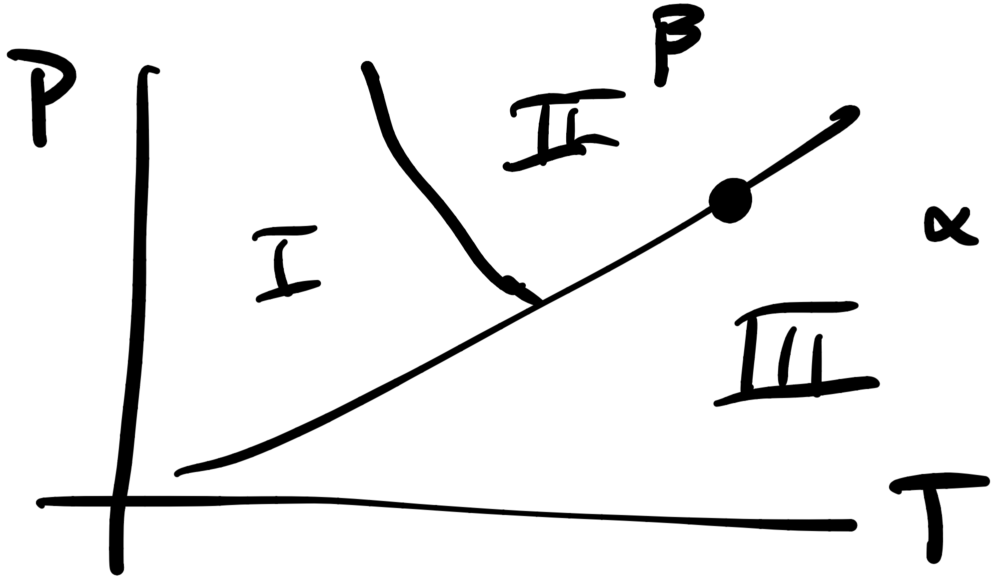
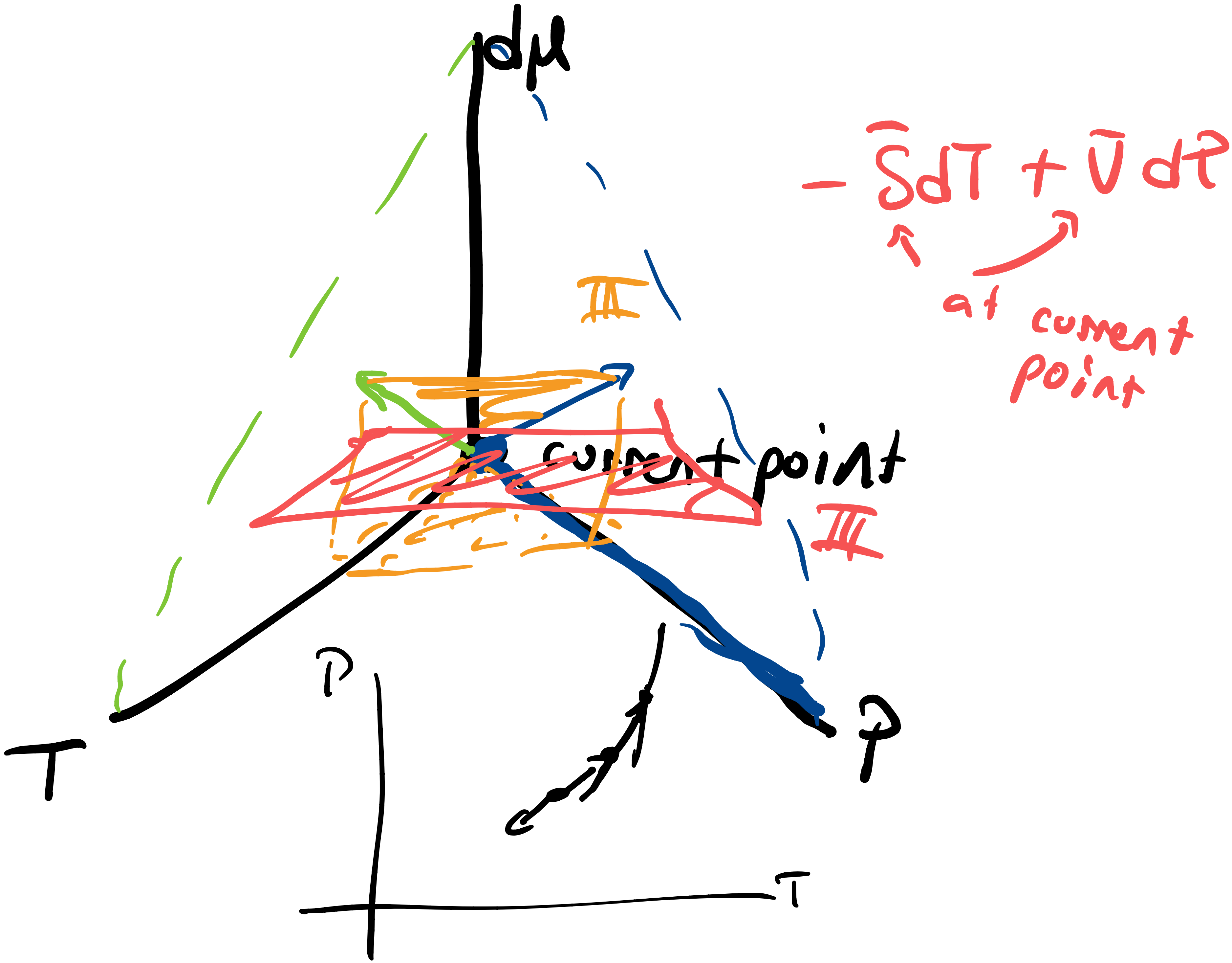


