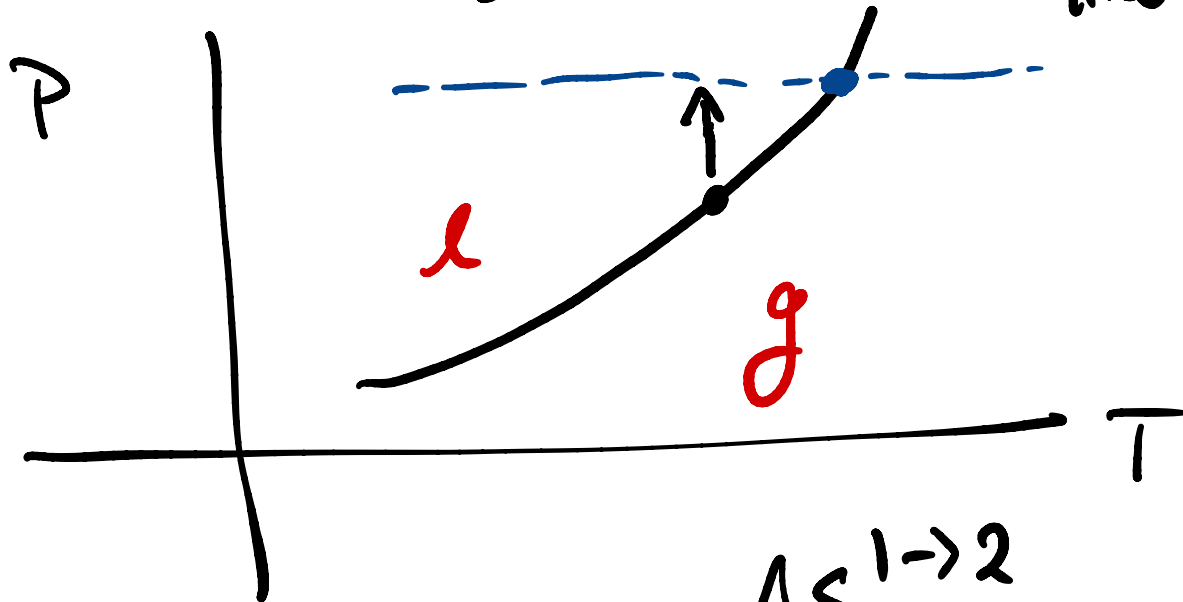


Clausius-Clapyron equation

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, of
vaporization)

for $l \rightarrow \text{gas}$

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

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

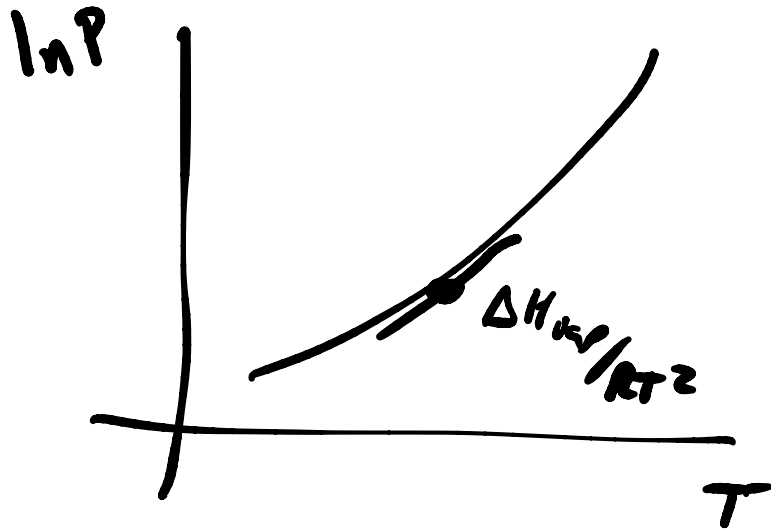
$$\frac{\partial \ln P}{\partial T} = \frac{\Delta \bar{H}_{\text{vap}}}{RT^2}$$

$$\int dP$$

$$\int dT$$

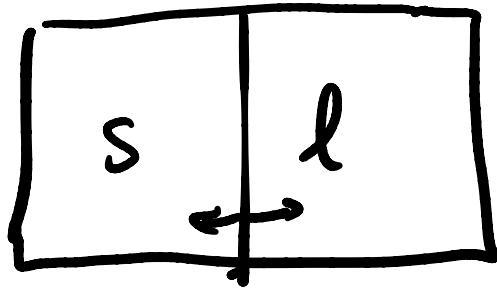
Assuming $\Delta \bar{H}_{\text{vap}}$ is const

