Last time

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Molecules convert from high μ state to a low μ state, until $\mu_i = \mu_j$

At const T & P

$$\mu_i = \bar{G}_i = G_i/n_i$$

$$G = \sum n_i \mu_i$$

how does μ depend on T & P?

Consider within one phase

$$\mu = \bar{G} = \bar{H} - T\bar{S}$$

$$G = H - TS$$

How does H & S depend on T & P

$$dH = d(E + pV) = dE + \underset{-}{\underline{pdV}} + V\underset{0}{\underline{dP}}$$

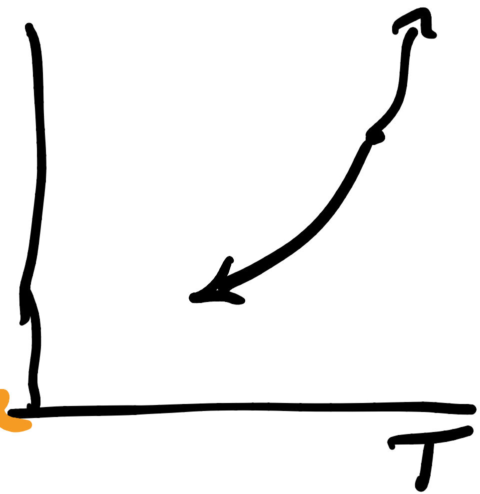
$$dE = dq - \underset{+}{\underline{pdV}}$$

