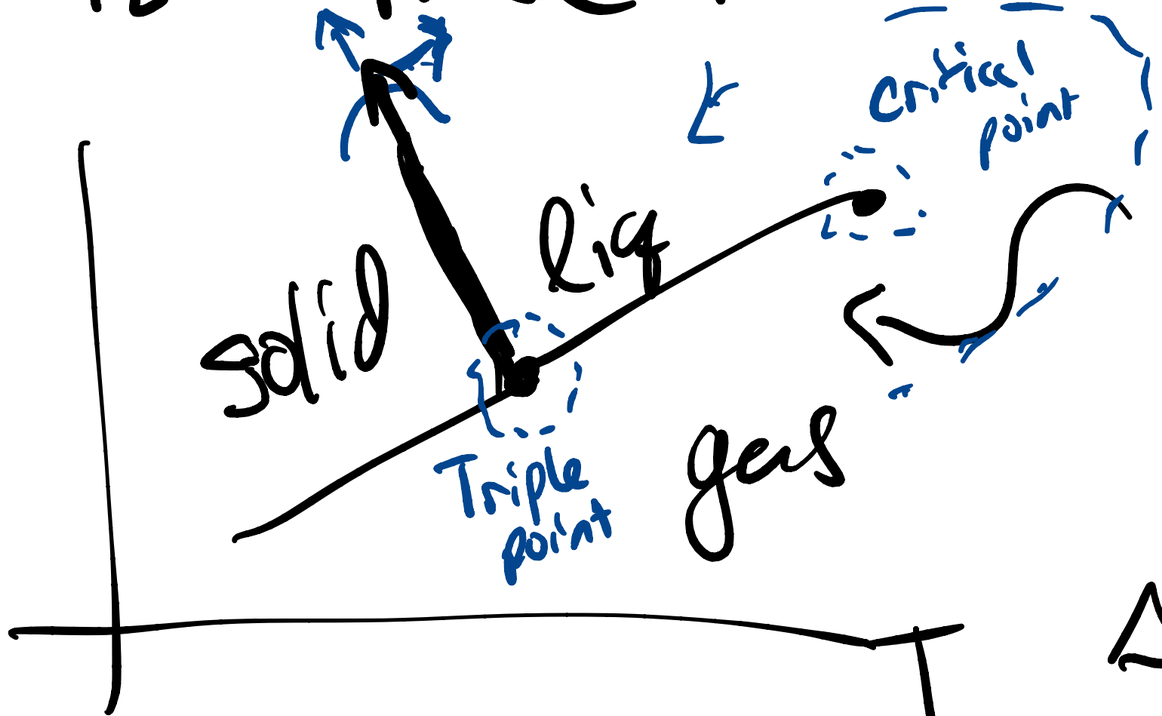
Lecture 12 - Phase transitions continued

Goal: P



lines mean

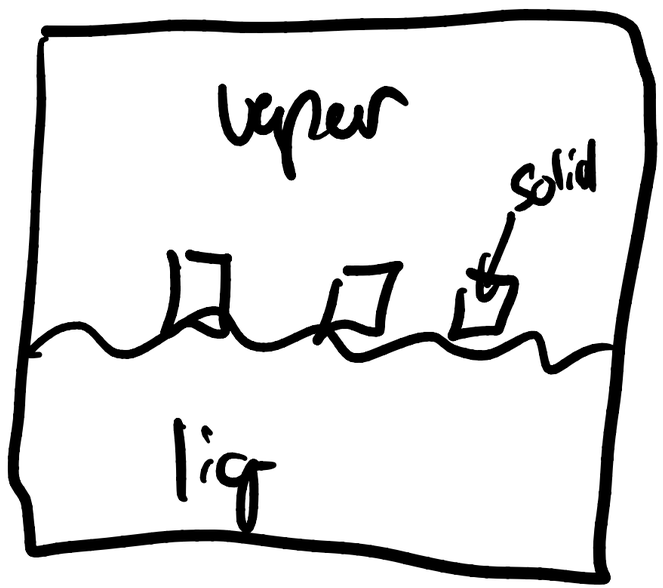
$\mu_{gas} = \mu_{liq}$ eq.