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

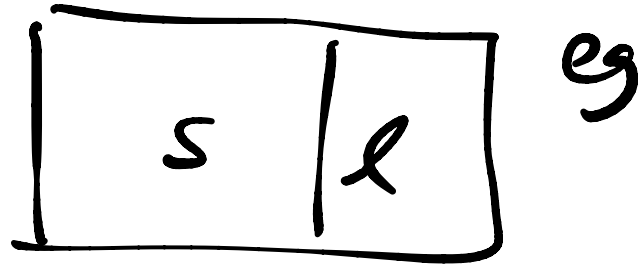


Chemical potentials and mixtures

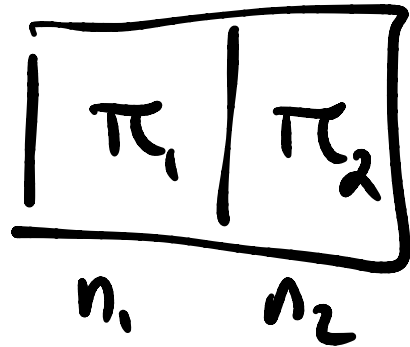
Similar to phase



→



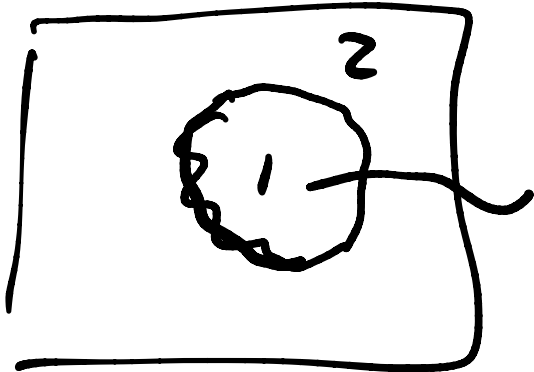
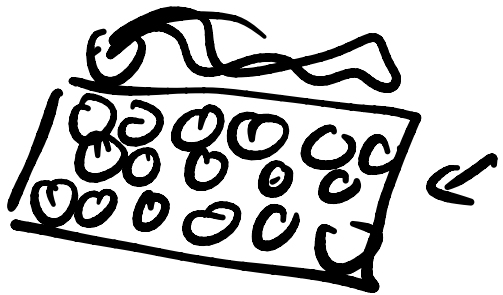
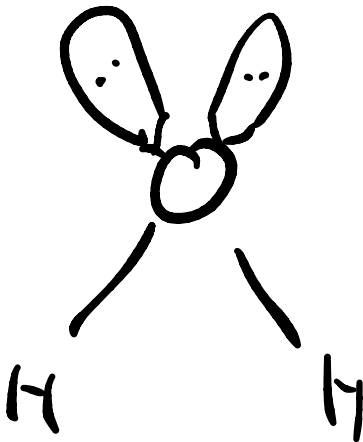
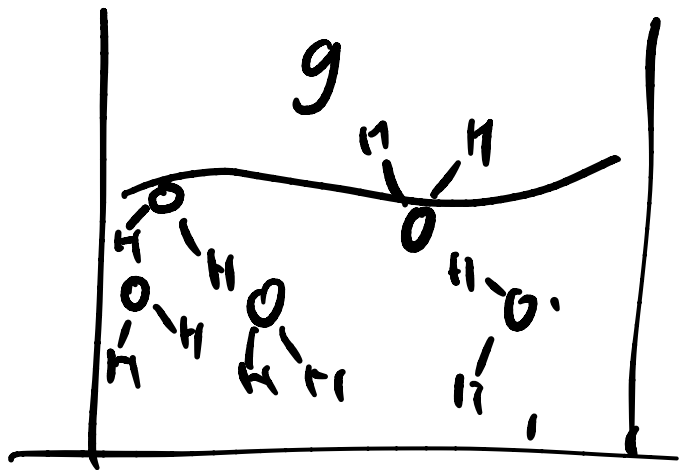
↙