@ const T & P

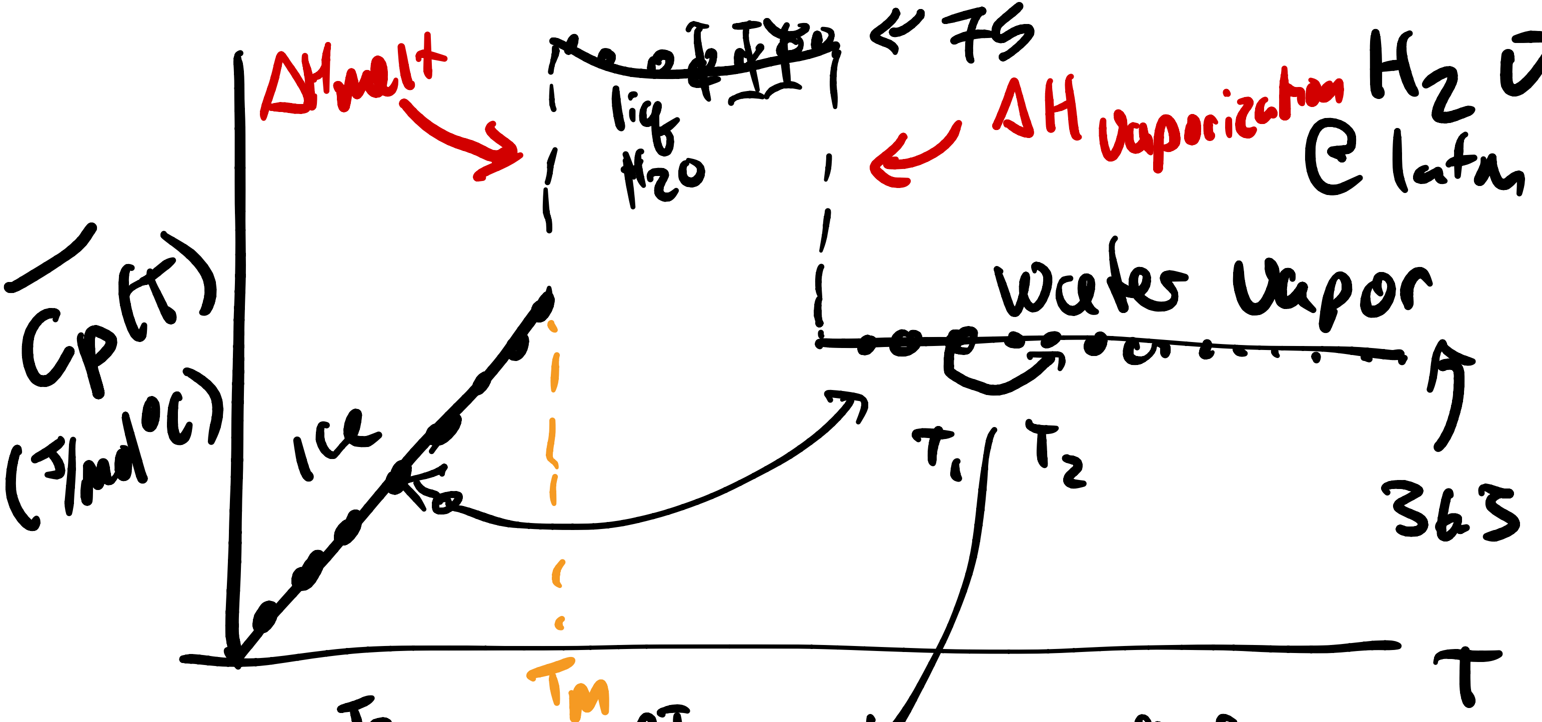
$$dH = dq = C_p\,dT$$

$$T\,dS = dq$$

$$\left.\begin{aligned} dH &= C_p\,dT \\ dS &= C_p/T\,dT \end{aligned}\right\}\ \text{need to integrate}$$



need to know C_p



$$\Delta H = \int_{T_1}^{T_2} dH = \int_{T_1}^{T_2} C_p(T)\,dT \overset{gas}{\approx} C_p^{gas}\,\Delta T$$

$$\Delta \bar{H} = \bar{C}_p^{gas}\,\Delta T$$

$$\bar{H}(T) = \bar{H}(T_{ref}) + \int_{T_{ref}}^{T} \bar{C}_p \, dT$$

