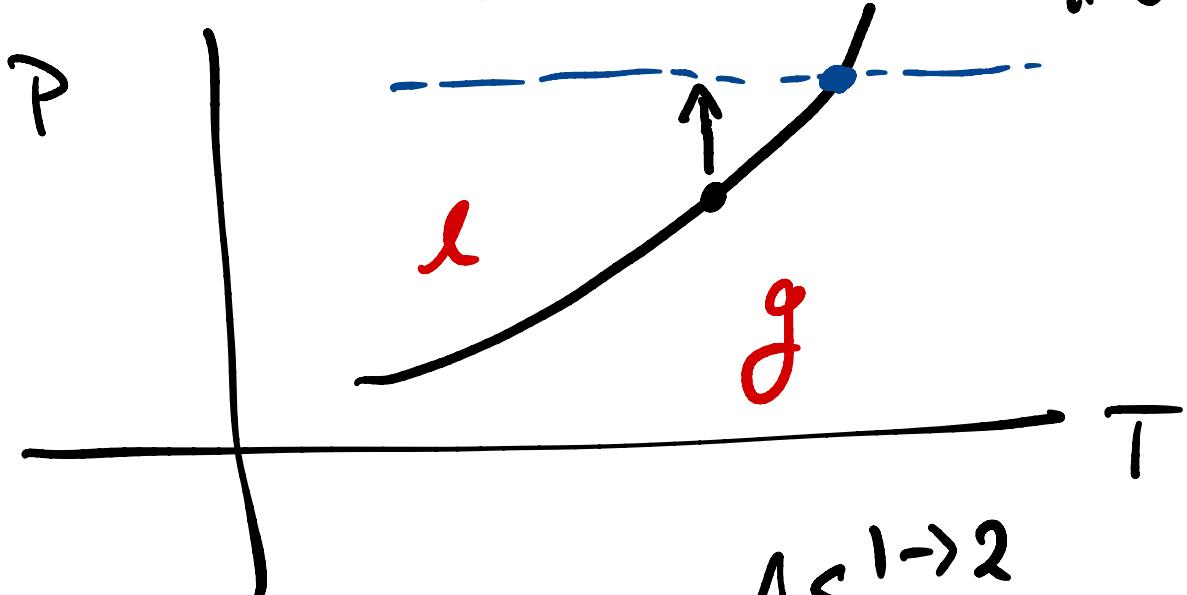


Claussius-Clapeyron equation

line - equal
chemical
potentials



$$\left(\frac{\partial P}{\partial T}\right)_{\mu \text{ phase 1} = \mu \text{ phase 2}} = \frac{\Delta S^{1 \rightarrow 2}}{\Delta V^{1 \rightarrow 2}}$$

$$\left(\frac{\partial P}{\partial T}\right) = \frac{\Delta \bar{S}^{1 \rightarrow 2}}{\Delta \bar{V}^{1 \rightarrow 2}} = \frac{\Delta \bar{H}^{1 \rightarrow 2}}{T \Delta \bar{V}^{1 \rightarrow 2}}$$

$$\Delta \bar{G} = \Delta \bar{H} - T \Delta \bar{S} = 0$$

$$\Rightarrow \Delta \bar{S} = \frac{\Delta \bar{H}}{T}$$

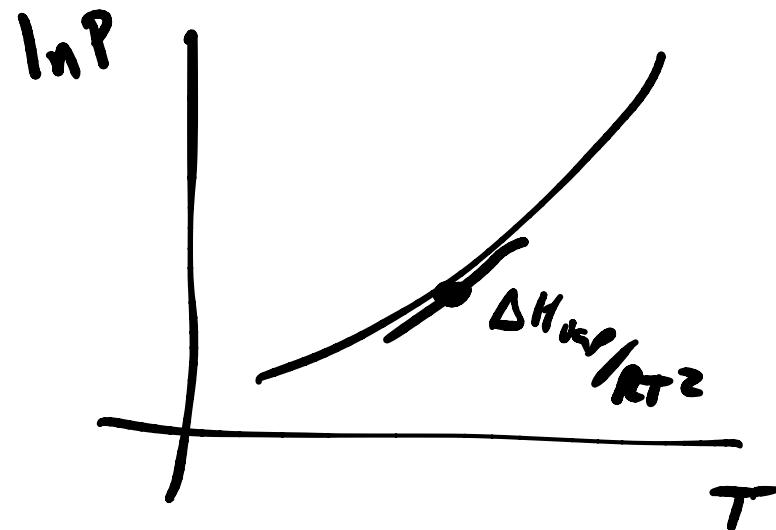
(of melting, or
vaporization)