←

$$G = n_1 \mu_1 + n_2 \mu_2 \text{ (+ interface)}$$

$$\approx n_1 \mu_1^* + n_2 \mu_2^*$$



$$\mu_1 n_1 \leftarrow U_1 + \mu_2 n_2 \leftarrow U_2$$

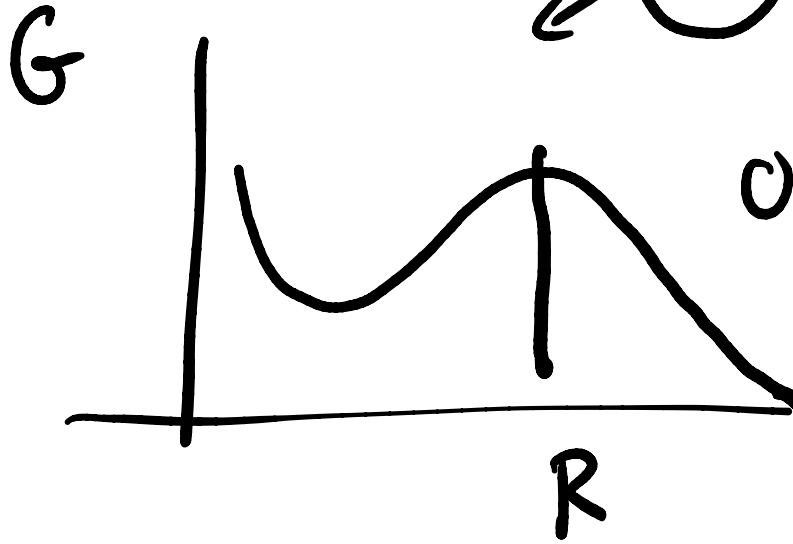
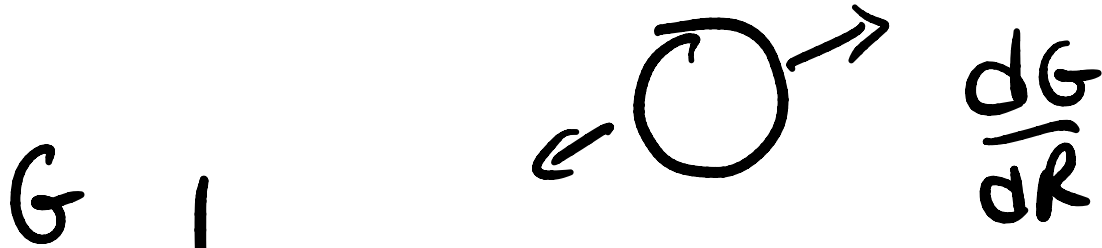
\uparrow l^{d-1}

$$+ \sigma \cdot l^{d-1} \leftarrow v^{2/3}$$

\uparrow
Surface
Tension

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

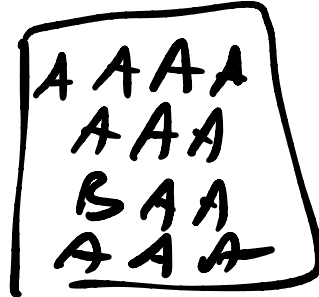
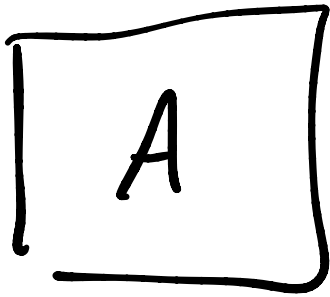
$$G = -\frac{4}{3}\pi R^3 \cdot \sigma + 4\pi R^2 \sigma$$



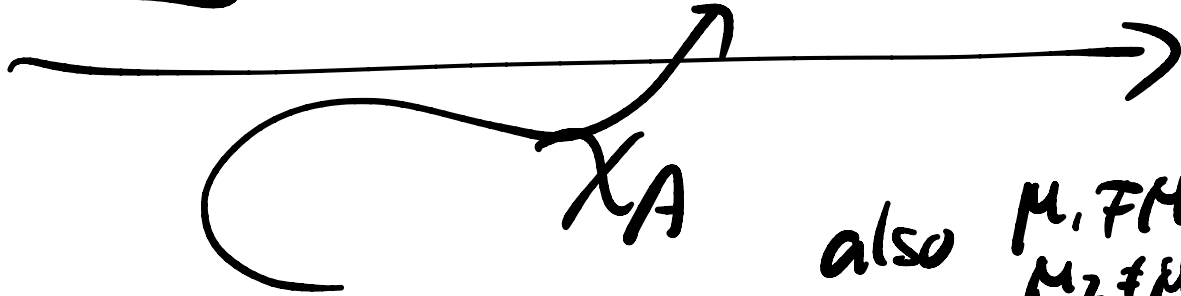
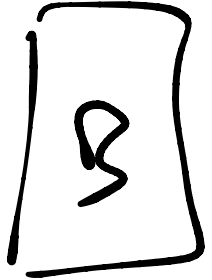
$$0 = -4\pi R^2 \sigma + 8\pi R \sigma$$
$$R^* = \frac{2\sigma}{\sigma}$$