$\Delta G = 0$ on line

$$G(P, T, n_1, n_2, \ldots)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \sum_i \underbrace{\left(\frac{\partial G}{\partial n_i}\right)}_{\mu_i} dn_i \quad \begin{matrix} n_i \neq n_j \\ T, P \end{matrix}$$

Why is a phase transition, similar to a mixture?



$$n_{total} = n_{liq} + n_{solid} + n_{gas} + n_{interfaces}$$

$$dG = VdP - SdT + \sum_{i=1}^{K} \mu_i dn_i$$

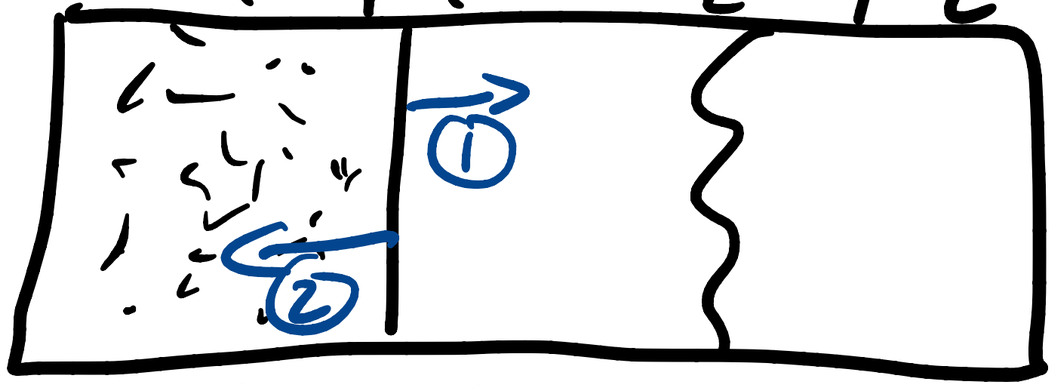
$$\underset{\substack{@\ dP=0 \\ dT=0}}{=} \sum_{i=1}^{K} \mu_i dn_i$$