$$d\mu^{\alpha} = -\bar{S}^{\alpha}dT + \bar{V}^{\alpha}dP$$

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


dμ
current point
II
III
T
P
P
T
$-\bar{S}dT + \bar{V}dP$
at current point

Slope of line of coexistance in P/T space

$$\left(\frac{\partial P}{dT}\right)_{\mu^{\alpha}=\mu^{\beta}} = \frac{\Delta \bar{S}^{\alpha \to \beta}}{\Delta \bar{V}^{\alpha \to \beta}}$$

liq → gas or solid → gas

$\bar{V}_{solid/liq} << \bar{V}_{gas}$

for an ideal gas, $\Delta \bar{V}_{g \to l} = \bar{V}_g - \bar{V}_l$

$= \bar{V}_g = \frac{RT}{P}$

$\Delta \bar{S} = \Delta \bar{H} / T$, b/c $\Delta \bar{G} = 0$

@cq

$$\left(\partial P/dT\right) = \frac{\Delta \bar{H}}{RT^2} \cdot P$$

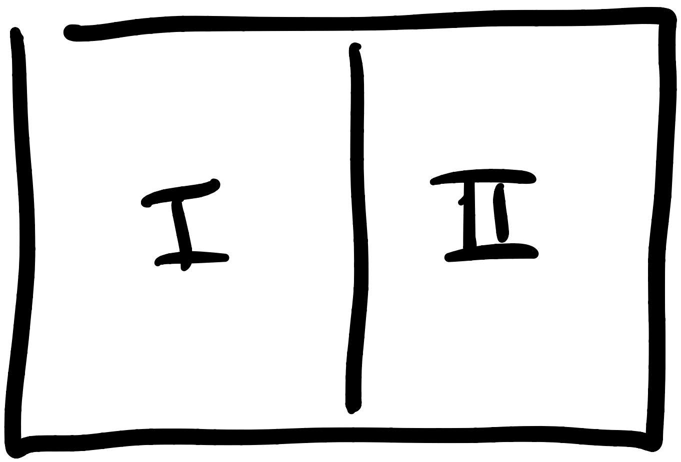
$$\frac{\partial (\ln P)}{\partial T} = \frac{\Delta \bar{H}}{RT^2}$$ @ eq

phase ΔH ↙

$$\ln P_2/P_1 = -\frac{\Delta \bar{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

