Lecture 11 - Phase Equilibria

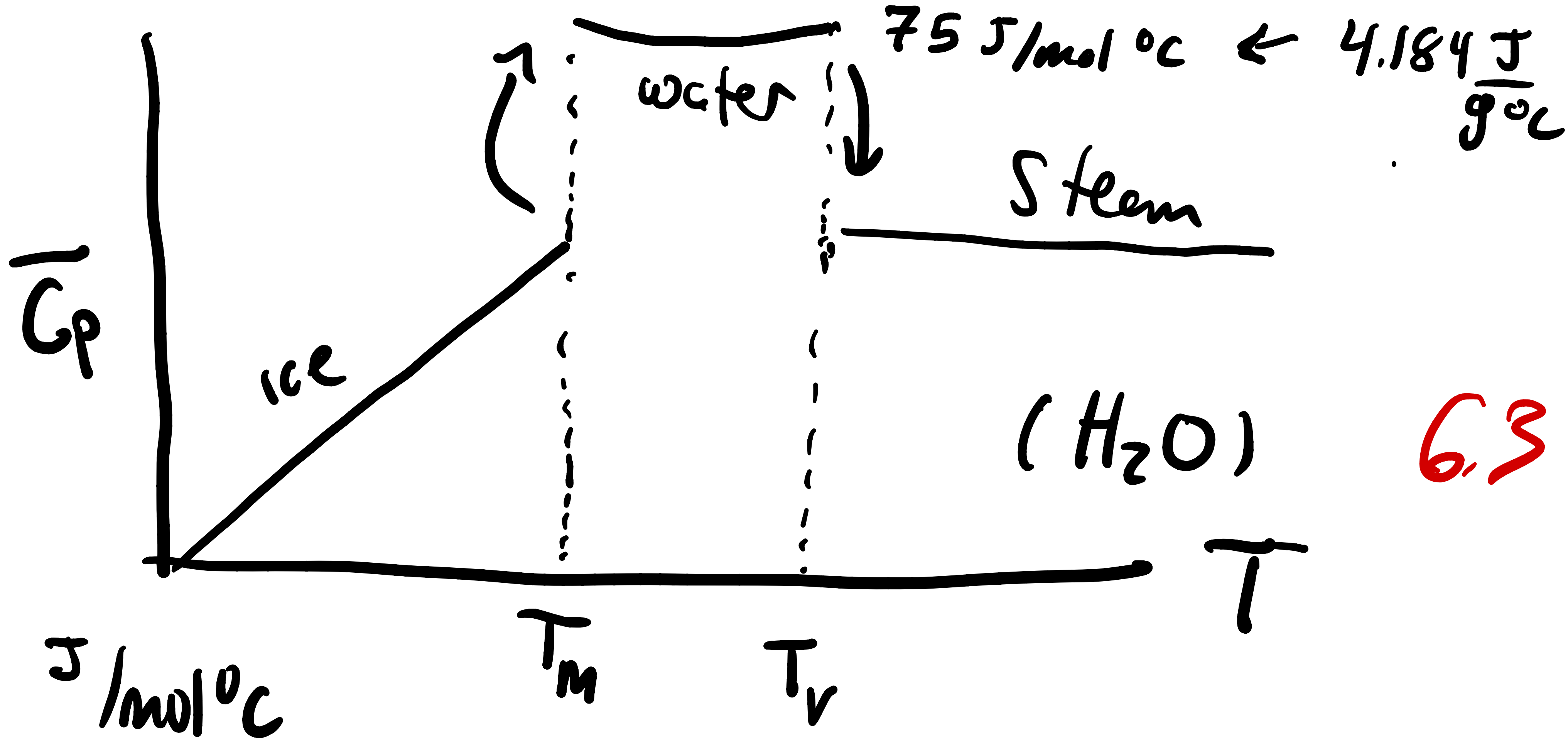
Why 1 phase over another

How does μ change with T & P

For each phase

$$\mu^{\pi} = \frac{G^{\pi}}{n^{\pi}} = \bar{H}^{\pi} - T\bar{S}^{\pi}$$

Heat capacity - depends on substance



6.3

? (low T heat capacity of solids)

$$C_p^{steam} = 36.3$$

$$C_p^{l} = a + bT + CT^2 = 101 - 0.165T + 2.56\times10^{-4}T^2$$

$$C_p^{s} = aT/(b+T) = \frac{228.3T}{1387+T}$$

want $\mu^{\pi} = \bar{H}^{\pi} - T\bar{S}^{\pi}$

$$dH = d(E + PV) = dE + pdV + Vdp$$

$$= (dq - PdV) + PdV + VdP$$

$$= dq + VdP = TdS + VdP$$

@ const P

$$dH = \underline{dq} = TdS = \underline{C_p dT}$$

$$dH = C_p dT$$

$$dS = \frac{C_p}{T} dT$$

To do integral, start at some reference temperature

$$S(T=0) = 0$$

$$H(T_m) = 0$$

$$S(T) = \int_0^{T_m} \frac{C_p^{solid}}{T'} dT' + \int_{T_m}^{T_v} \frac{C_p^{liq}}{T'} dT'$$