for $l \rightarrow \text{gas}$

$$\Delta \bar{V} = \bar{V}_{\text{gas}} - \bar{V}_{\text{liq}} \approx \bar{V}_{\text{gas}} \approx \frac{RT}{P}$$

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

$$\frac{\partial \ln P}{\partial T} = \frac{\Delta \bar{H}_{vap}}{RT^2}$$

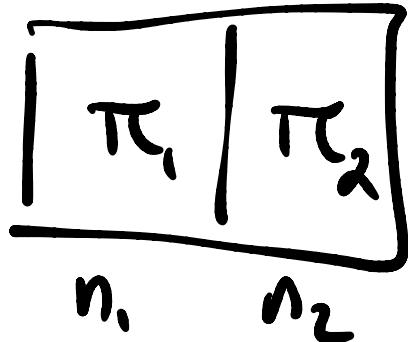
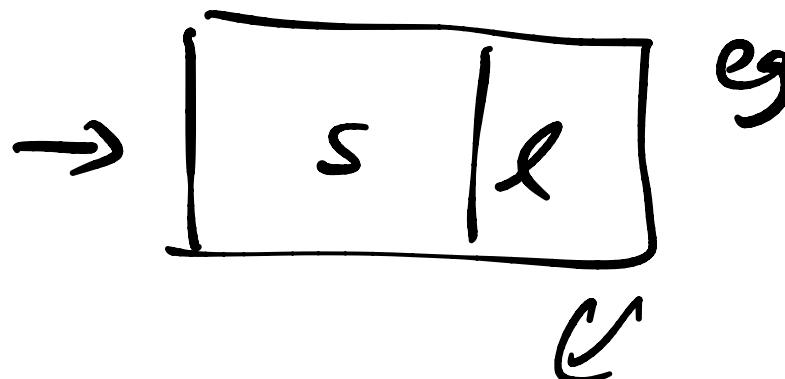
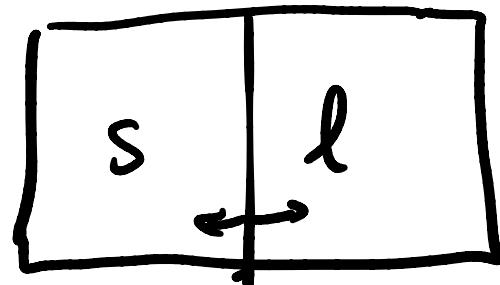