$$\bar{S}(T) = \bar{S}(T_{ref}) + \int_{T_{ref}}^{T} \frac{\bar{C}_p}{T} \, dT$$

T_{ref} for H is T_{melt}, $\bar{H}(T_m) = 0$ solid phase

T_{ref} for S, $\bar{S}(T_{ref} = 0) = 0$

ΔS_{melt} ΔS_{vap}

$$\Delta \bar{G} = \bar{G}(\text{liq}, T_m) - \bar{G}(\text{solid}, T_m) = 0$$

@ T_m liq & solid are in equilibrium

$$\mu_{liq} = \mu_{sold}$$

$$0 = \Delta \bar{H}_{melt} - T_m \Delta \bar{S}_{melt}$$

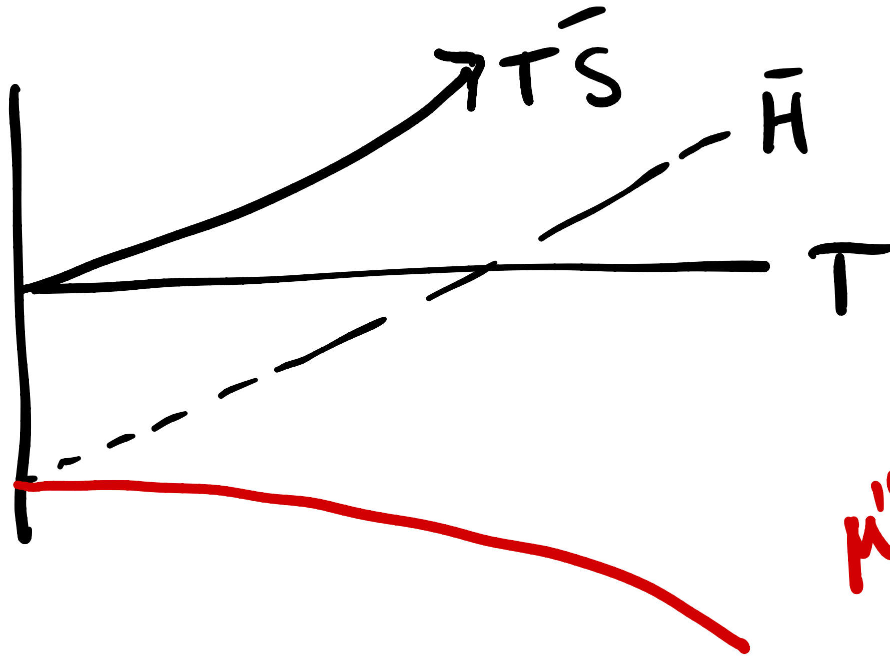
$$\Delta \bar{S}_{melt} = \frac{\Delta \bar{H}_{melt}}{T_m}$$

