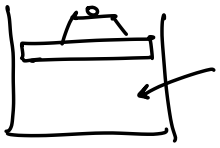
always need to undercool or overheat for a transformation.




at $T < T_{transformation}$ ; $\Delta G < 0$

* Significance of $\Delta H$: (at constant $T$ & $p$)

- Consider a system at constant $T$ & $p$ transforming from a metastable state to a stable state



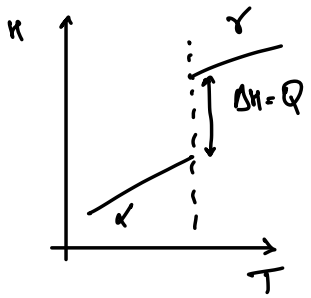
- change of state accompanied by a change in Volume ($\Delta V$) [for example $H_2O$ @ 0°C; $\bar{V}^{solid} > \bar{V}^{liquid}$]

$\Rightarrow$ environment performs $-p\Delta V$ work on the system

I Law: $\Delta U = Q - p\Delta V \Rightarrow \boxed{Q = \Delta U + p\Delta V = \Delta H}$

during the transformation latent heat is given off or absorbed due to a change in enthalpy

$$\Delta H = H^{\alpha} - H^{\gamma}$$




ASIDE: How do we determine $H^{\alpha}(T)$?

$$dH_p^{\alpha} = C_p^{\alpha}\, dT$$

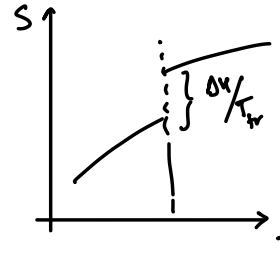
$$\Rightarrow \boxed{H^{\alpha}(T) - H^{\alpha}(T_0) = \int_{T_0}^{T} C_p^{\alpha}\, dT}$$

* Significance of $\Delta S$:

at the transition temperature $\Delta G = 0$

$$\Rightarrow \Delta H = T\Delta S$$

$$@ \quad \Delta S = S^{\alpha}(T=T_{tr}) - S^{\gamma}(T=T_{tr}) = \frac{H^{\alpha}(T=T_{tr}) - H^{\gamma}(T=T_{tr})}{T_{transition}}$$




ONLY VALID AT THE TRANSITION TEMPERATURE

* Approximating $\Delta G$:

$$\Delta H_{PT} = T_{PT}\, \Delta S_{PT}$$

↳ phase transition

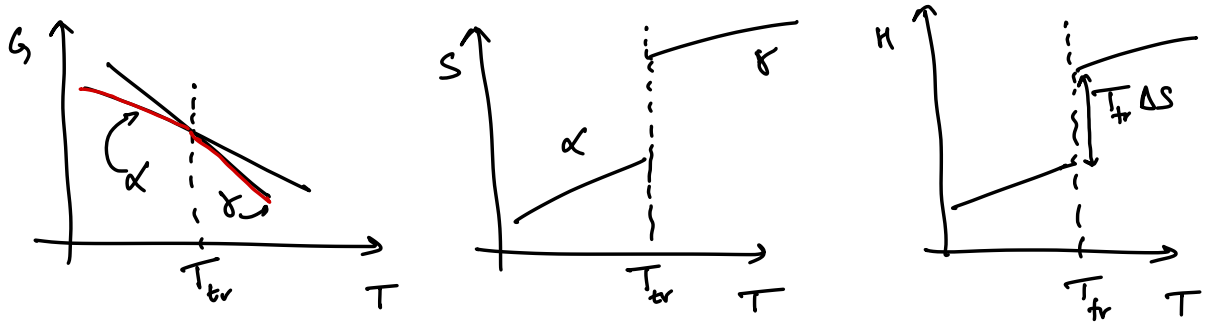
$\Delta G = \Delta H - T\Delta S$

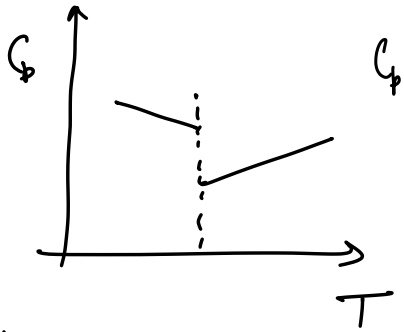
Linearize $\Delta G$

$$\Delta G = \Delta H_{PT}\left(1 - \frac{T}{T_{PT}}\right)$$ ← VERY USEFUL!!