$\int dP$ $\int dT$ assuming $\Delta \bar{H}_{vap}$ is const

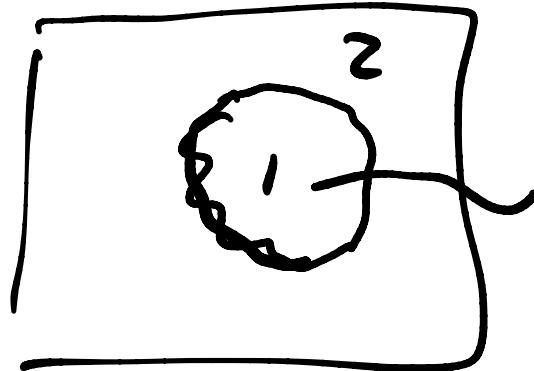
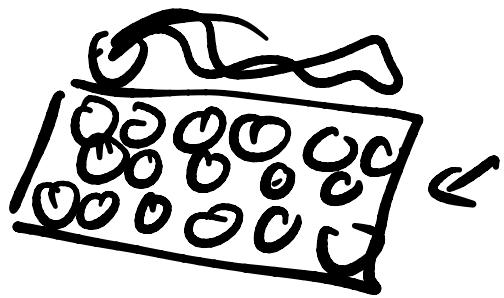
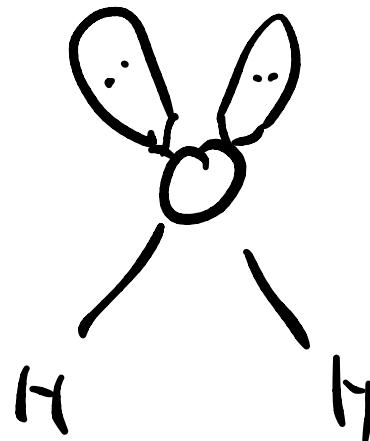
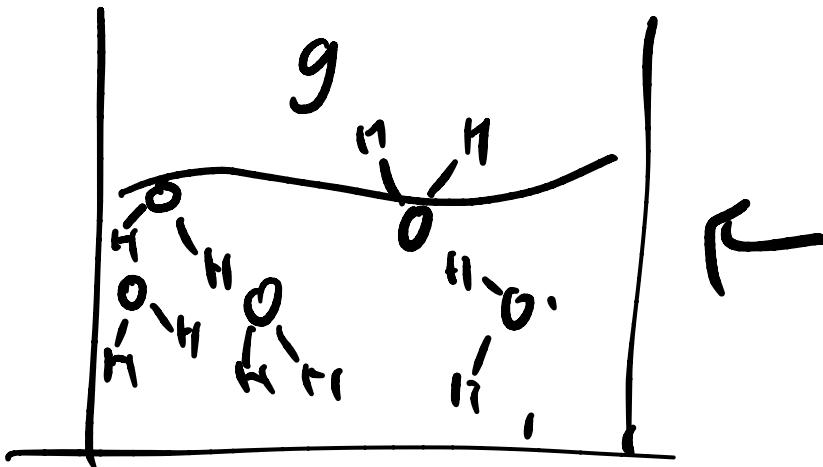
$$\ln \frac{P}{P_{ref}} = - \frac{\Delta \bar{H}_{vap}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right)$$

Chemical potentials and mixtures

Similar to phase



$$G = n_1 \mu_1 + n_2 \mu_2 \text{ (+ interface)}$$
$$\tilde{n}_1 \cdot h_1 \mu_1^* + n_2 \mu_2^*$$

