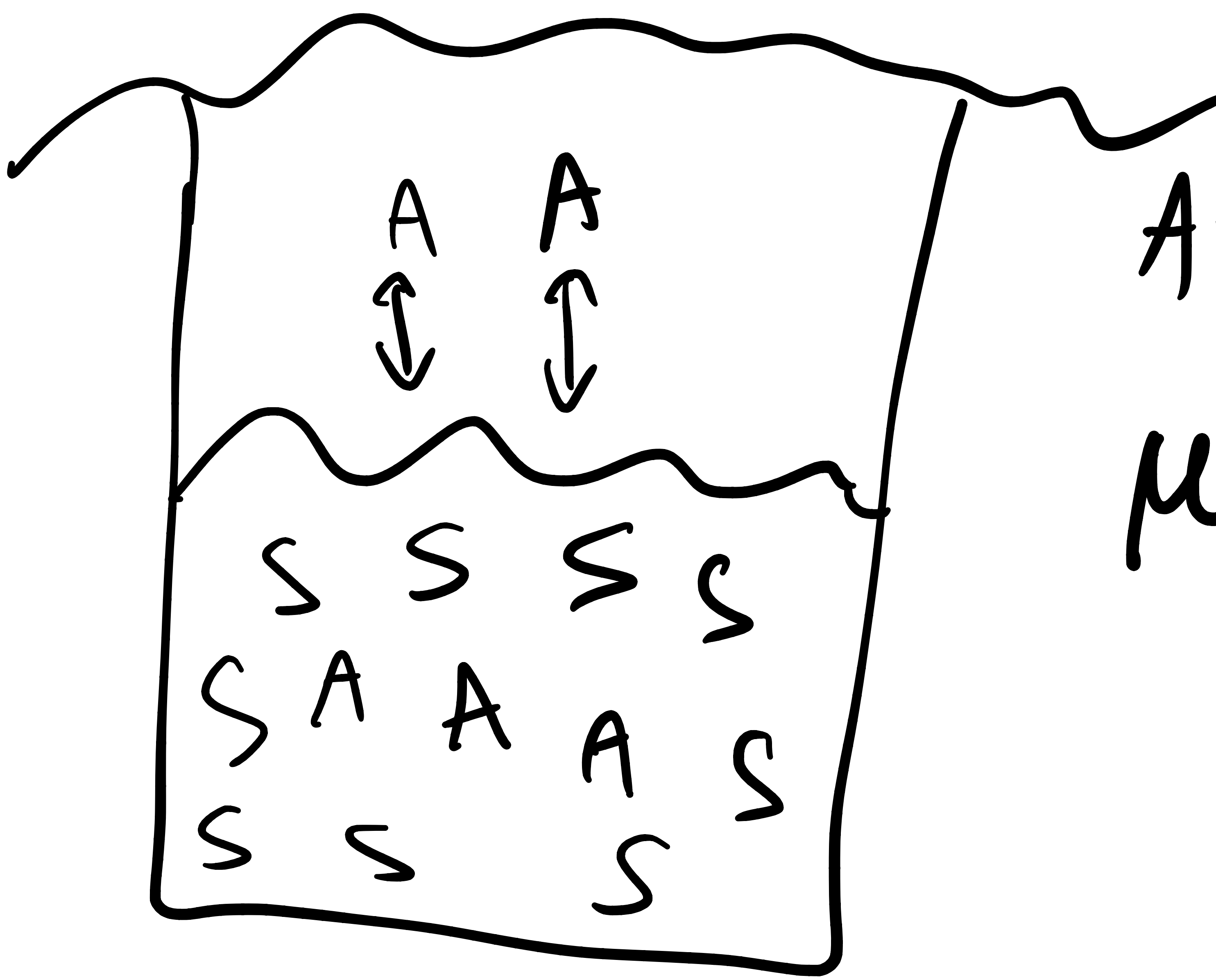
Lecture 14

Consider dissolved solute in solvent



A + eq.