## EHRENFEST CLASSIFICATION OF PHASE TRANSITIONS:

① 1st order phase transitions:

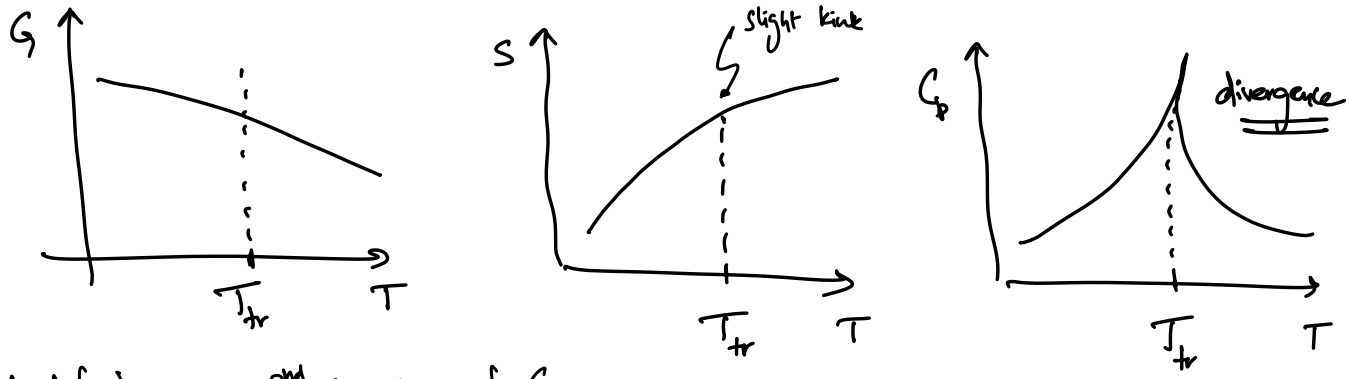



$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

KINETICALLY; 1st order phase transitions involve a NUCLEATION AND GROWTH mechanism
- supercool, small nuclei form which then grow

② 2nd order phase transition: 2nd derivative of G is discontinuous:



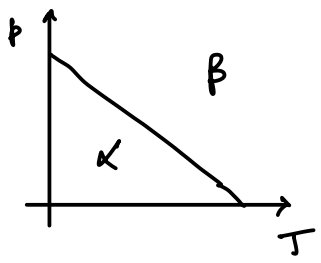

original definition → 2nd derivative of G is discontinuous.
in reality → response functions diverge

KINETICALLY: 2nd order phase transitions occur uniformly and continuously
(NO NUCLEATION AND GROWTH)

Classical thermodynamics breaks down in the vicinity of a 2nd order phase transition. → presence of large fluctuations.

* EQUILIBRIUM CRITERIA FOR MULTICOMPONENT SYSTEMS → Subject of problem set (3)

# CLAUSIUS-CLAPEYRON:



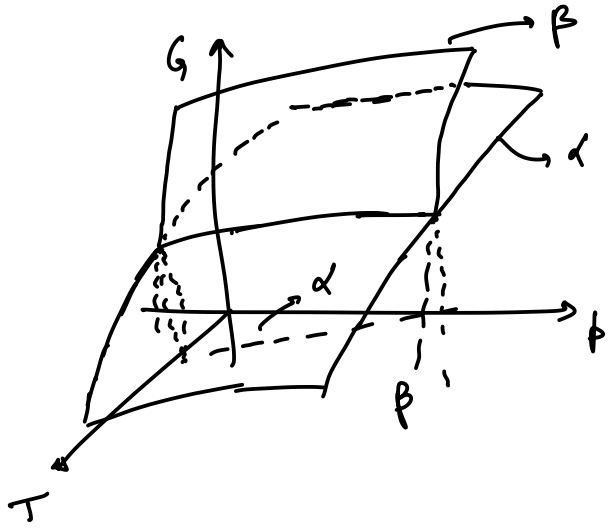

- Can we say anything about the slope of the coexistence lines in a T-p diagram?

Coexistence line defined by:

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

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

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




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

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

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

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

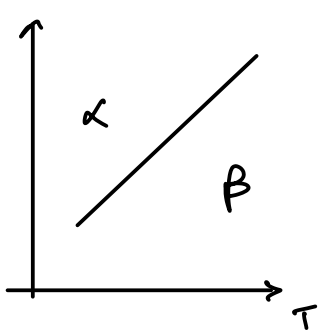
↳ gives the slope of the coexistence line

* Going from a low-temperature phase ($\alpha$) to a high-temperature phase ($\beta$)

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

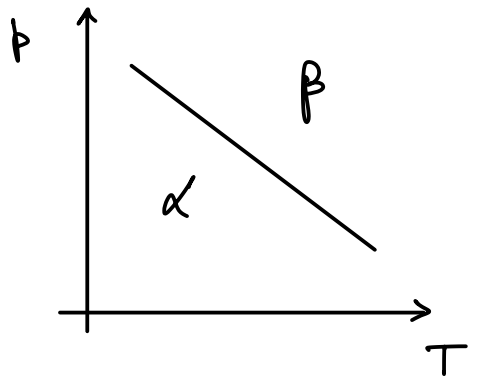
- if $\Delta V^{\alpha \to \beta} > 0$ (expands upon transformation)