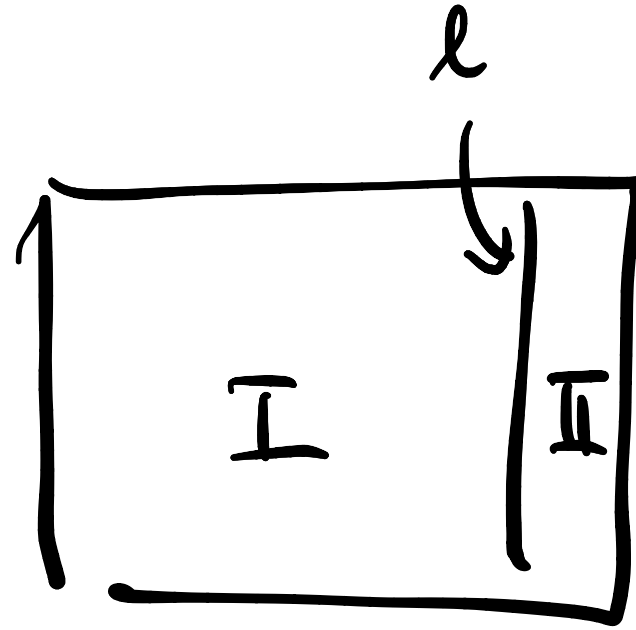
Chemical potentials of mixture

2 phase



not @ eq

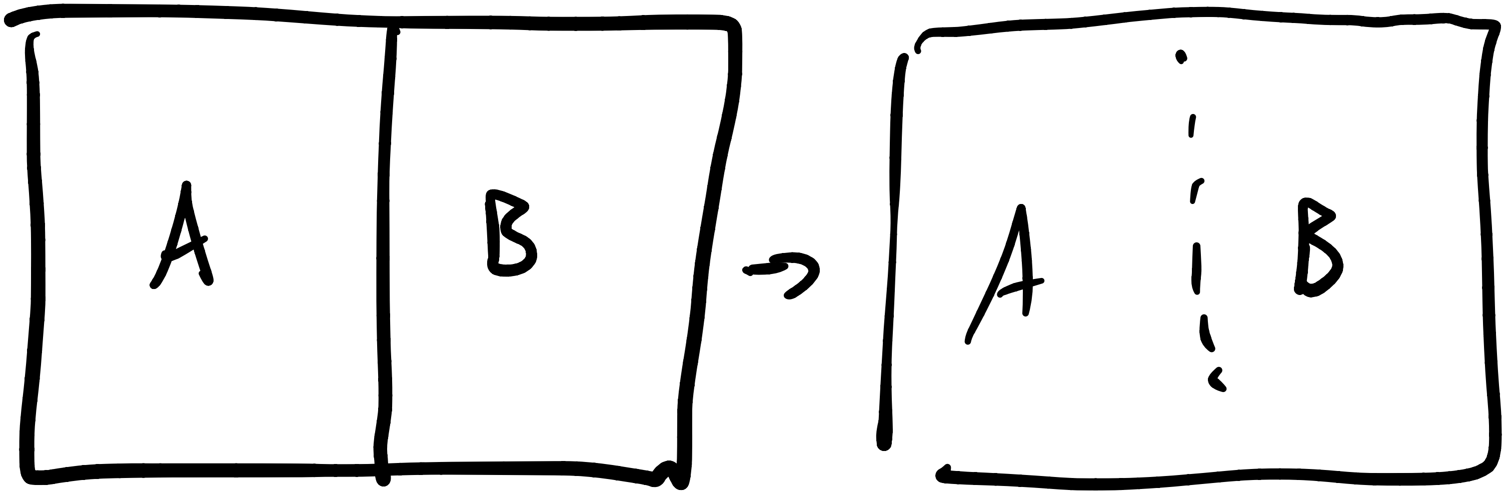
$\longrightarrow$ n_I & n_{II} change until $\mu_I = \mu_2$