$$+ \int_{T_v}^{T} \frac{C_p^{gas}}{T'} dT' + \Delta S^{fus}$$

$$+ \Delta S^{vap}$$

@ phase transition

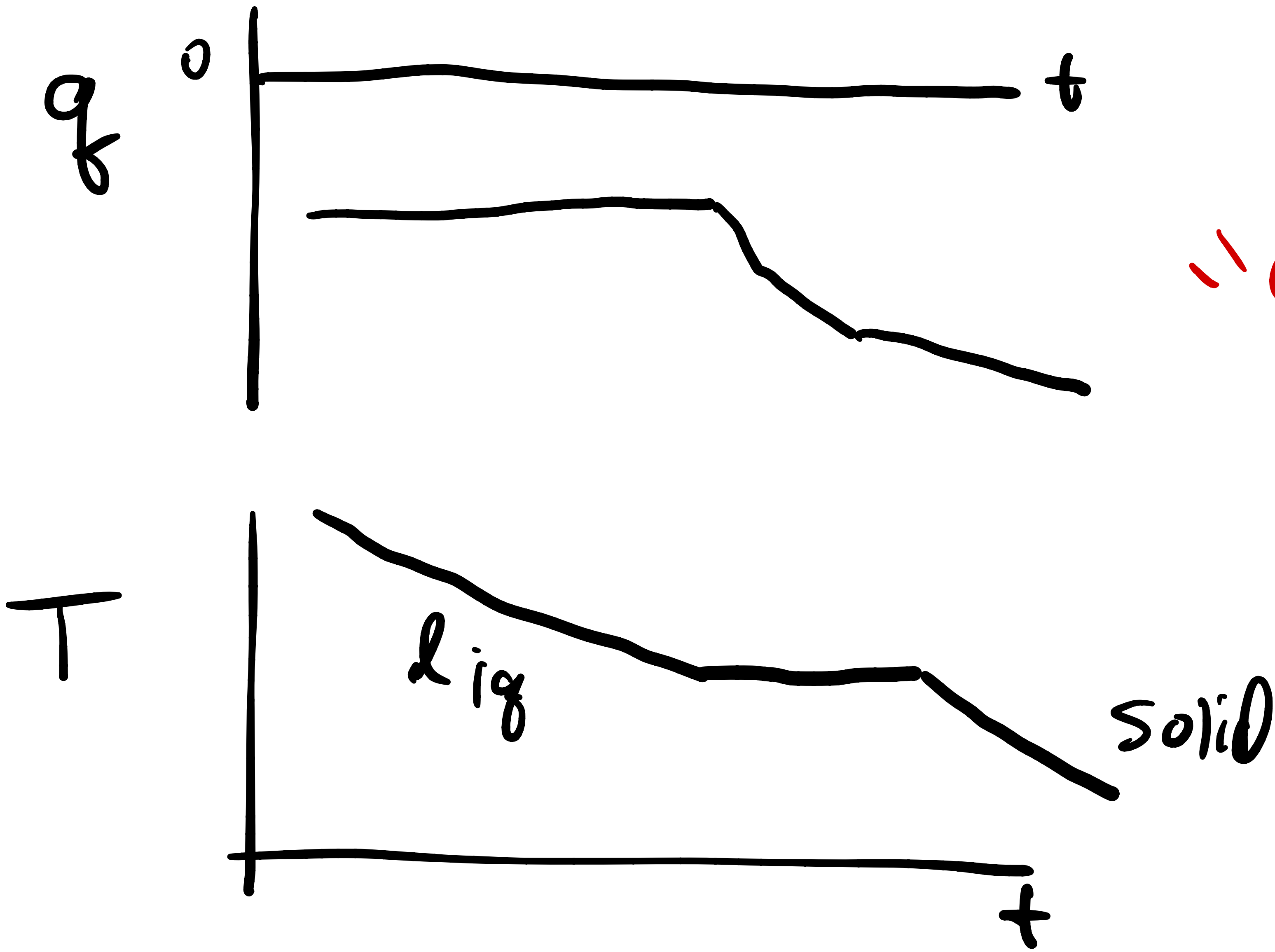
$$\Delta G^{fus} = 0 = \Delta H^{fus} - T_m \Delta S^{fus}$$

$$\Delta S^{fus} = \Delta H^{fus} / T_m$$

$$\Delta S^{vap} = \Delta H^{vap} / T_v$$

T_v & T_m come from discontinuities

$$\Delta H^{vap} = q^{vap} \qquad \Delta H^{fus} = q^{fus}$$



"cartoon"