$$\mu_i^{liq} = \mu_i^{gas}$$

$$= \mu_i^{\circ} + RT\ln\left(P_i / P_i^{\circ}\right)$$

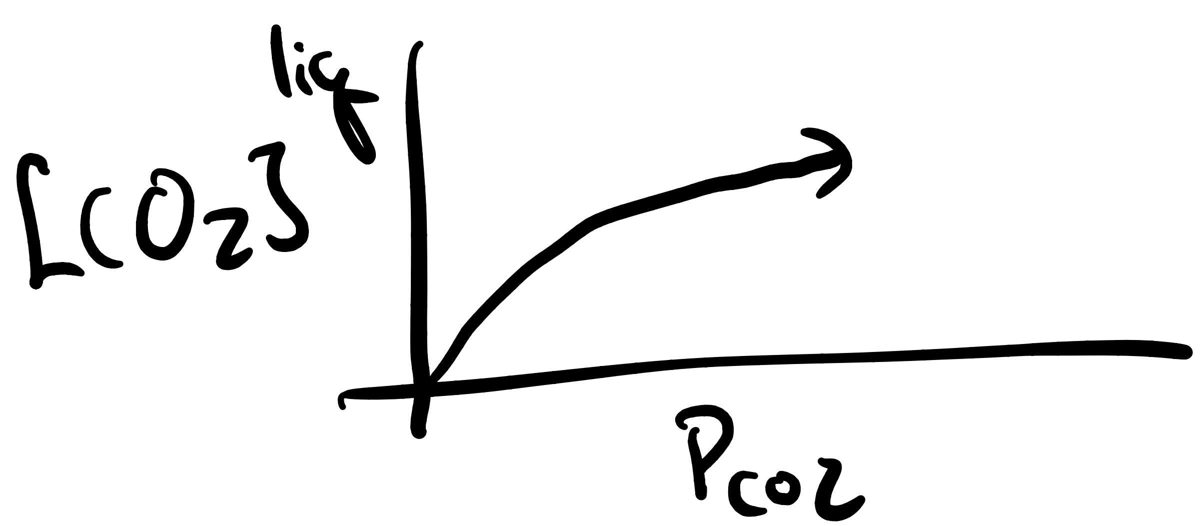
1 atm

If increase gas pressure by adding molecules

$\mu_i^{gas} \uparrow$ then $\mu_i^{gas} > \mu_i^{liq}$

then expect gas to $\underbrace{\text{absorb}}$ until

$\mu_i^{gas} = \mu_i^{liq}$ (dissolve)