Gibbs-Duhem relation $dG = VdP - SdT + \sum n_i d\mu_i$

$$dG = \sum_{i=1}^{K} n_i d\mu_i = 0 \quad @ \text{ eq}$$

think about only 2 components

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad @ \text{ equilibrium}$$



① $T < T_m$

② $T > T_m$

$$dG = \mu^s dn^s + \mu^l dn^l$$

$$n_{total} = n^l + n^s$$

$$dn_{total} = 0 = dn^l + dn^s$$

$$dG = \mu^s dn^s + \mu^l dn^l$$

$$0 = dn^s + dn^l \Rightarrow dn^s = -dn^l$$

$$dG = (\mu^s - \mu^l) dn^s$$

$$= (\mu^l - \mu^s) dn^l$$

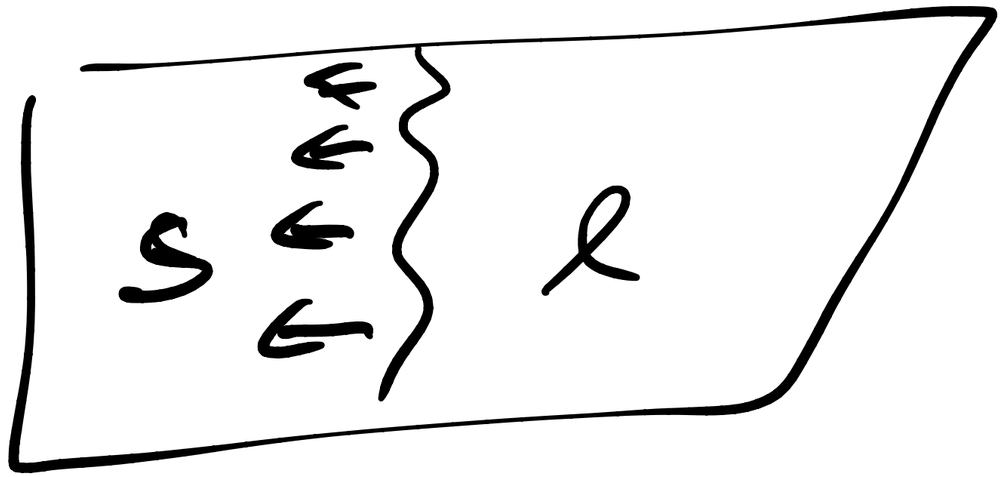
Spontaneous event $dG < 0$

$$(\mu^s - \mu^l) dn^s < 0$$

<0 >0

>0 <0

becomes equal when $\mu^s = \mu^l$



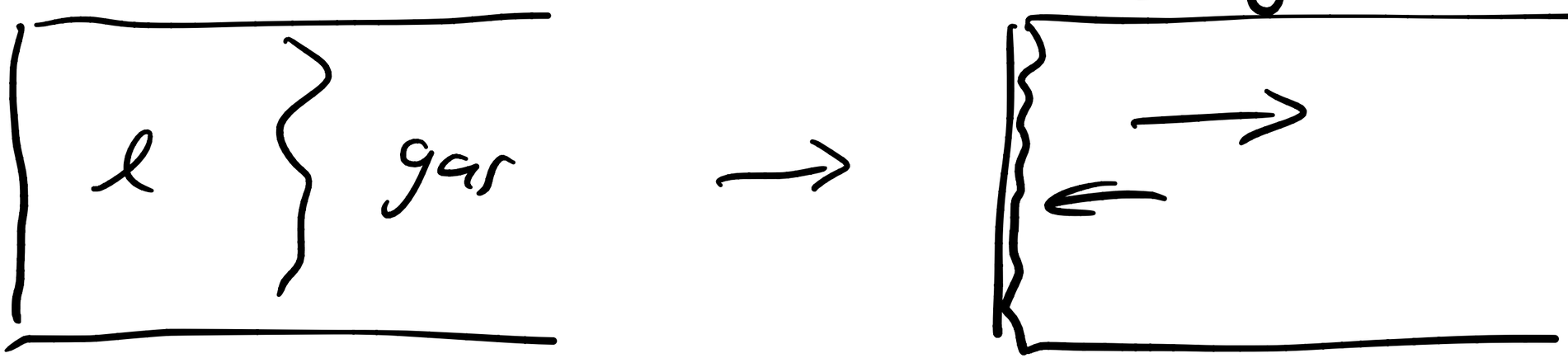
eq $T > T_m$ wants to melt

$\mu^s > \mu^l$

$dn^s \downarrow \quad dn^l \uparrow$

"coexistance"

@eq $\mu^l = \mu g$



$$\Delta V = (\bar{V}^s - \bar{V}^l)\,dn^s = (\bar{V}^l - \bar{V}^s)\,dn^l$$

ΔV: molecules occupying

when you melt, $dn^s < 0$

So does volume go up or down when you melt

Most materials, $\bar{V}^l > \bar{V}^s$.