Book: details of integrals

$\bar{H}(T)$ for H_2O

$\bar{S}(T)$ for H_2O

read section

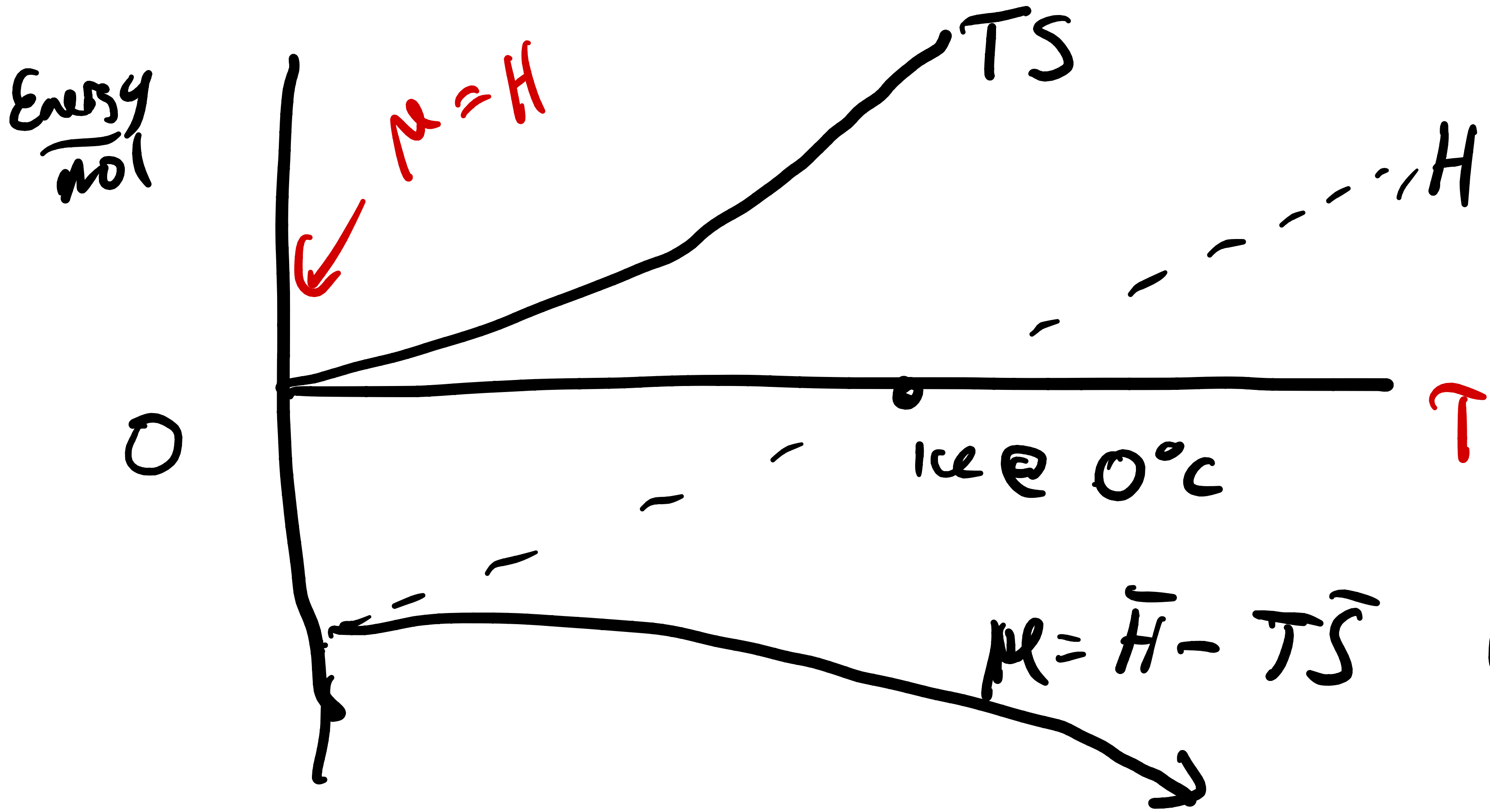
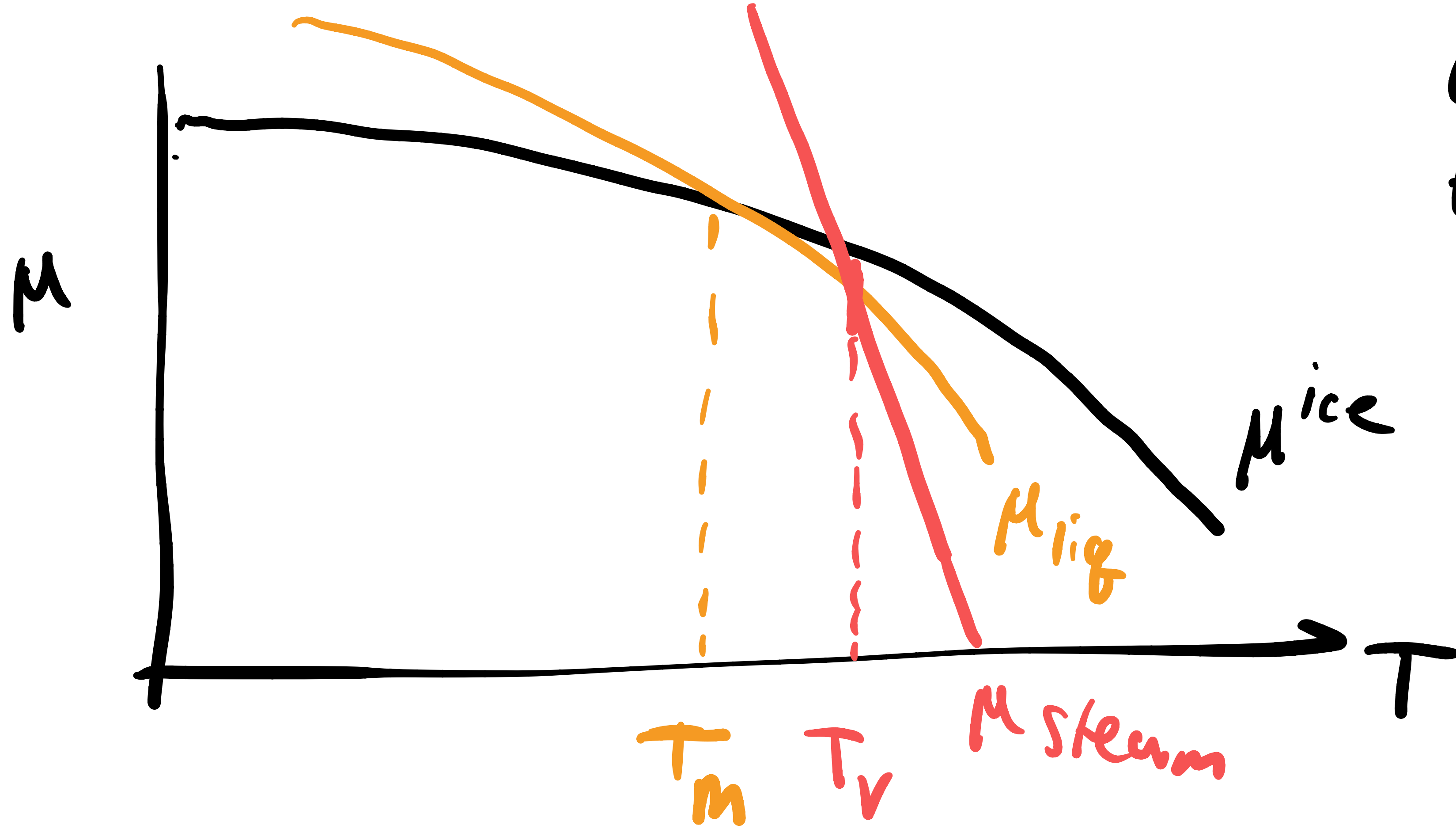