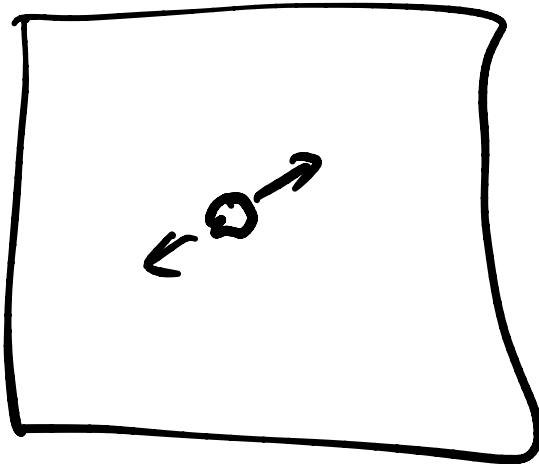


$$\mu_1 n_1 \leftarrow v_1 \\ \uparrow l^d + \mu_2 n_2 \leftarrow v_2$$

$$+ \gamma \cdot l^{d-1} \leftarrow r^{2/3}$$

Surface
Tension

$$10^{14} / 10^{21}$$



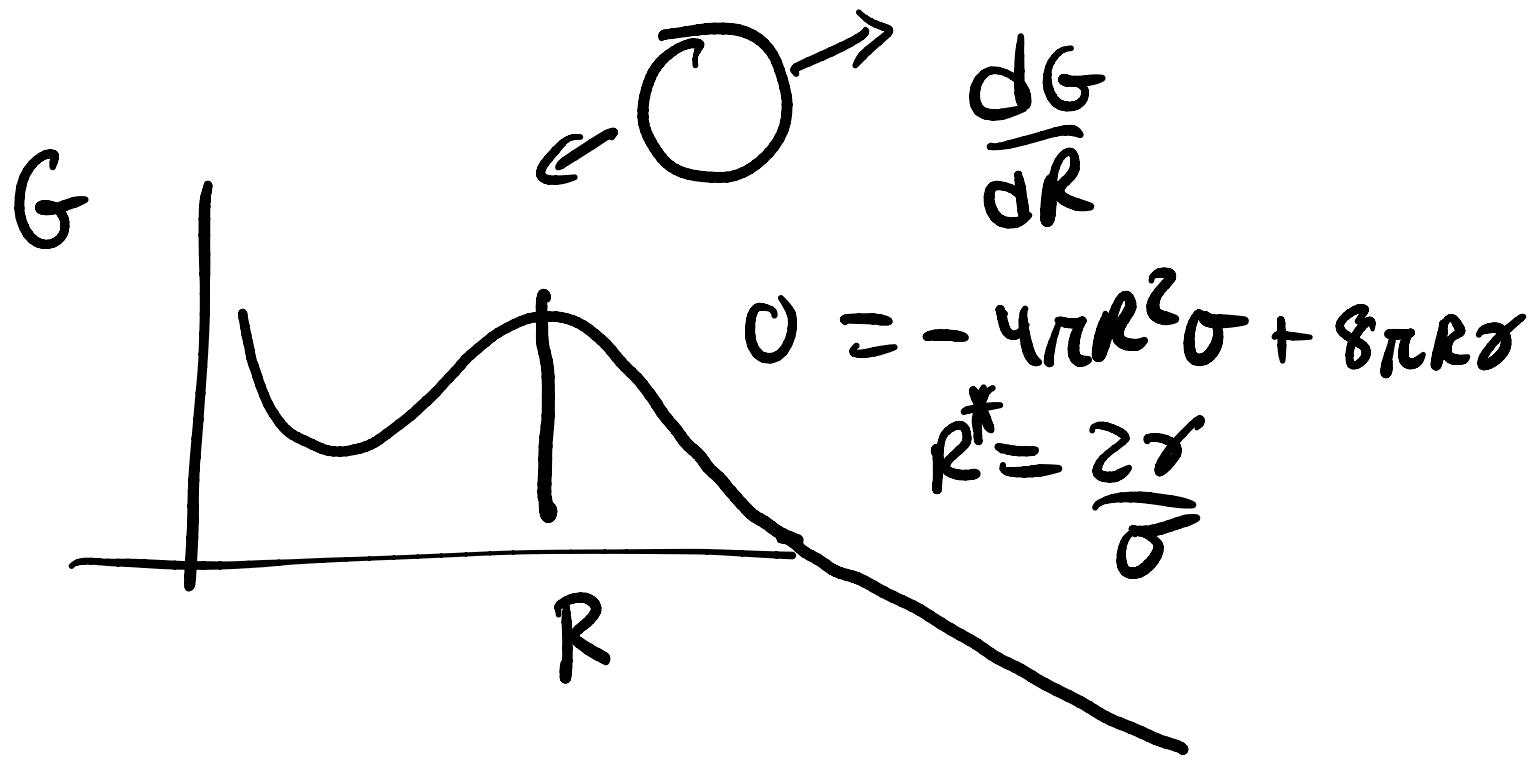
Crystallization
classical nucleation
theory