Main exception is water, opposite is true

Another key quantity, heat flow

(turns out) $dq = (\bar{H}^s - \bar{H}^\ell) dn^s$

melting $dn^s < 0$

usually $\bar{H}^s < \bar{H}^\ell$

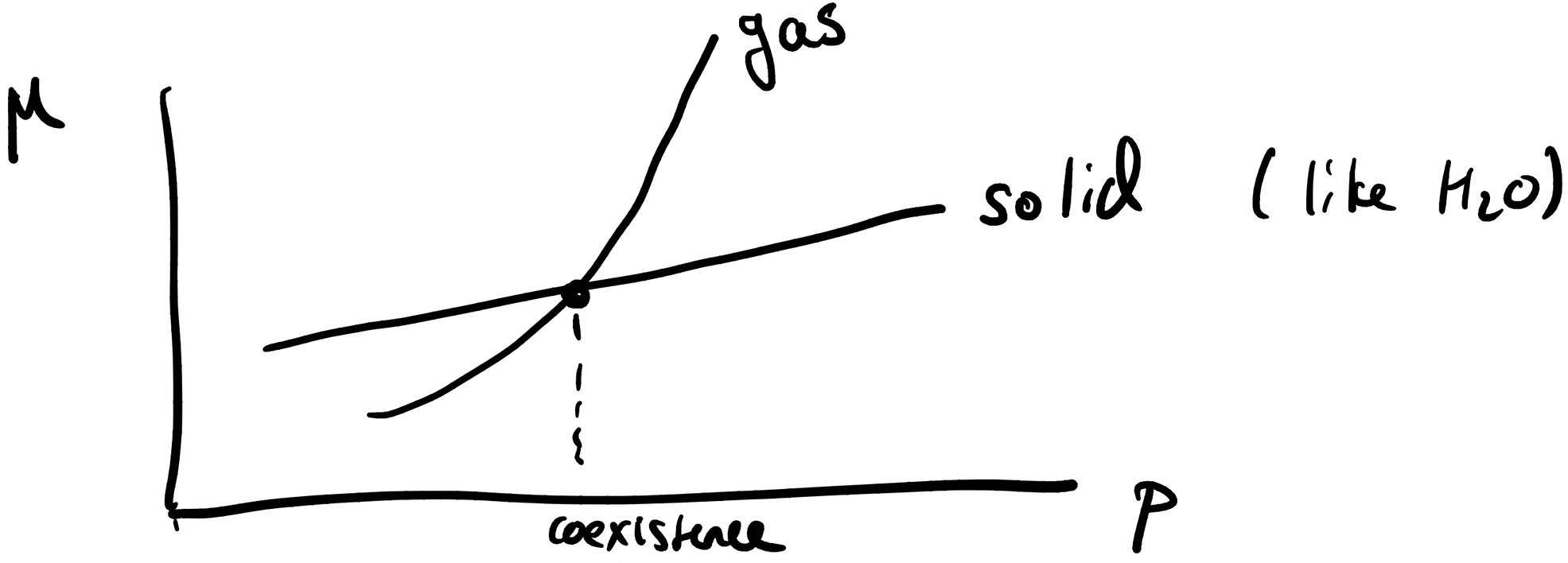
but you need to know H

$dH = c_p dT = dq$

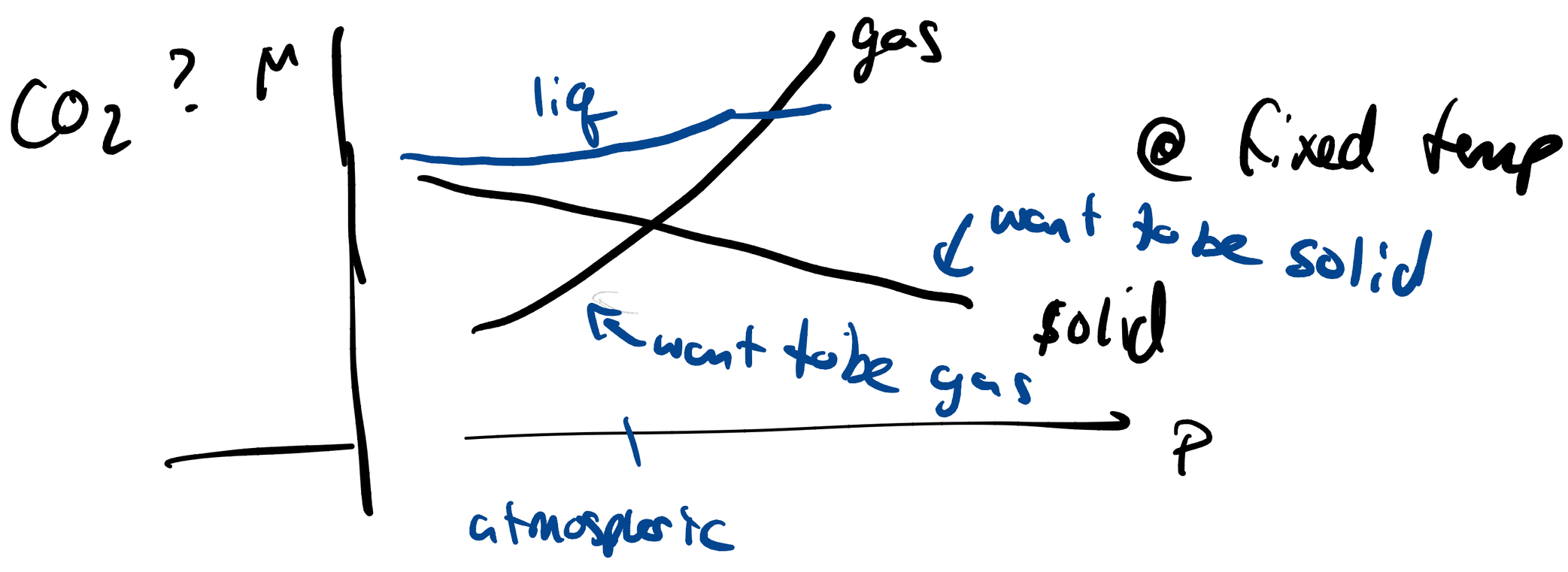
When are two phases equally likely

$$\mu^\alpha = \mu^\beta$$

how does μ depend on P, T