Fig 6.4

6.5 fig



$$\mu = \frac{G}{n}$$

$$G = H - TS$$

$$\mu = \frac{H}{n} - T\frac{S}{n}$$

$$= \bar{H} - \tilde{S}$$

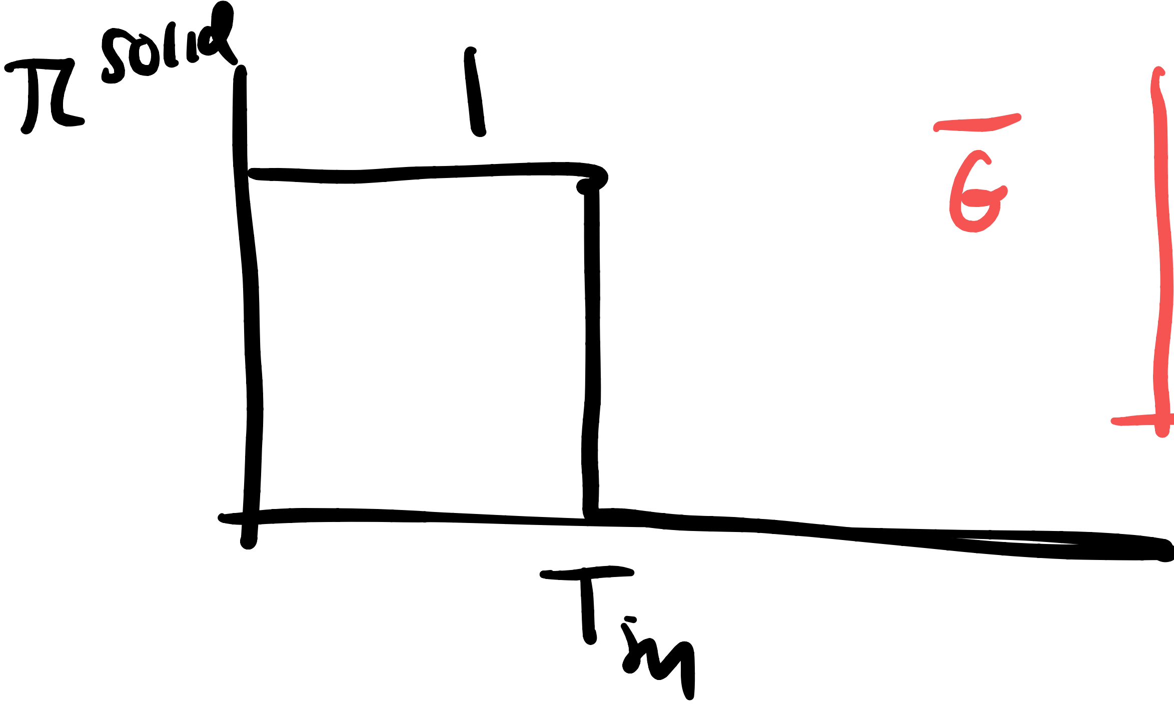
mixtures

$$\chi^{\pi} = \frac{n^{\pi}}{n_{total}}$$

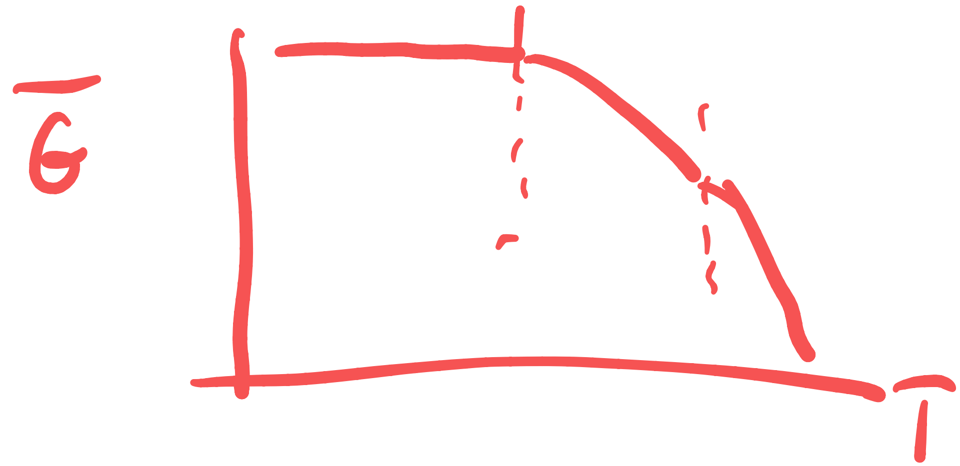
eg

$$\chi^{gas} = \frac{n^{gas}}{n_{solid} + n_{liq} + n_{gas}}$$