$$G = -\frac{4}{3} \pi R^3 \cdot \sigma + 4 \pi R^2 \gamma$$

↑
energy/volume

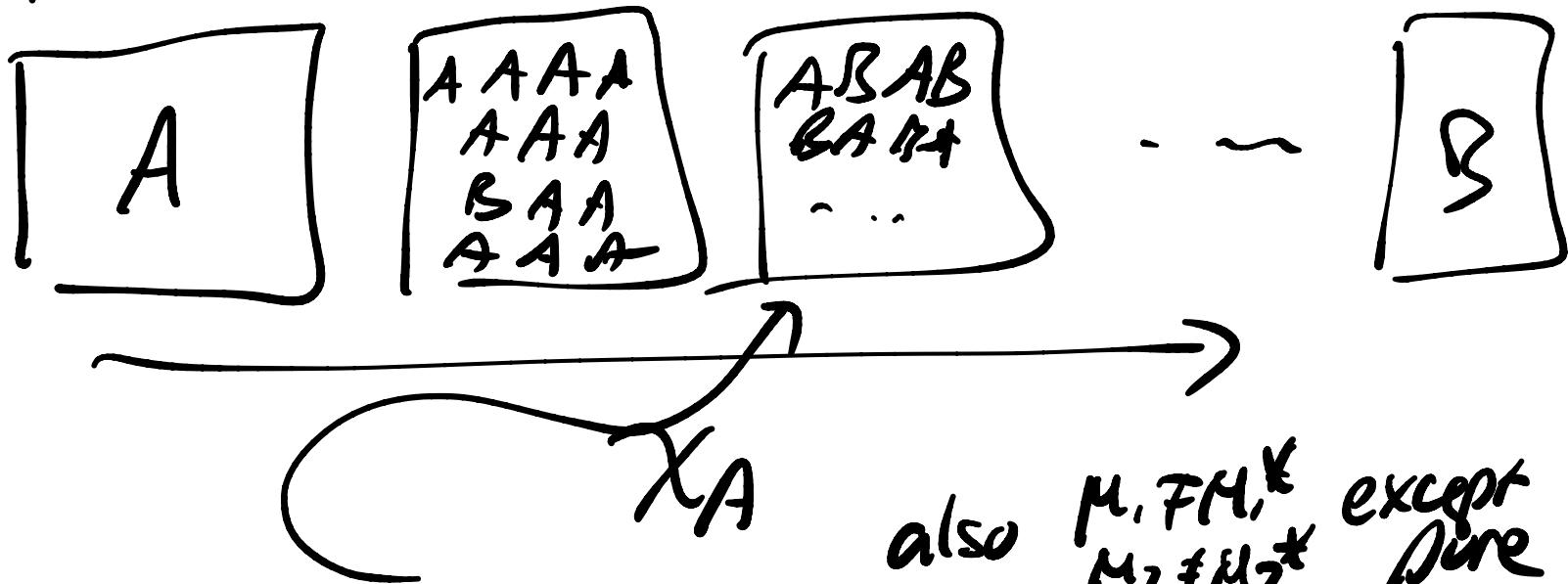
↑
surface
tension

$$G = -\frac{4}{3}\pi R^3 \cdot \sigma + 4\pi R^2 \gamma$$

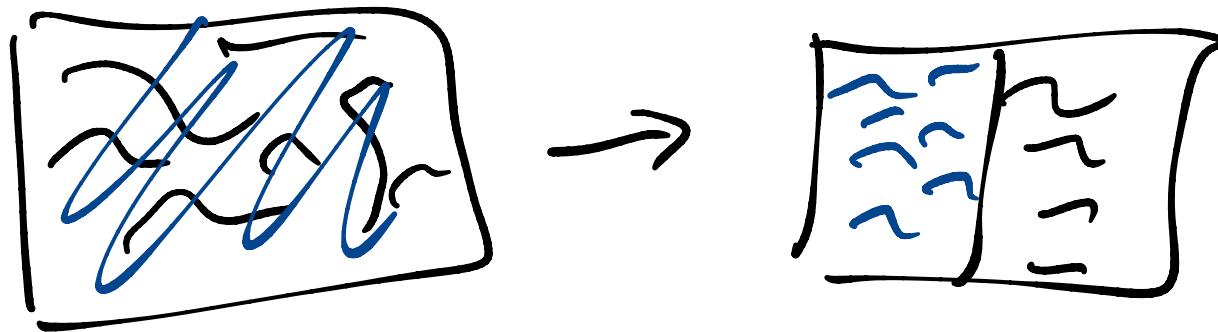


Mixture

A & B



$$G = n_1 M_1 + n_2 M_2 \neq n_1 \mu_1^* + n_2 \mu_2^*$$



2 reasons $\mu \neq \mu^*$

$$\mu_i = \overline{H}_i - T \overline{S}_i$$

\curvearrowleft interaction energy \curvearrowright bigger
than pure state

Standard state. consider gases

G - D relation

$$\sum n_i d\mu_i = V dP \underset{T}{-} S dT$$

$$V = \sum n_i \bar{V}_i \quad S = \sum n_i \bar{S}_i$$

M equations $d\mu_i = \bar{V}_i dP - \bar{S}_i dT$

Partial pressures

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 + \dots$$

$$P = P_1 + P_2 + \dots$$

\hat{P} partial pressure

$$d\mu_i = \bar{V}_i dP - \bar{S}_i dT$$

constant
 T_j const
 $P_j \neq i$

$$dP = dP_1 + dP_2 + \dots + dP_m$$

$$\Rightarrow d\mu_i = \bar{V}_i dP_i$$

ideal gas

$$\bar{V} = RT/P$$