which line is lower



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

@ eq $\quad \bar{H}^{l} - T^{*}\bar{S}^{l} = \bar{H}^{s} - T^{*}\bar{S}^{s}$

$$T_m = T^{*} = \Delta\bar{H} / \Delta\bar{S}$$

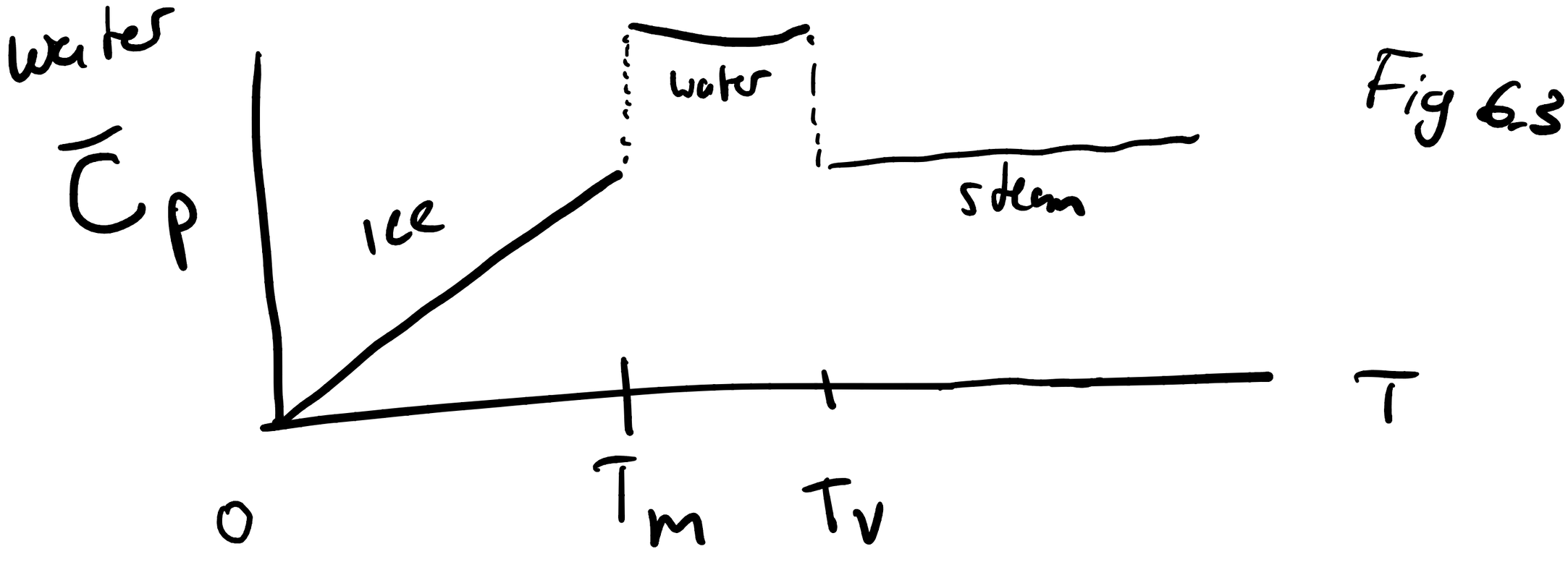


Fig 6.3

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

$$dH = C_p dT \quad > \quad d\bar{H} = \bar{C}_p dT$$

$$dS = C_p/T \, dT \qquad d\bar{S} = \bar{C}_p/T \, dT$$