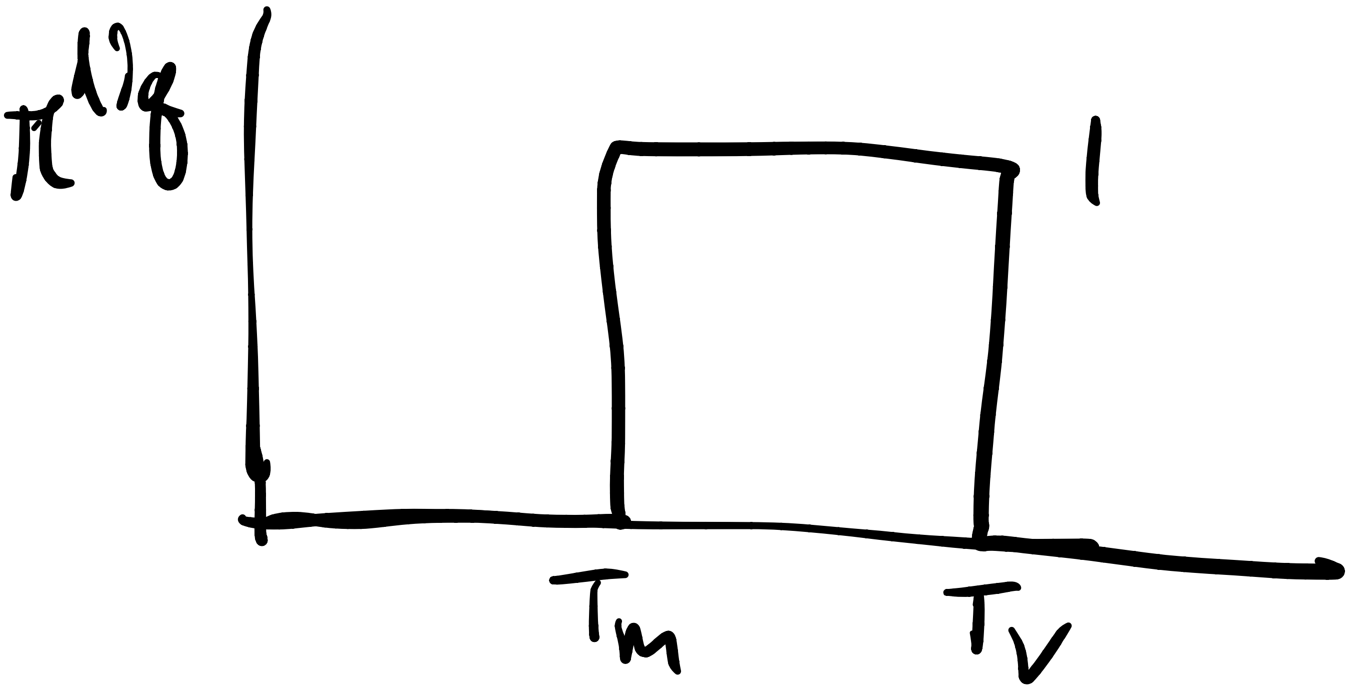
$$\overline{G} = \sum_{\pi} \chi^{\pi} \mu^{\pi}$$



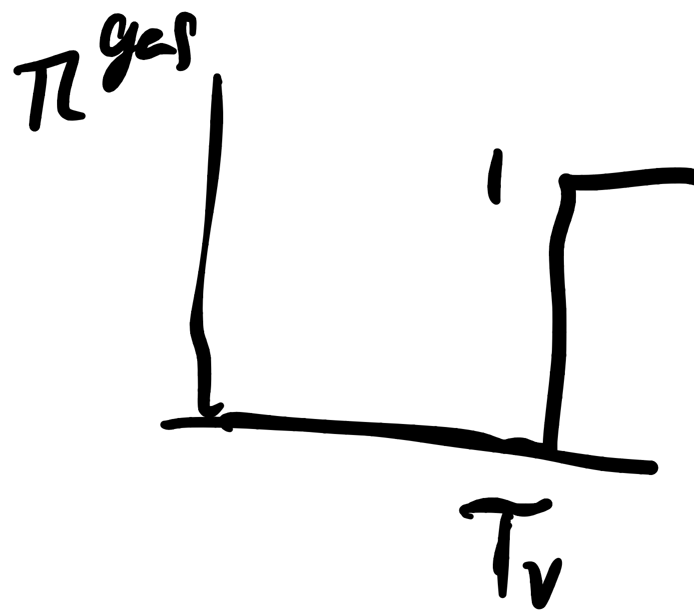
π^{solid}
1
T_m



$\bar{G}$
T



π^{liq}
1
T_m
T_v



π^{gas}
1
T_v

That was all constant pressure

What is effect of
being @ different fixed pressures

Biggest effect on gas
(What is the compressibility)