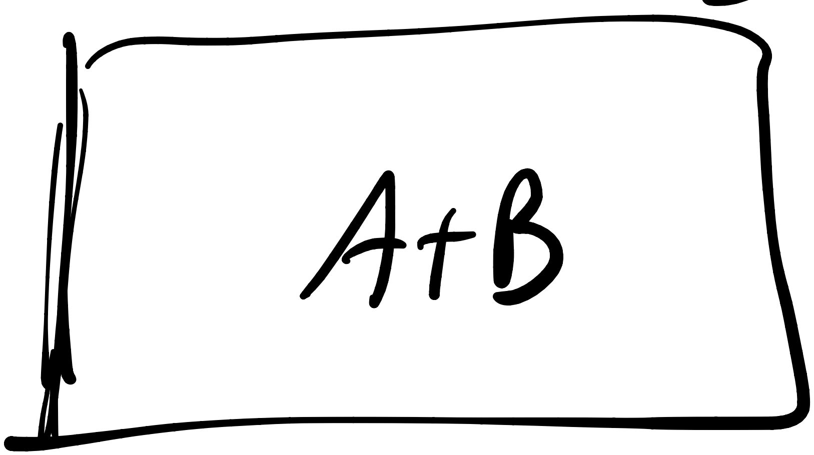
$$G = n^{I} \underline{\mu^{*I}} + n^{II} \underline{\mu^{*II}} + (\text{interface})$$

pure phase (under μ^{*I}), pure phase (under μ^{*II}), (negligible) (under interface)

In a solution



$G_{start} = n_A \mu_A^* + n_B \mu_B^*$



$G_{mix} = n_A \mu_A + n_B \mu_B$

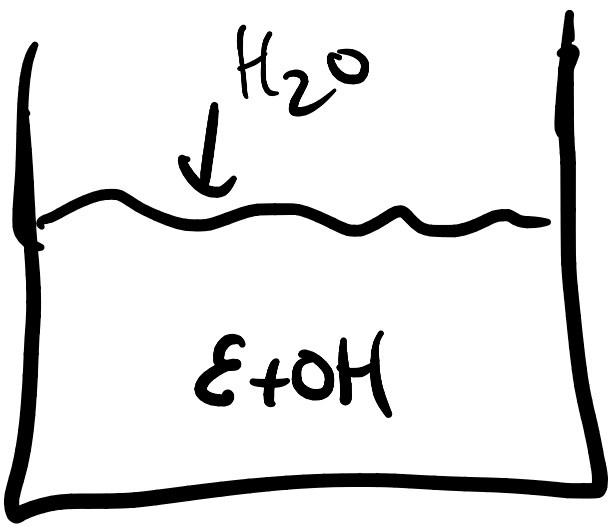
not μ_A^* μ_B^*

$\Delta G = ?$

$$d\mu^\alpha = \cancel{-\bar{S}^\alpha dT} + \bar{V}^\alpha dP$$

$$P_{total} = \sum_{i=1}^{k} P_i$$

$$d\mu^\alpha = \bar{V}^\alpha dP^\alpha$$ in solution

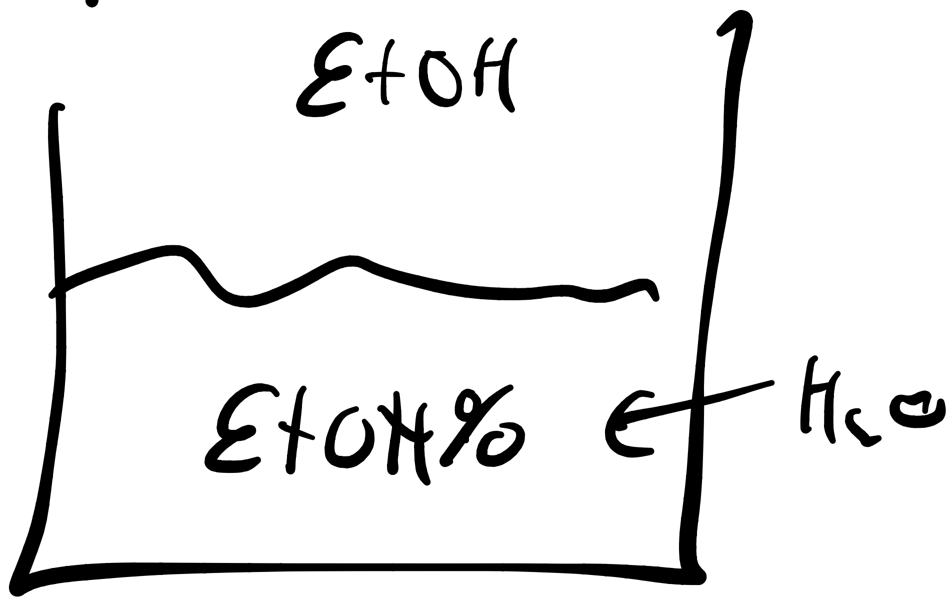


$$\mu^{EtOH}_{solution} = \mu^{EtOH}_{gas}$$

↑ ideal gas

$$\int_{\mu^\circ} d\mu^\alpha = \int_{P^\circ} \frac{RT}{P^\alpha} dP^\alpha$$

$$\mu^{\alpha} = \mu^{\circ\alpha} - RT\ln\left(P_{\alpha}/P_{\alpha}^{\circ}\right)$$



