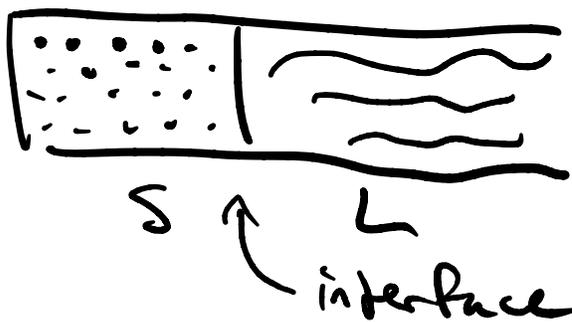When are two phases in equilibrium
   with eachother?

Give each phase a chemical potential
   $\mu^\alpha, \mu^\beta, \mu^\sigma$ etc

Stick with one componet for now

Consider pure liq & solid

S ↑ L
  └ interface

what happens?

Suppose constant temp & pressure
then $dG = \mu^S dn^S + \mu^\ell dn^\ell$ (+ interfacial
                                          (neglect)
   Interested in case where
   $n_+ = n^S + n^\ell \Rightarrow$
      $dn^S = -dn^\ell$

So $dG = dn^S(\mu^S - \mu^\ell) = dn^\ell(\mu^\ell - \mu^S)$
Spontaneous change will decrease dG ($dG < 0$)
Suppose $\mu^S > \mu^\ell$, $dn^S < 0 \Rightarrow S \to L$

atoms flow from high to low
Chemical potential !

Volume & Enthalpy will change

$$\Delta V = (\bar{V}^S - \bar{V}^\ell) dn^S \qquad \text{suppose } \bar{V}^S < \bar{V}^\ell$$

then $dn^S < 0$, melting, means volume ↑

heat change $q = (\bar{H}^S - \bar{H}^\ell) dn^S$

need molar enthalpies

$$\left[dH = TdS + Vdp = TdS = dq \overset{C_p dT}{\underset{\text{phase}}{\text{in each}}} \right]$$

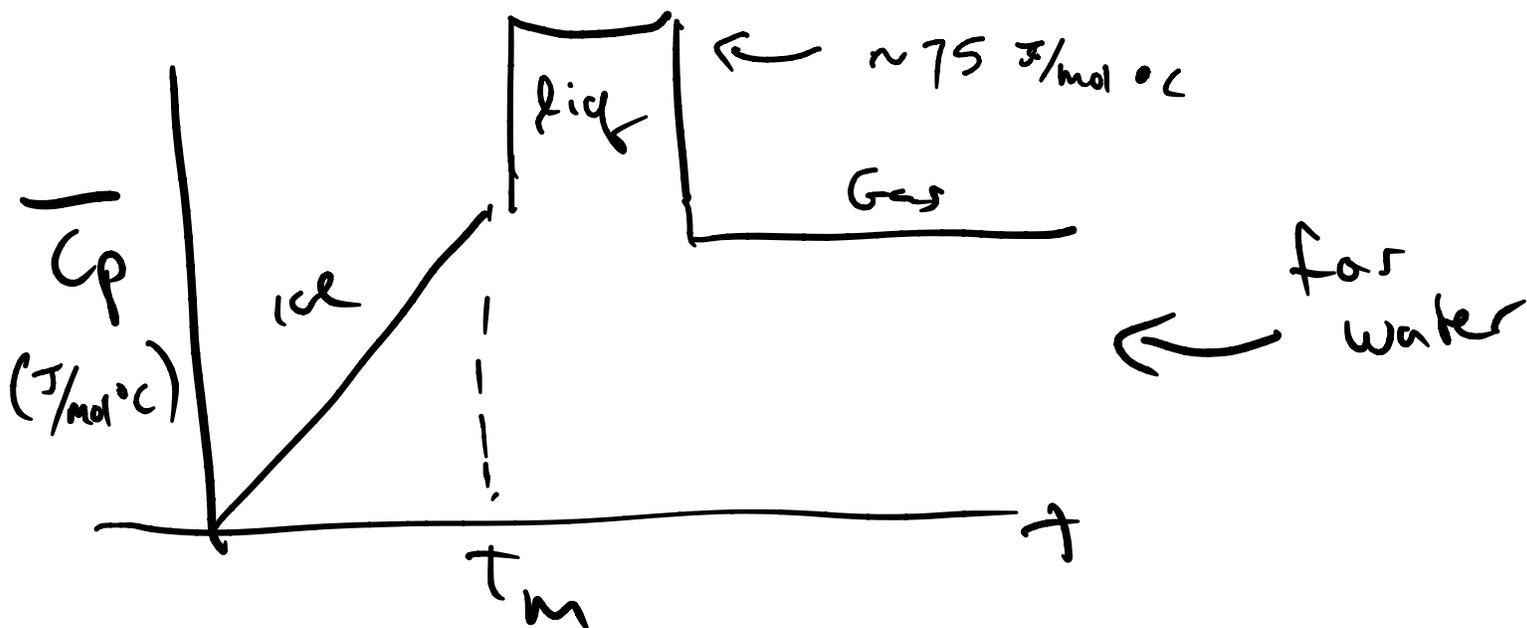If μ's equal at certain p, T,
then phase. coexistence