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



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

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



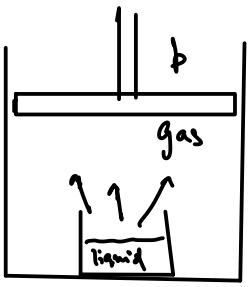

NOTICE: increase pressure ⟶ favor the phase with the smaller volume

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

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

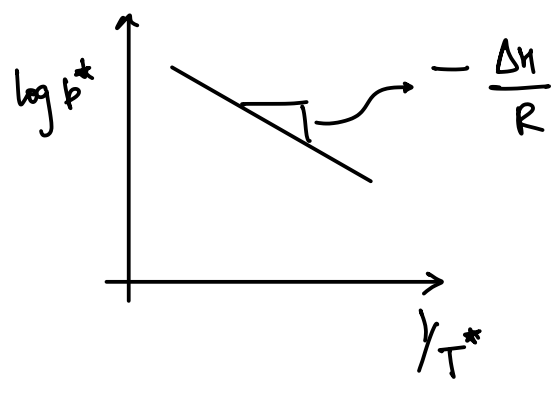
$$\frac{nR\,dp^*}{p^*} = \frac{\Delta H^{l \to g}}{T^{*2}} dT^*$$

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

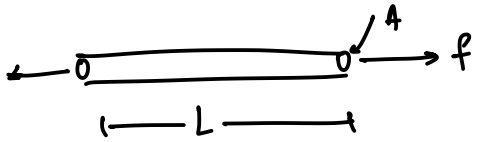
$$nR \log\left(\frac{p^*}{p_0^*}\right) = -\Delta H^{l \to g}\left(\frac{1}{T^*} - \frac{1}{T_0^*}\right)$$

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

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



# ✱ More fun with phase diagrams:




at constant $T$

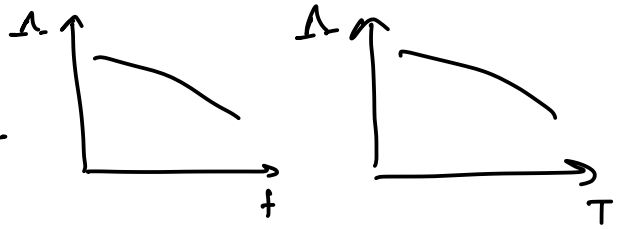
$dU = TdS + fdL$

we control $f$ & $T$

$\Lambda = U - TS - fL$

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

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

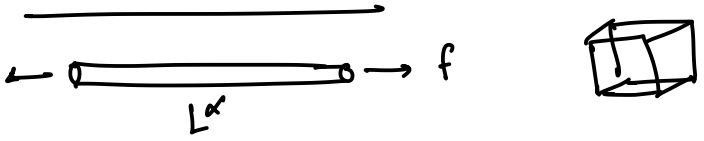


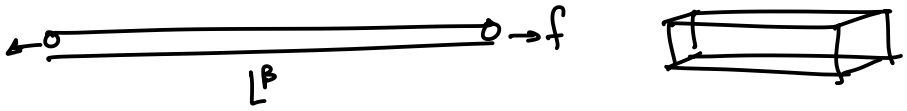

Response functions:

$$T\left(\frac{\partial S}{\partial T}\right)_f = C_f \qquad \frac{A_0}{L_0}\left(\frac{\partial L}{\partial f}\right)_T = \frac{1}{E} \quad \text{where } \sigma = E\varepsilon$$

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

Martensitic phase transformations:




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


2- phase coexistence line is determined by:

$$\Lambda^\alpha = \Lambda^\beta$$

$$d\Lambda^\alpha = d\Lambda^\beta$$

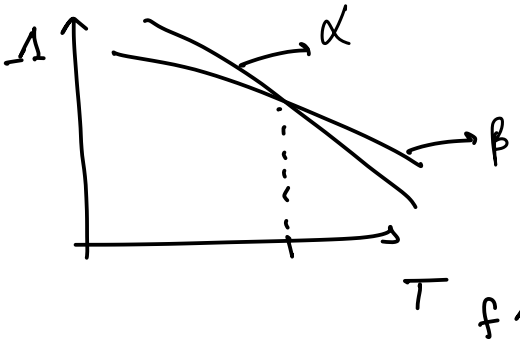
$$-S^{\alpha} dT^{*} - L^{\alpha} df^{*} = -S^{\beta} dT^{*} - L^{\beta} dT^{*}$$

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

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

what about $S^{\beta}, S^{\alpha}$ ??

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




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

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