Do integral from $T=0$ up to T of system

Have to have a reference temperature for S & H

$S(T=0) = 0$ (3rd law of thermo. for a perfect crystal) or a reference

$H(T=T_m) = 0$ of crystal

for S

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

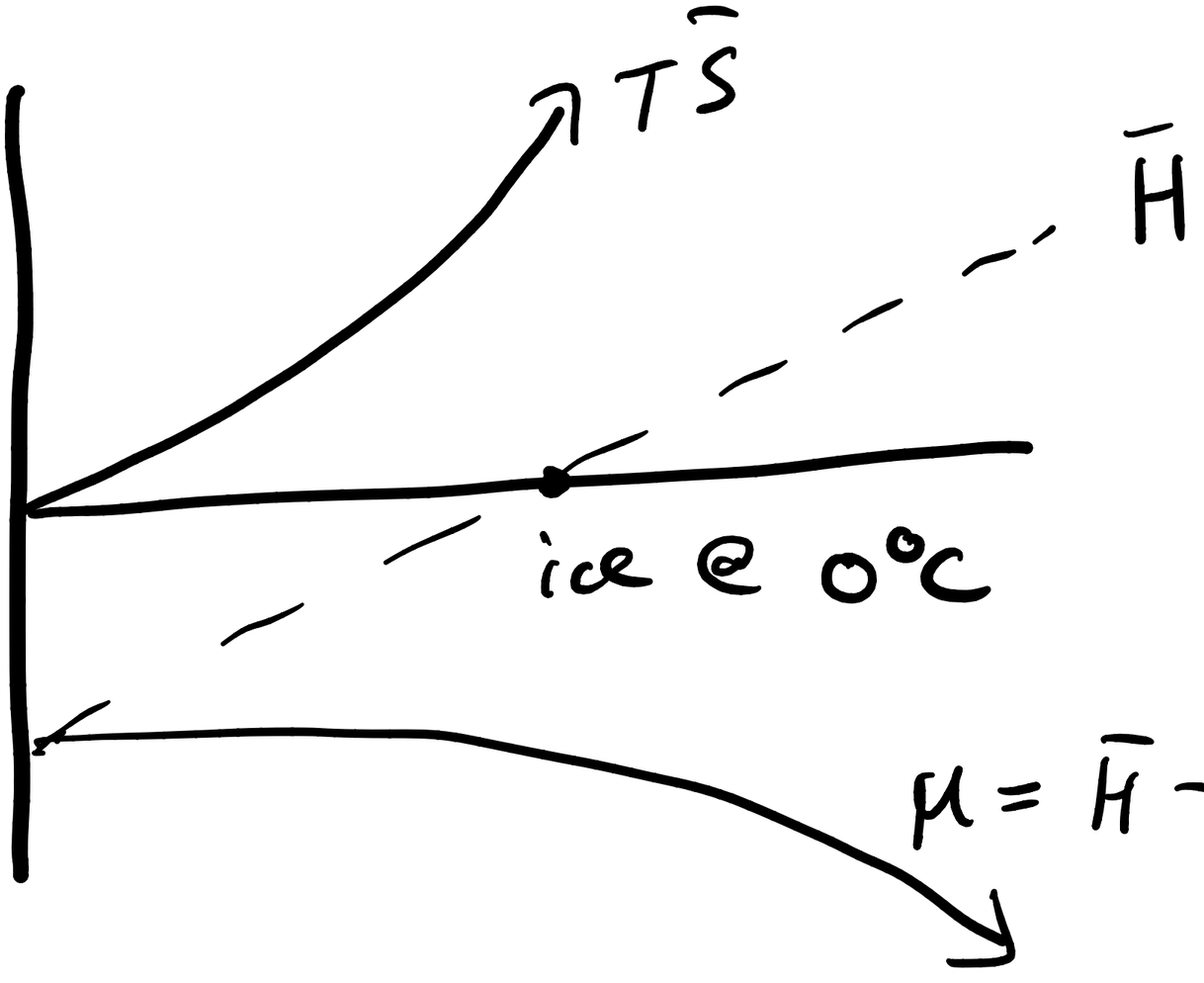
$$+ \int_{T_v}^{T'} \frac{C_p^{gas}(T)}{T} dT + \Delta S^{fus} + \Delta S^{vap}$$