But when would this happen?
Depends on how μ depends
on T & p in each phase

In each phase, $G = H - TS$ so
$$\mu = \bar{H} - T\bar{S}$$

Hence, need temp dependence of $\bar{H}$ & $\bar{S}$, which depends on the substance and is fit to data

$\bar{C_p}$ ($J/mol \cdot c$) ... ice ... liq ... Gas ... $\sim 75\ J/mol \cdot c$ ... for water ... T_m

Measure in stable phase

$$\bar{C_p}^{gas} = 36.3 \quad \leftarrow flat$$

$$\bar{C_p}^{\ell} = a^{\ell} + b^{\ell}T + c^{\ell}T^2 = 101 - 0.163T + 2.56\times10^{-4}T^2$$

$$\bar{C_p}^{s} = \frac{a^{s}T}{b^{s} + T} = \frac{229.3T}{1387 + T} \quad \curvearrowright goes\ to\ 0 @ 0$$

Need a reference condition and get
H & S relative to that

$G = H - TS$ so @ low T, H dominates

$\Rightarrow$ phase at low T is also low H (large negative)

Pick Enthalpy of ice $= 0$ @ T_m

$S(T=0) = 0$.

Have to determine T_m, T_v from filling!

Since $dG = 0$ @ transition

$$\Delta S_m = \Delta \bar{H}_m / T_m \quad \& \quad \Delta S_v = \Delta \bar{H}_v / T_v$$
$$\underbrace{}_{\text{defined}} \quad \underbrace{\phantom{\Delta \bar{H}_v / T_v}}_{\text{measured}}$$

In each phase $d\bar{H} = \bar{C}_p \, dT$, $d\bar{S} = \bar{C}_{p/T} \, dT$

So $\bar{H}(T) - \bar{H}(T_r) = \int_{T_r}^{T} \bar{C}_p \, dT$

$$\bar{S}(T) - \bar{S}(T_r) = \int_{T_r}^{t} \bar{C}_p / T \, dT$$

Then add $\Delta \bar{H}$ & $\Delta \bar{S}$ of transitions

For water fit:

Ice at temp $T < T_m$:

$$\bar{H}(T) - \bar{H}(T_m) = \int_{T_m}^{T} C_p^{ice} \, dT$$

$$= \int_{T_m}^{T} \frac{a^{ice} T}{b^{ice} + T} \, dT$$

$$1 - \frac{b}{x+b} = \frac{x}{x+b}$$

$$= a^{ice}(T - T_m) - a^{ice} b^{ice} \ln\left(\frac{b^{ice} + T}{b^{ice} + T_m}\right)$$

$$H^{ice}(T_m) = 0$$

$$H^{liq}(T_m) = \Delta \bar{H}_m = 6.01 \quad \leftarrow \text{check} \, \checkmark$$