$$d\mu^{\pi} = \underbrace{-\bar{S}^{\pi} dT}_{@\,dT=0} + \bar{V}^{\pi} dP$$

$PV = nRT$

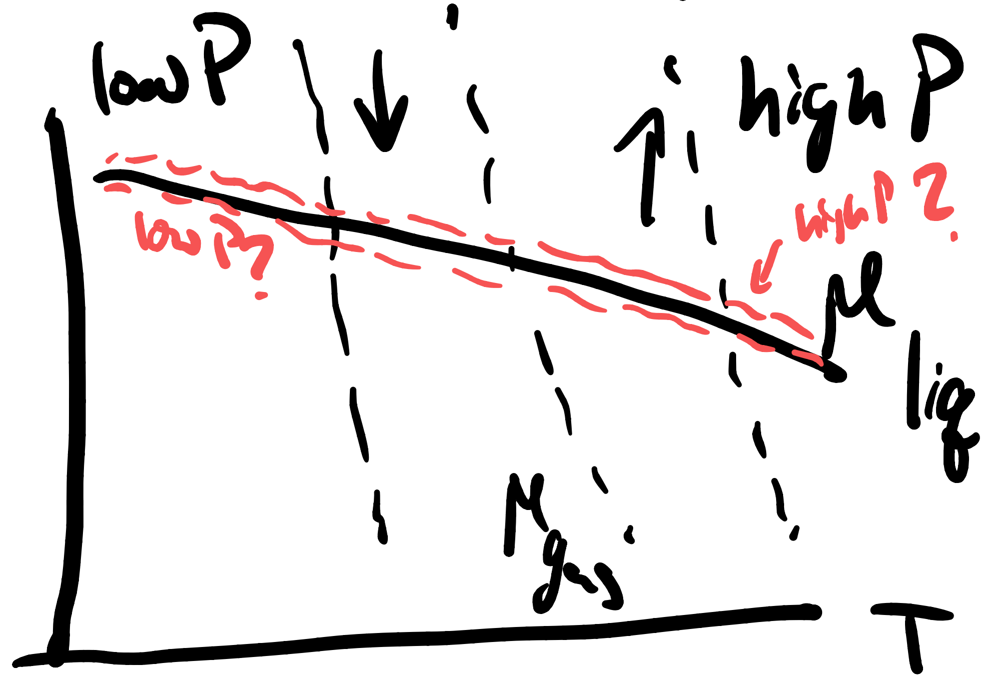
$\bar{V} = V/n$

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

if ideal gas

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