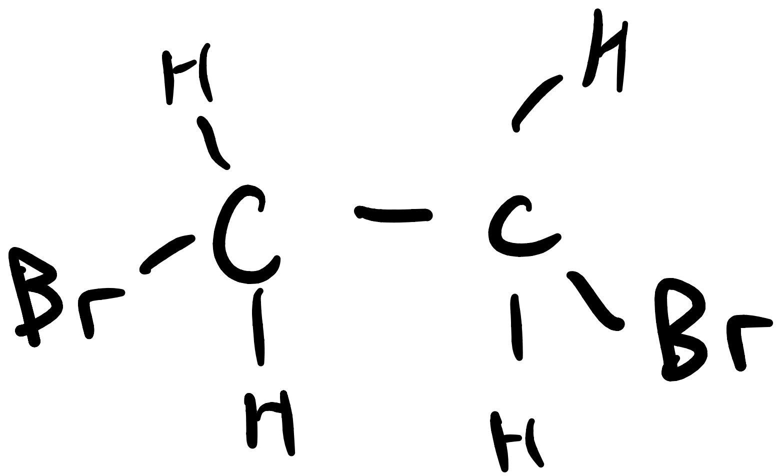
see discussion (pg ?) about different standard states

Raoult's Law (ideal solution approximation)

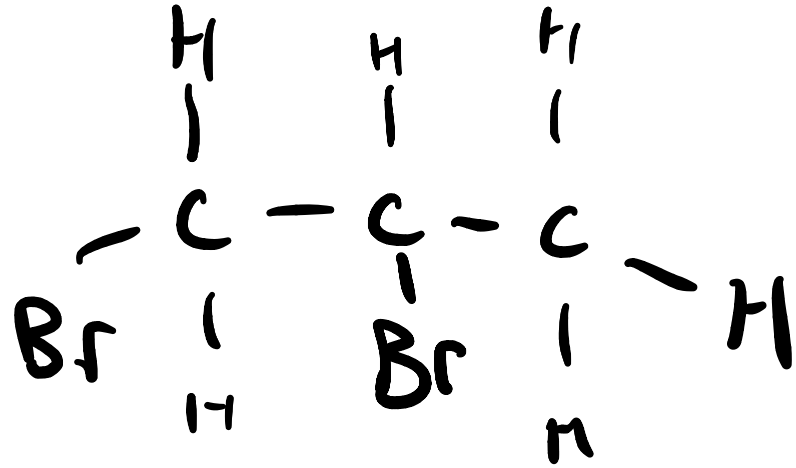
Partial pressure of a mixture
is given by the individual
partial pressures ...