Entropy

$$\Delta S^{ice} = \bar{S}^{ice}(T) = \int_0^T \frac{C_p^{ice}}{T} \, dT$$

$$= a^{ice} \ln\left(\frac{b^{ice} + T}{b^{ice}}\right)$$

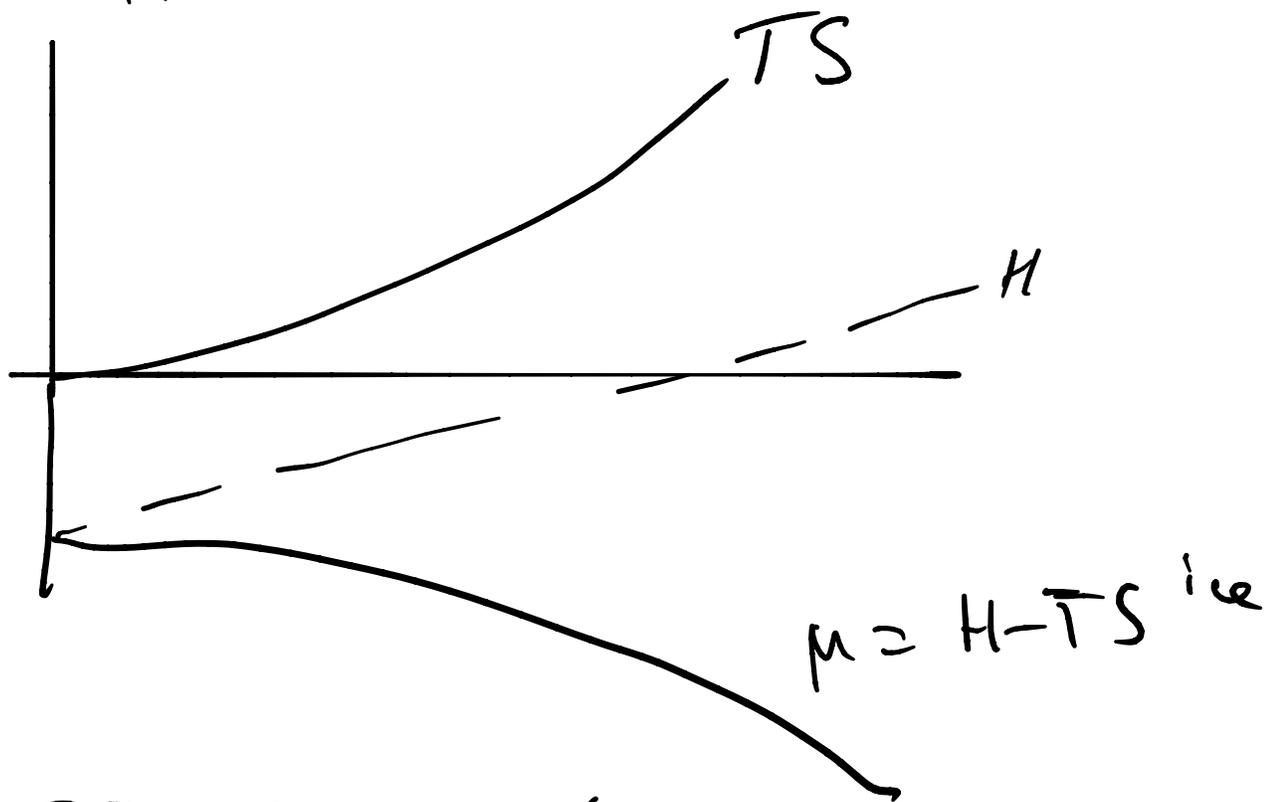$$\Delta S^{ice}(T_m) = 0.041$$

$$\Delta S^{liq}(T_m) = S^{ice} + 0.063$$

To get to T_v

$$H^\ell(T_v) = H^\ell(T_m) + \int_{T_m}^{T_v} C_p^{liq} \, dT$$

$$S^\ell(T_v) = S^\ell(T_m) + \int_{T_m}^{T_v} C_p^{liq}/T \, dT$$

can you do it?