$$= RT \ln(P / 1\,atm)$$

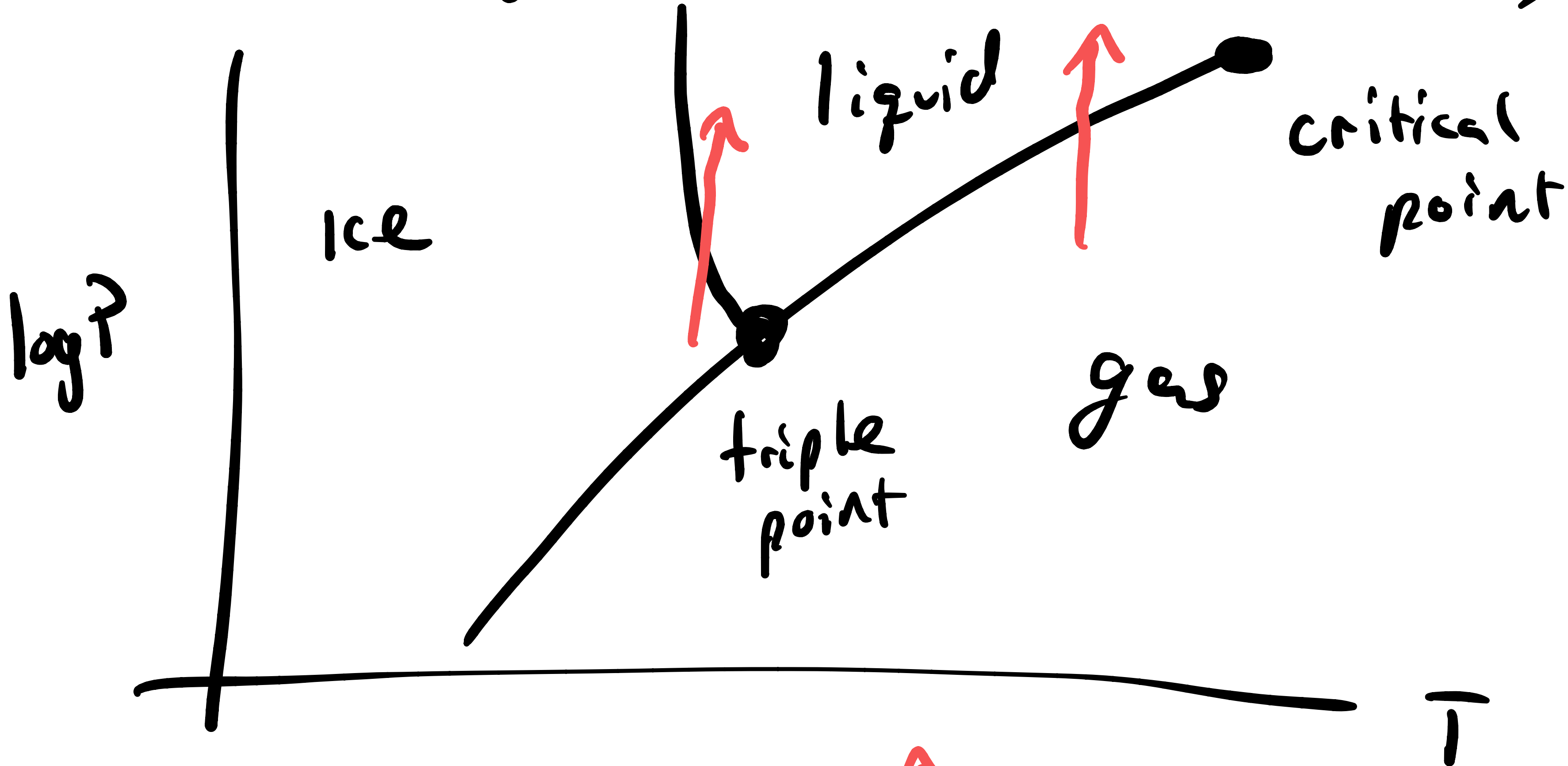


higher pressures
favor <u>phases</u> that are <u>denser</u>

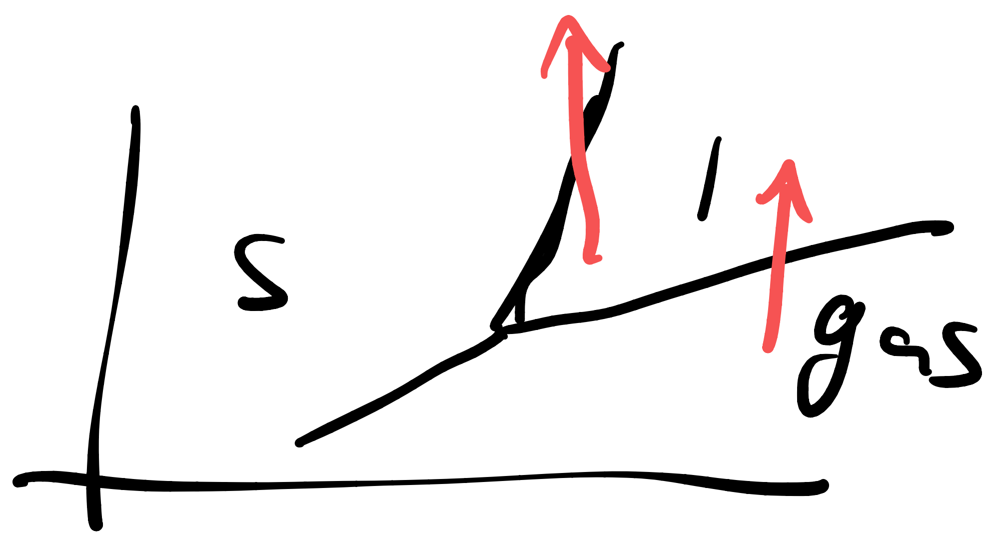
for water:
liq water is more dense
then solid ice

ice: $P\uparrow$ $T_m\downarrow$

Phase diagram of a system (H_2O)