Kelvin

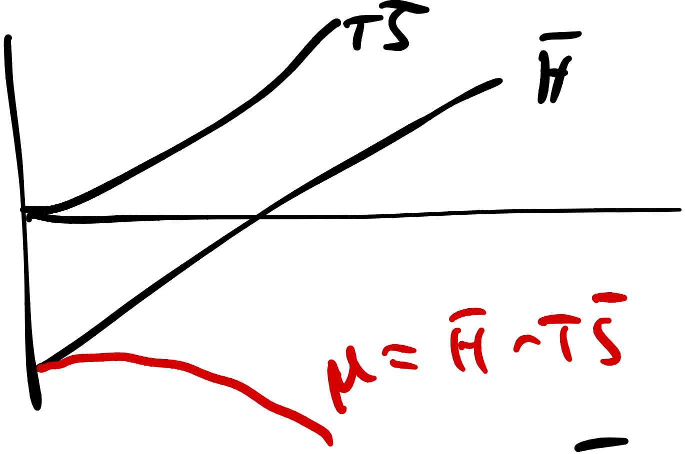
$$\Delta \bar{H}_m = \bar{H}^{liq}(T_m) - \cancel{\underbrace{\bar{H}^{sol}(T_m)}_{0}}$$

have functions fit for $\bar{C}_p(T)$

Plot H^{ice}, TS^{ice}



$\mu^{ice} = \bar{H} - T\bar{S}$, goes down w/T



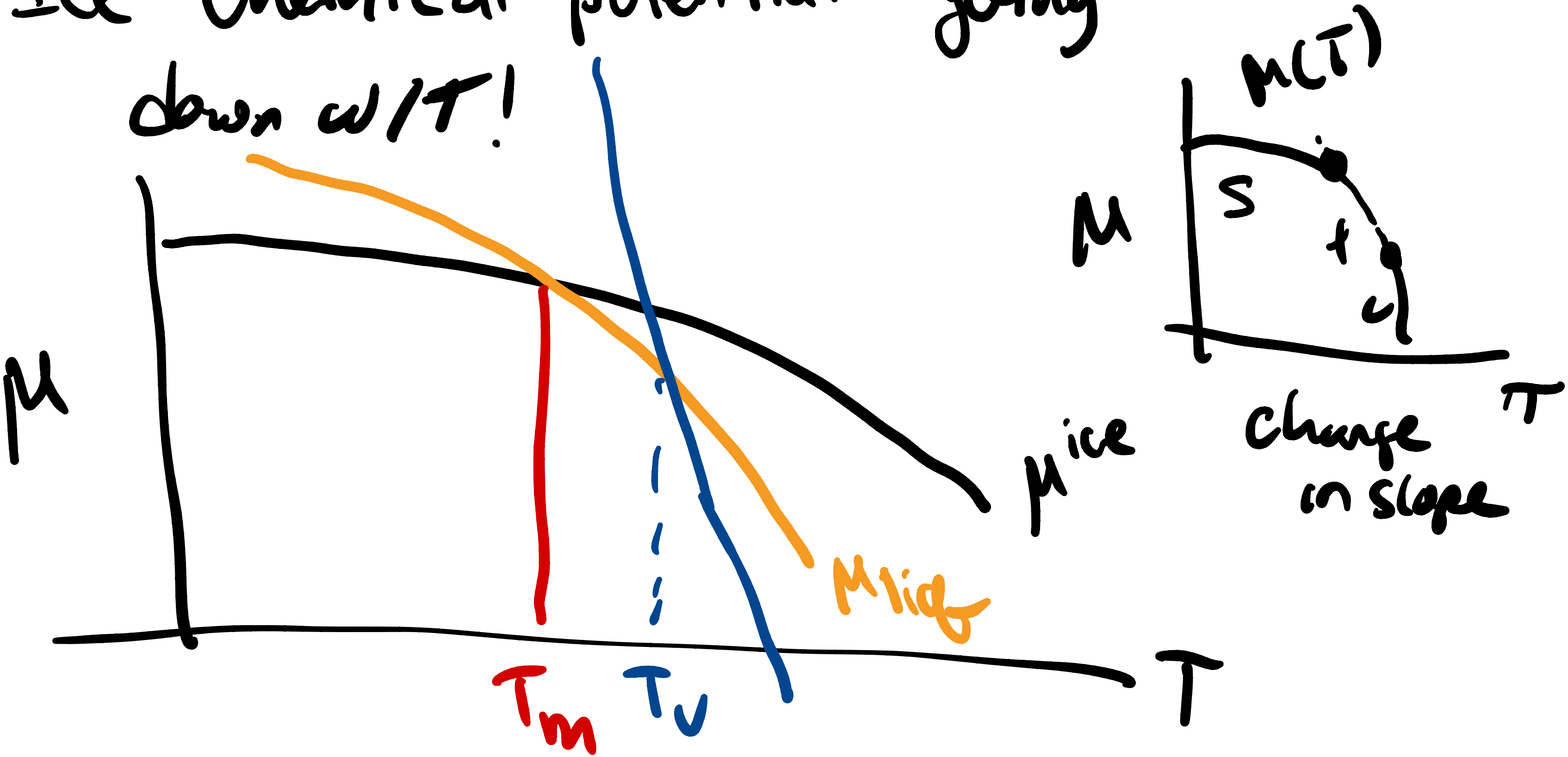
④ $\left(\frac{\partial \mu}{\partial T}\right)_p = -S$ decreasing