Plot H^{ice} & TS^{ice}

① @ $T = 0$, $\mu = H$

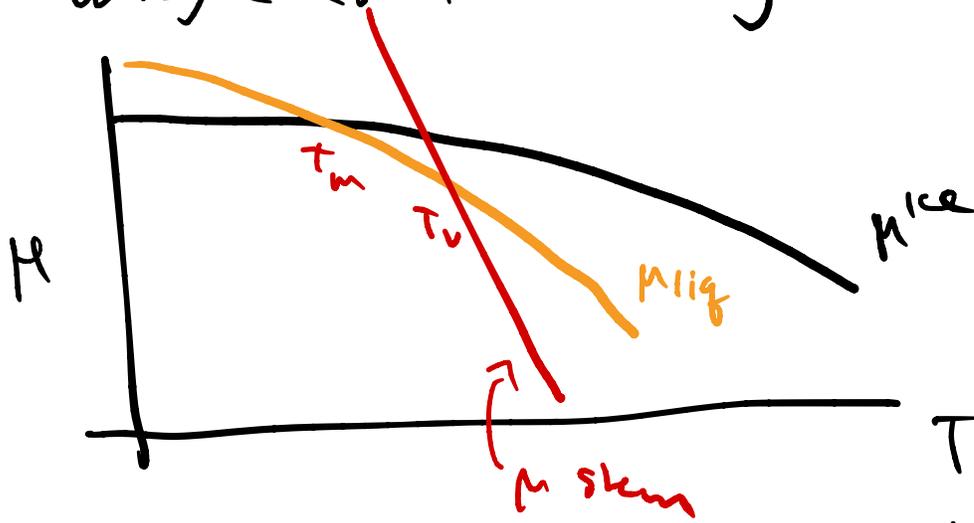② $\overline{C_p}^{ice} = \left(\frac{\partial H^{ice}}{\partial T} \right)$ ⟹ slope > 0 always for H

③ $\left(\frac{\partial S}{\partial T} \right)_p = \overline{C_p}/T$ ⟹ S increases w/ T

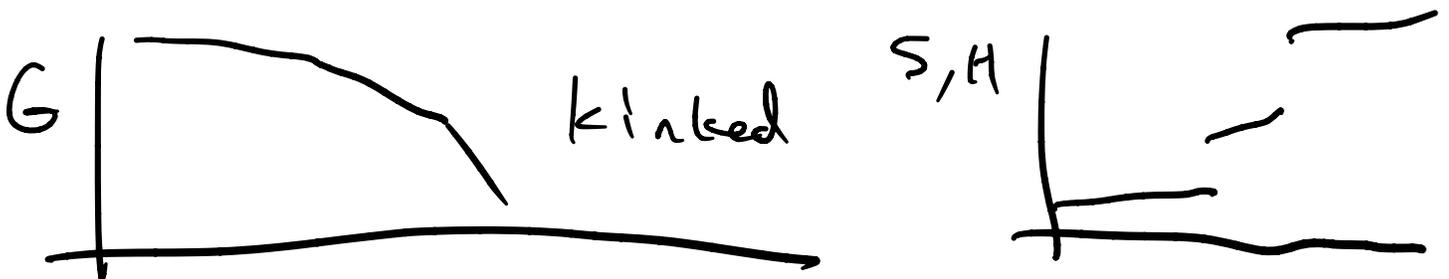④ $\left(\frac{\partial \mu}{\partial T} \right)_p = -S$, decreases
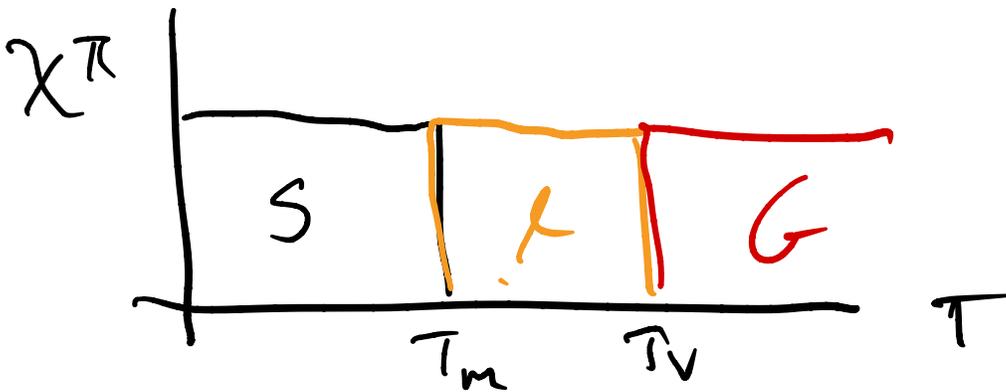
⑤ $\frac{\partial^2 \mu}{\partial T^2} = -\frac{\partial S}{\partial T} = -C_p/T$ so concave down