Mixture

A & B

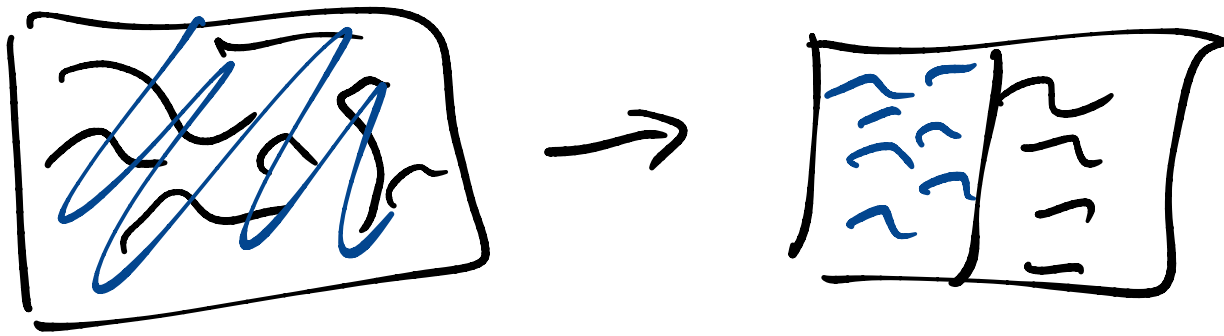


...



also $\mu_1 \neq \mu_1^*$
 $\mu_2 \neq \mu_2^*$ except pure

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



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

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

\curvearrowright interactions change

\nwarrow bigger than pure state

Standard state. consider gasses

G-D relation

$$\sum n_i d\mu_i = V dP - S dT$$

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

m equations

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

Partial pressures

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

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

$\hat{=}$ partial pressure

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

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

constant
 T , const
 $P_j \neq i$

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

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

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

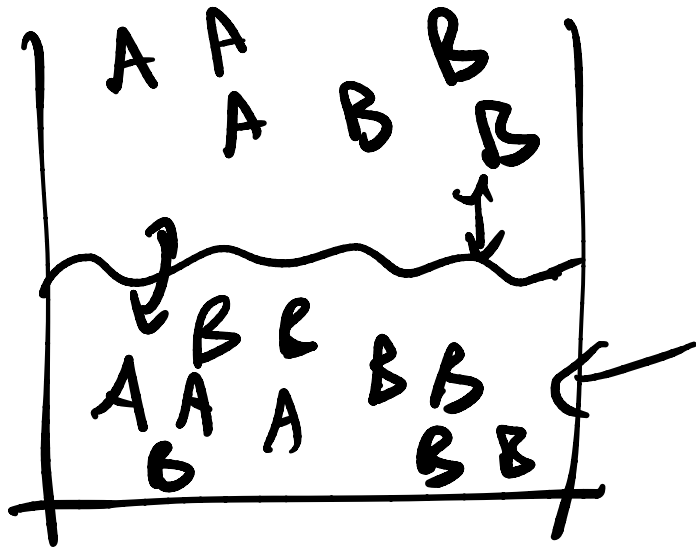
$$\mu - \mu_{ref} = RT \ln(P/P_{ref})$$

Standard pressure, 1 atm

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

$$\mu_i = \mu_i^\circ + RT \ln(P_i/P_i^\circ)$$

$$P_i^\circ = 1 \text{ atm} \quad = \mu_i^\circ + RT \ln(P_i)$$



Gibbs free energy
matters at const P?

Solvent in eq. with gas/liquid

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



Other standard states

• - partial pressure ~~of everything later~~
later

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

useful for low concentration mixtures

$$X_i^* = 1 \quad \text{pure state}$$

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

note: possible to have

$$P_1 = P_2 = P_3 \dots P_m = \text{later}$$

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

★ can't have $\chi_1 = \chi_2 = \dots \chi_m = 1$ ✗

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