① @ $T = 0$ $\mu = \bar{H}$

② $\bar{C}_p^{ice} = \left(\frac{\partial H^{ice}}{\partial T}\right)_p > 0$ every whe

⑤ $\left(\partial S / \partial T\right)_p = \bar{C}_p / T > 0$ S increases with T

Ice chemical potential going down w/T!



If small (nano scale) system
no true true phase transitions

$$G^{system} = \frac{n_{solid}}{n_{tot}} \mu_{solid} + \frac{n_{liq}}{n_{tot}} \mu_{liq} + \frac{n_{vap}}{n_{tot}} \mu_{vap}$$

$$= \sum_{\pi} \chi^{\pi} \mu^{\pi}$$

$\pi \sim$ solid, liq, vapor ?

How does pressure affect μ

P biggest effect on gasses

Gibb-Duhem

Cs $d\mu^{\pi} = -\bar{S}^{\pi} dT + \bar{V}^{\pi} dP$

@ const T

$= \bar{V}^{\pi} dP$

how does $\bar{V}$ in $\overbrace{\text{liq, solid or gas}}^{\pi}$ change

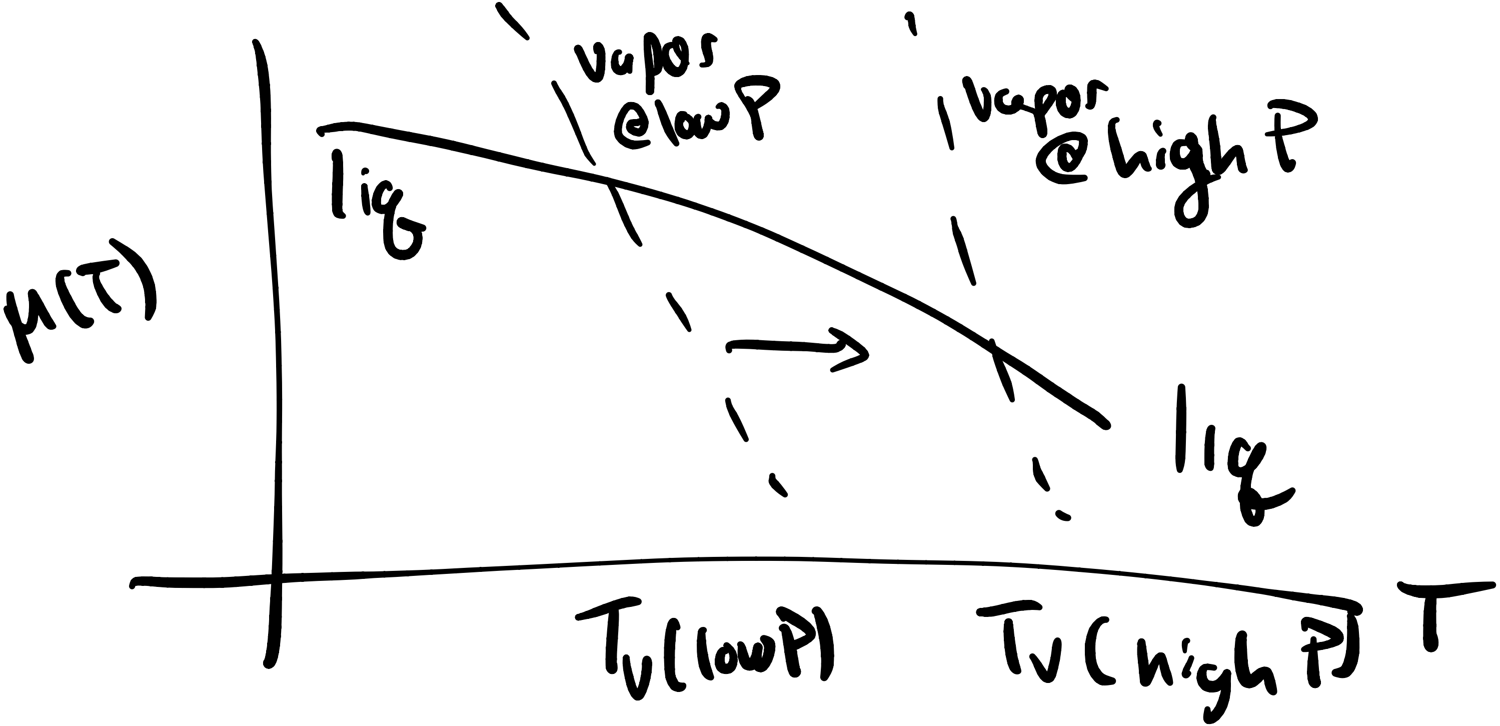
$$d\mu^{gas} = \bar{V}\,dp \approx \frac{RT}{P}\,dP$$