$$P_i = \chi_i P_i^*$$

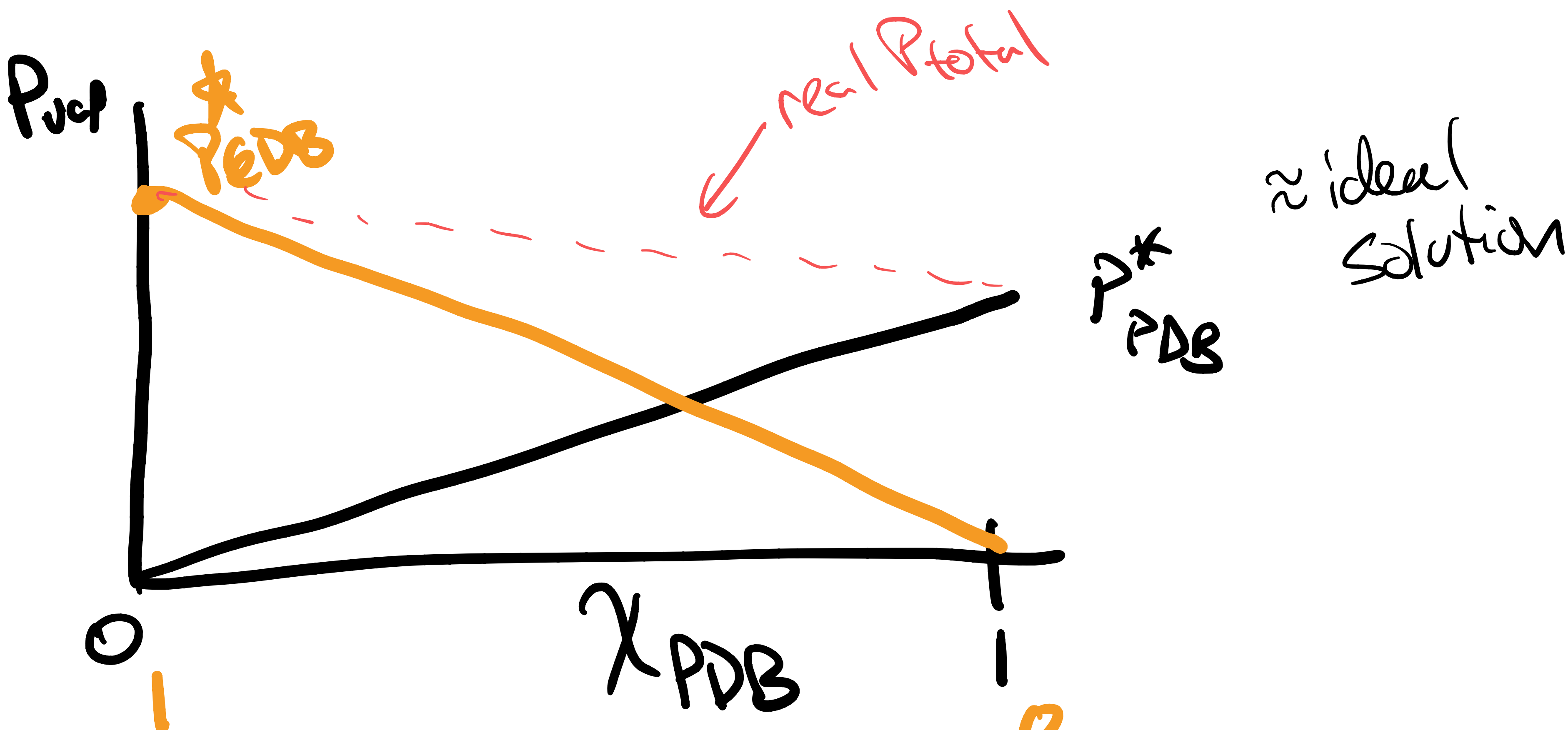
Called ideal solution
"as if the molecules don't interact"



EDB



PDB



Do they mix (ideal solution)

$\Delta G < 0$?

$= G_{mixed} - G_{unmixed}$

$= (n_A\mu_A + n_B\mu_B) - (n_A\mu_A^* + n_B\mu_B^*)$

$\mu_i = \mu_i^* + RT\ln x_i$ [comes from Raoult approx]

$\Delta G_{mixing}^{ideal} = n_A RT\ln x_A + n_B RT\ln x_B$ ← divide by $n_A + n_B$

$\Delta \bar{G}_{mixing} = x_A RT\ln x_A + x_B RT\ln x_B$

$$\Delta \bar{G} = \underline{RT} \left(x_A \ln x_A + x_B \ln x_B \right)$$

only temp dependence

↕

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

$$\Delta \bar{S} = -R \left(x_A \ln x_A + x_B \ln x_B \right)$$

always negative

and $\Delta \bar{H} = 0$

(Abnormal)