other

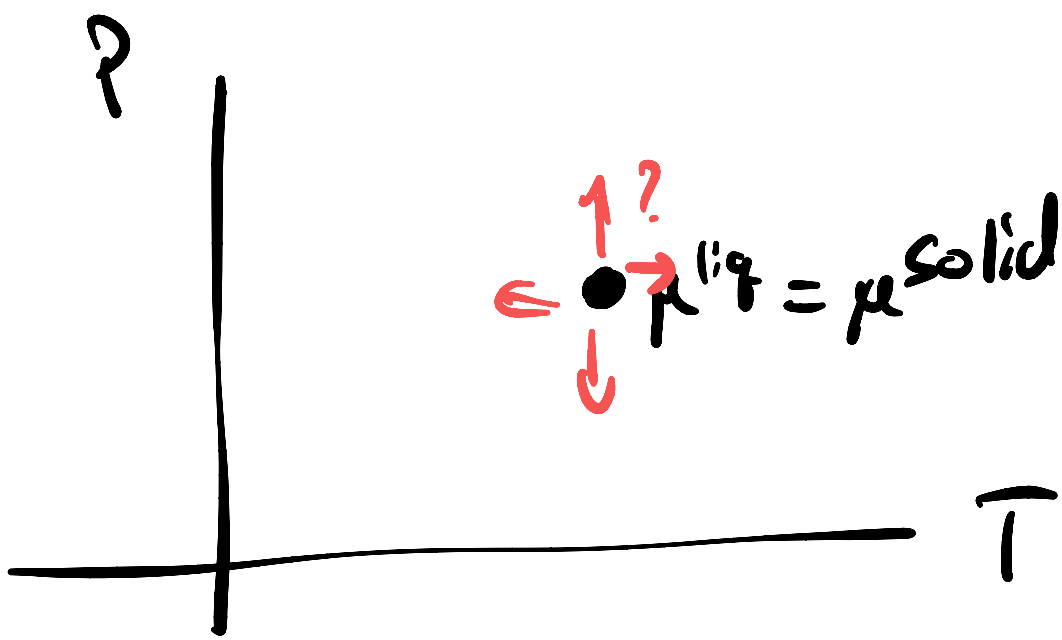


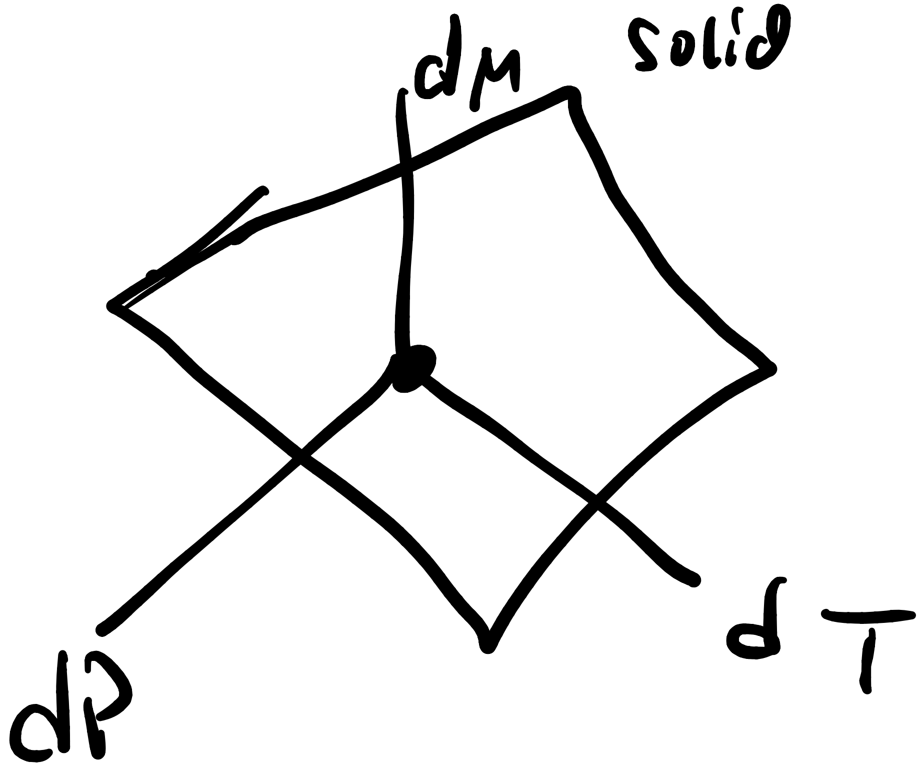
Restrictions on phase diagram

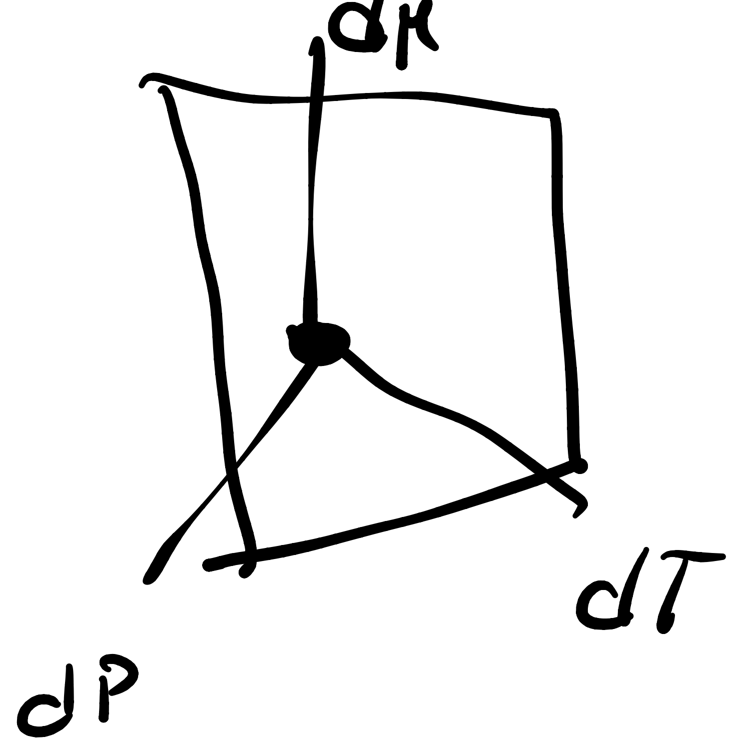
$$d\mu^{\pi} = \bar{V}^{\pi} dP - \bar{S}^{\pi} dT$$

One equation for each phase

when can they be equal







Intersect along a line

one line coexistence

Only 1 point where 3 phases can intersect this line has a slope

$$\left({}^{dP}/_{dT} \right) = \frac{\Delta \bar{S}^{1 \to 2}}{\Delta \bar{V}^{1 \to 2}}$$ ← next time

Claussius-Clapyron Equation

Gibbs-Phase Rule

components - # coexisting + 2 = Degrees of freedom

Things you can change & maintain eq