So ice seems to be getting lower in Chemical potential w/ $T \rightarrow$ why doesn't it stay ice?

μ^{ice}
μ^{liq}
T_m
T_v
μ steam
μ
T

In practice, only in most stable phase

$$G = \sum x^\pi \mu^\pi \qquad H = \sum x^\pi \bar{H}^\pi \qquad S = \sum x^\pi \bar{S}^\pi$$

x^π
S   l   G
T_m T_v T

G   kinked

S, H

C $\Leftarrow$ diverges at special pts

How does pressure influence
chemical potential/phase?
Strongest influence on gas

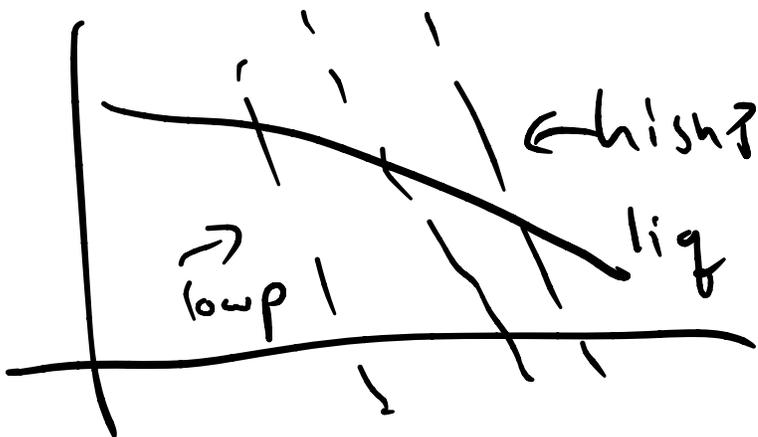$$d\hat{G}^{\pi} = d\mu^{\pi} = -\bar{S}^{\pi}dT + \bar{V}^{\pi}dp$$

@ const T

$$d\mu^{steam} = \bar{V}dP = \frac{RT}{P}dp \quad \overset{ideal\ gas}{}$$

$$\Delta\mu = \int_{1atm}^{P} d\mu = RT\ln P/P_{ref}$$

$$= RT\ln p \quad \Leftarrow in\ atm\ units$$

Effect of pressure is to
shift μ steam line

←this?

liq

low p

shift boiling pt
@ 0.005 atm,
triple point
@ very high P, T
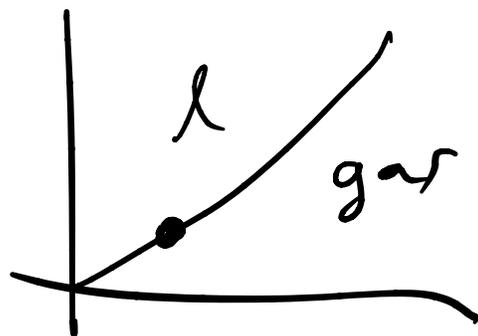critical pt, every prop same