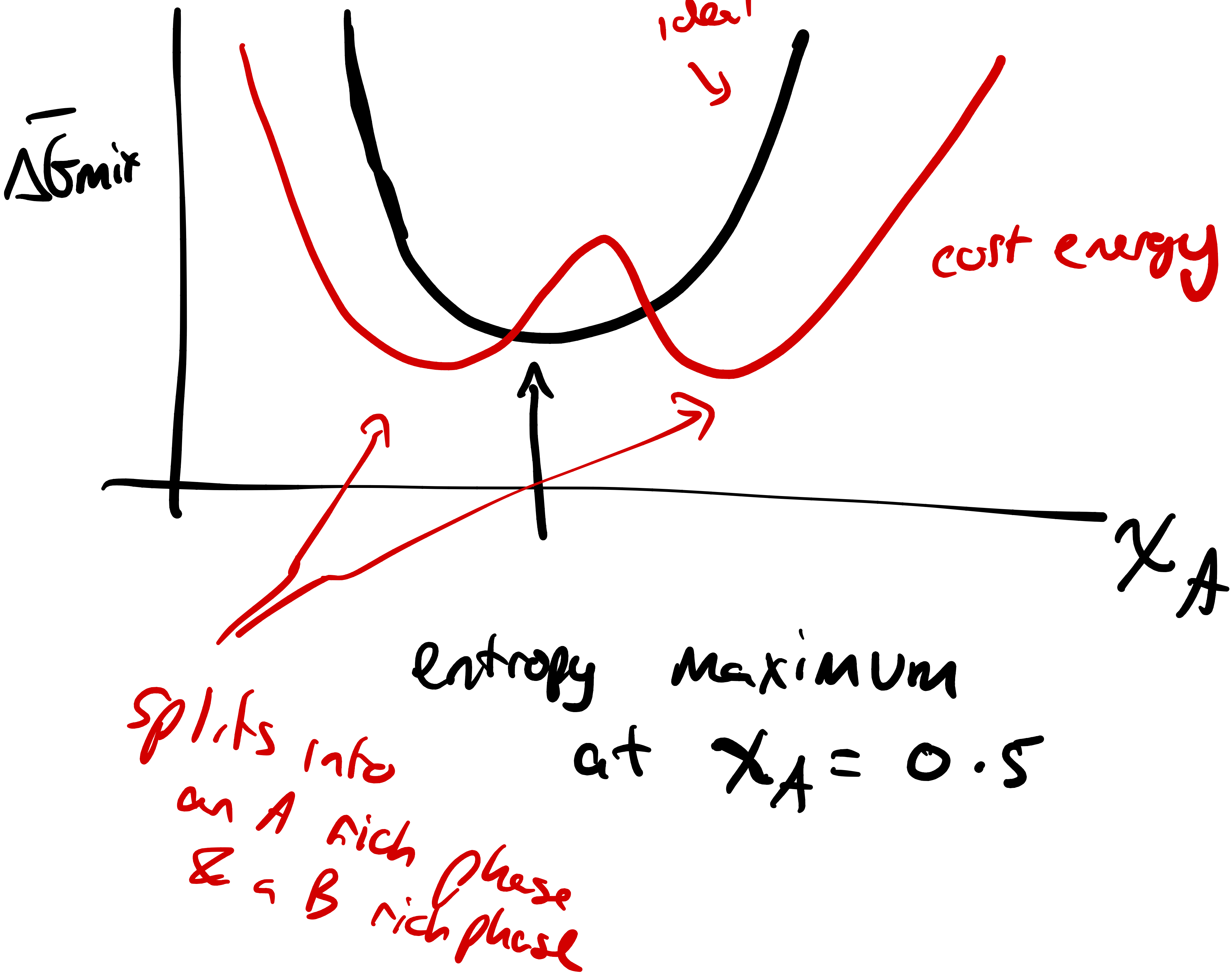
$\Delta\bar{H} \approx 0$ ideal

$\Delta\bar{H} > 0$ mixing costs energy

$\Delta\bar{H} < 0$ mixing lowers energy

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

↕ similar to prev


$\Delta \bar{G}_{mix}$
ideal
cost energy
x_A
entropy maximum at $x_A = 0.5$
splits into an A rich phase & a B rich phase

Preview: chemical reactions

$$aA + bB \rightleftarrows cC + dD$$

$\Delta G =$ depends on $\mu_A, \mu_B, \mu_C, \ldots$
and $a, b, c \ldots$

$$\Delta \bar{G} = -RT \ln K_{eq}$$

$$K_{eq} = \frac{[D]^d [C]^c}{[A]^a [B]^b}$$