$$PV = nRT$$

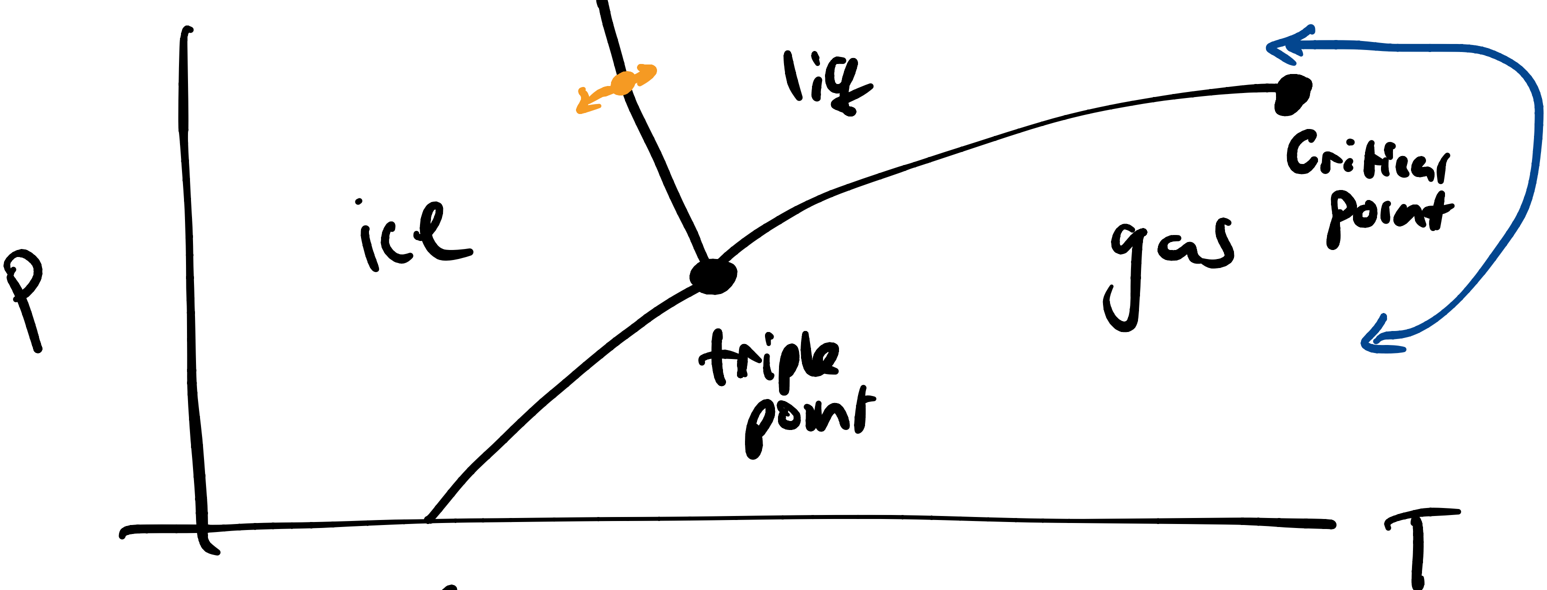
$$V/n = \frac{RT}{P}$$

$$\Delta\mu = \int_{1atm}^{P} d\mu = \int_{1atm}^{P} \frac{RT}{P}\,dP$$

$$= RT\ln\left(P/atm\right)$$



boiling point elevation

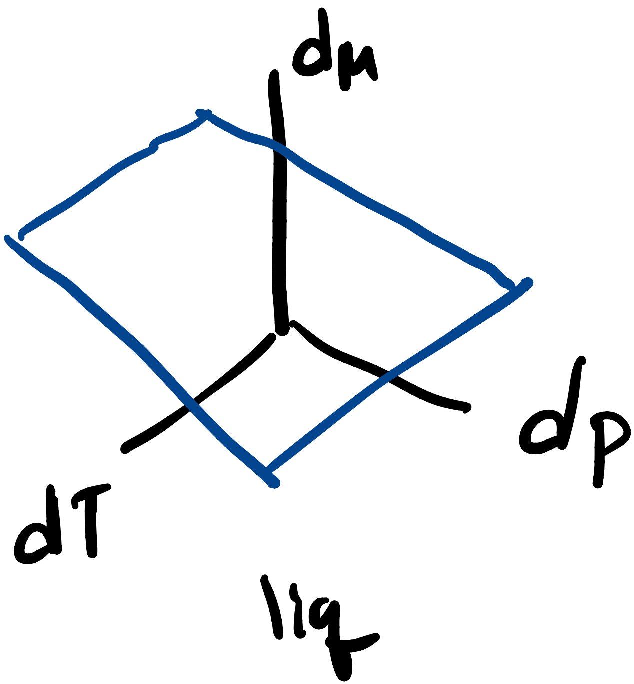


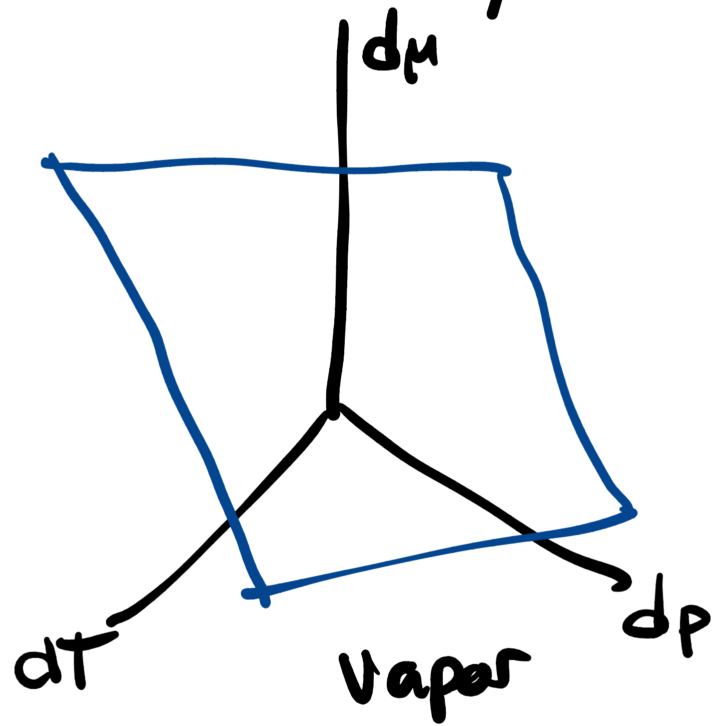
line: $\mu^{\pi_1}(T,p) = \mu^{\pi_2}(T,p)$