Similarly for H

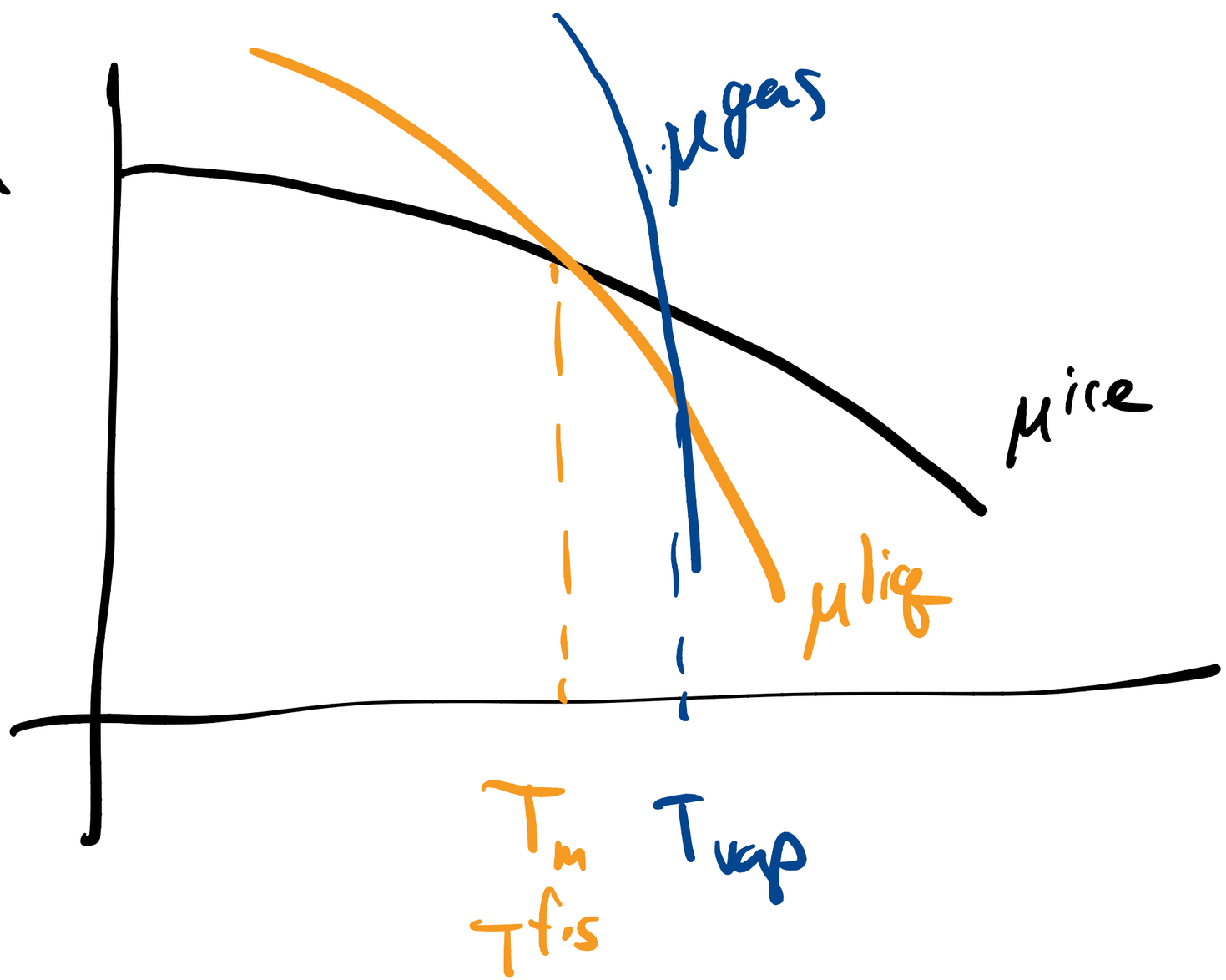
$$T^* = \frac{\Delta H^*}{\Delta S^*}$$

$\Delta S^{fus} = \Delta H^{fus} / T^{fus}$ ← heat that flows in

for water, fig 6.4



looks like ice becomes more favorable as $T\uparrow$



@ const P