Restrictions on phase diagram

$$n\,d\mu + s\,dT - V\,dp = 0 \quad \text{GD eqn}$$

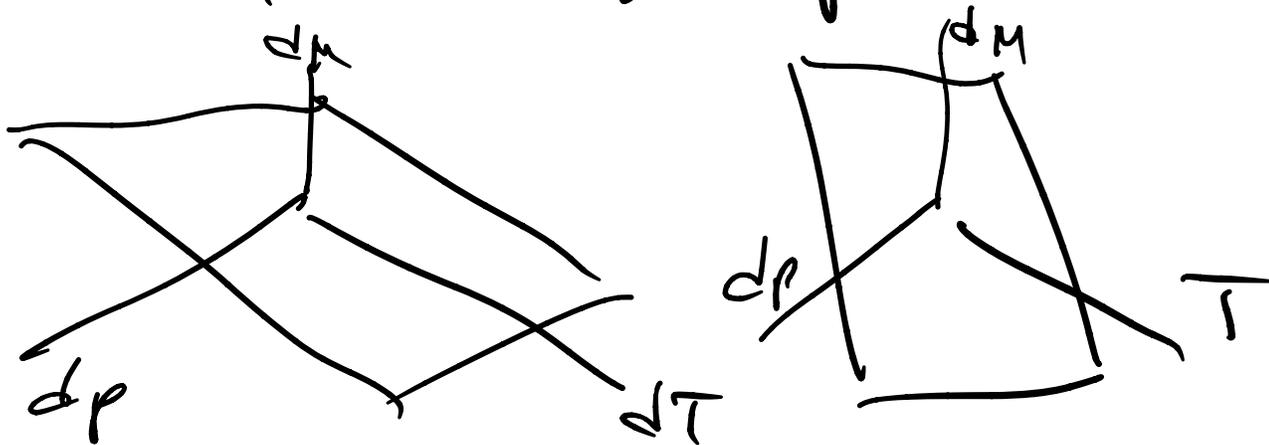$$\Rightarrow d\mu = -\bar{s}\,dT + \bar{V}\,dp,$$

one equation for each phase

Suppose

@ T & p where
μ's equal

most dT or dp Change μ by diff amnts

These eqns both give planes

Intersect at $dp = dT = 0$

also along a line

Can show from finding this line

that $\left(\frac{\partial p}{\partial T}\right)_{\substack{\mu \, phase \, 1 = \\ \mu \, phase \, 2}} = \frac{\Delta S^{1 \to 2}}{\Delta V^{1 \to 2}}$ ✳ ← eg $l \to v$

Claussius Clapyron Eqn

For most substances ΔV increases
(& ΔS always does) & positive
Water is notable exception (at room temp)
1 atm

Last, what about adding another phase & plane? Can show this puts a big restriction and $d\mu$'s all equal only at a point so there can be only one triple point for a single component

Gibbs phase rule

#Components − #phases + 2 = Degrees of freedom
                Coexisting

Dof is things you can vary and maintain equilibrium

1 component:	#phases		dof	
	1		2	P, V, T only 2 independent
	2		1	change T, have to change p also, etc

Last: for liq → gas

$$\left(\frac{\partial P}{\partial T}\right) = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

if $\Delta\bar{V} = \bar{V}^{gas} - \bar{V}^{solid/liq}$

@ $\bar{V}_{gas} \gg \bar{V}^{s/l}$

@ ideal $\Delta\bar{V} = \frac{RT}{P}$

Then $\frac{1}{P}\frac{\partial P}{\partial T} = \frac{\partial \log P}{\partial T} = \frac{\Delta\bar{H}}{RT^2}$

boil when pressure curves equal, 1 atm = 760 torr