T.P. $\mu^{ice} = \mu^{water} = \mu^{gas}$, 5×10^{-3} atm

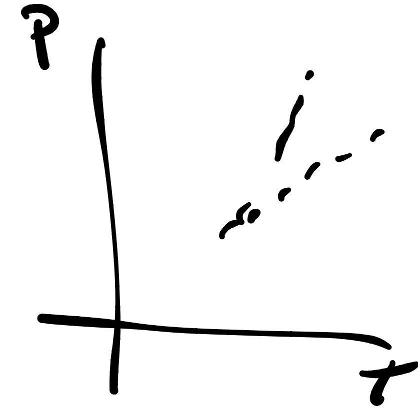
GD eqn $\quad d\mu + \bar{S}\,dT - \bar{V}\,dp = 0$

one equation for μ in each phase





2 planes of $\mu(T,P)$ intersect along a line



Can show

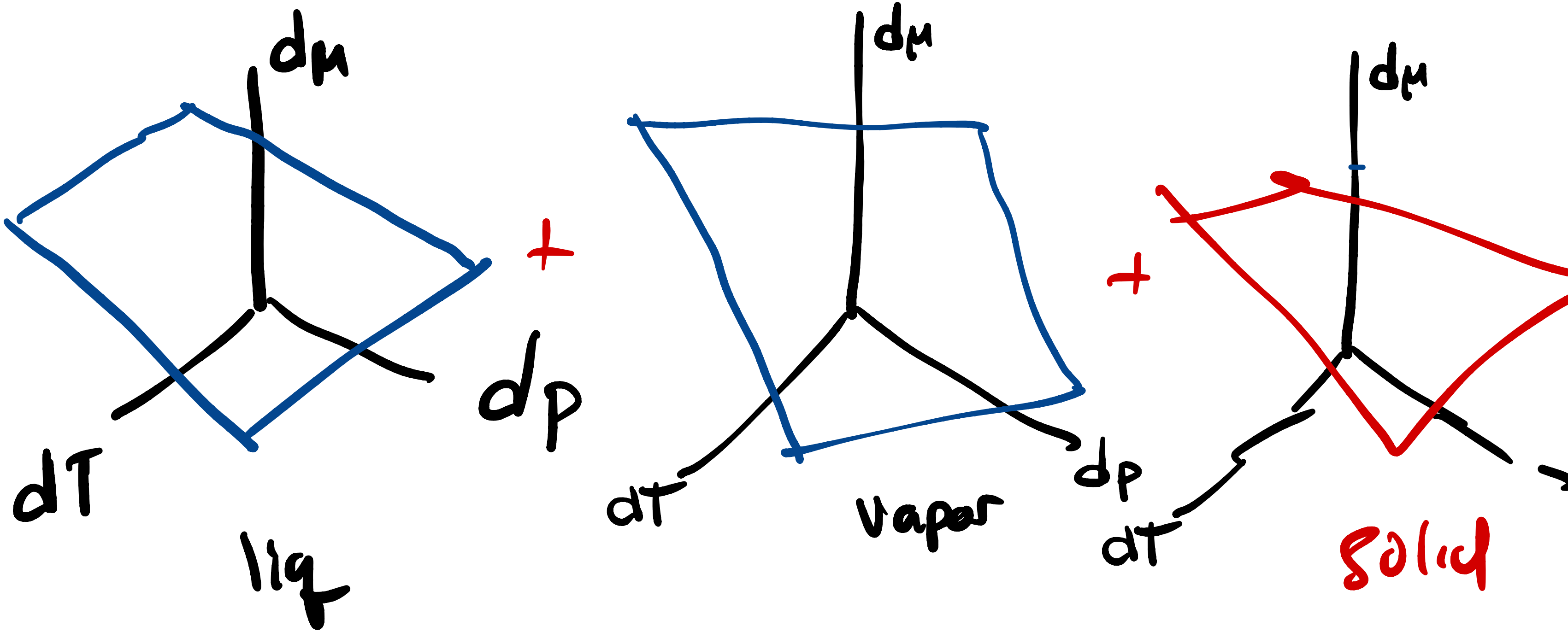
$$\left(\partial P / dT\right)_{\mu_{phase 1} = \mu_{phase}} = \frac{\Delta S^{1\to 2}}{\Delta V^{1\to 2}}$$

> for almost everything

eg $l \to vap$

Claussius - Clapyron equation

H_2O exception



3 planes can intersect only at a point

Gibbs phase rule

d.o.f. = # components − # coexisting phases + 2

things you can change & still coexist

1 component	#	d of	
	1 phase	2	P, T
	2 phases	1	change T also change P