$$d\mu = \int_{P_{ref}}^P \frac{RT}{P} dP$$

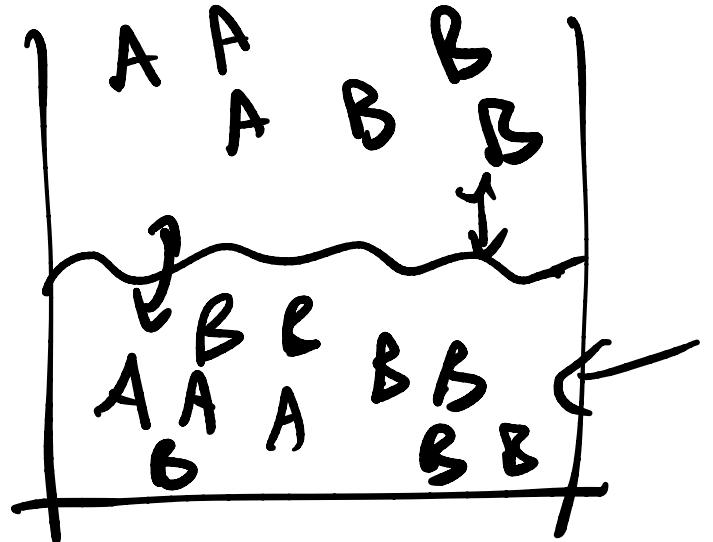
$$\mu - \mu_{ref} = RT \ln(P/P_{ref})$$

Standard pressure, (atom)

$$\mu - \mu_{\text{ref}} = RT \ln\left(\frac{P}{P_{\text{ref}}}\right)$$

$$\dot{\mu}_i = \dot{\mu}_i^{\circ} + RT \ln\left(\frac{P_i}{P_i^{\circ}}\right)$$

$$P_i^{\circ} = 1 \text{ atom} = \dot{\mu}_i^{\circ} + RT \ln(P_i)$$



Gibbs free energy
minimizes at const?

Solvent in eq. with gas/vapor

$$\mu_i \text{ in mixture} = \mu_i \text{ gas} = \mu_i^\circ + RT \ln(P_i)$$



Other Standard States

- partial pressure ~~of everything taken~~

$$[i]^0 = 1 \text{ molar} \quad \text{for all } i$$

useful for low concentration mixtures

$$\chi_i^* = 1 \text{ pure state}$$

$$\frac{n_i}{n_{\text{total}}} = 1 \quad (\text{high conc})$$

note: possible to have

$$P_1 = P_2 = P_3 = \dots = P_m = 1 \text{ atm}$$

$$\{1\} = \{2\} = \{3\} = \dots = \{m\} = 1 \text{ molar}$$

* can't have $x_1 = x_2 = \dots = x_m = 1$ \times

Note 2 $\mu_i \neq \mu_j$ in general