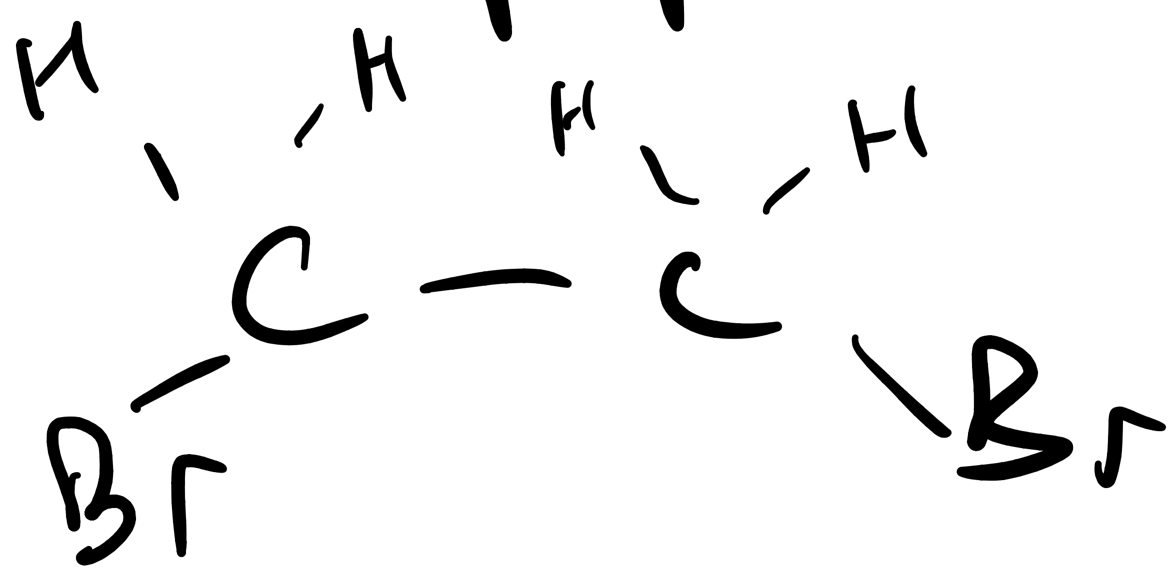
P_i is the vapor pressure

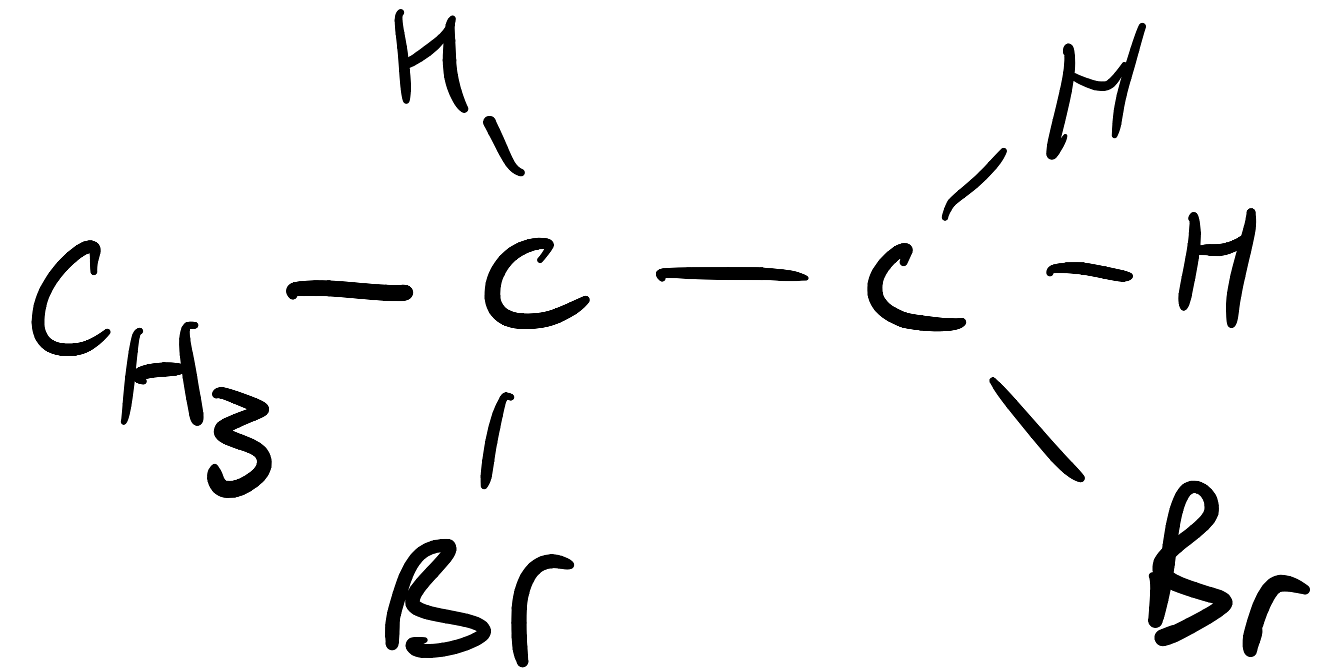
for small X_{solute},

Ideal example:

Ethelyne dibromide

propelene dibromide





Ideal $\quad P_{vap} = \sum_i x_i P_i^*$

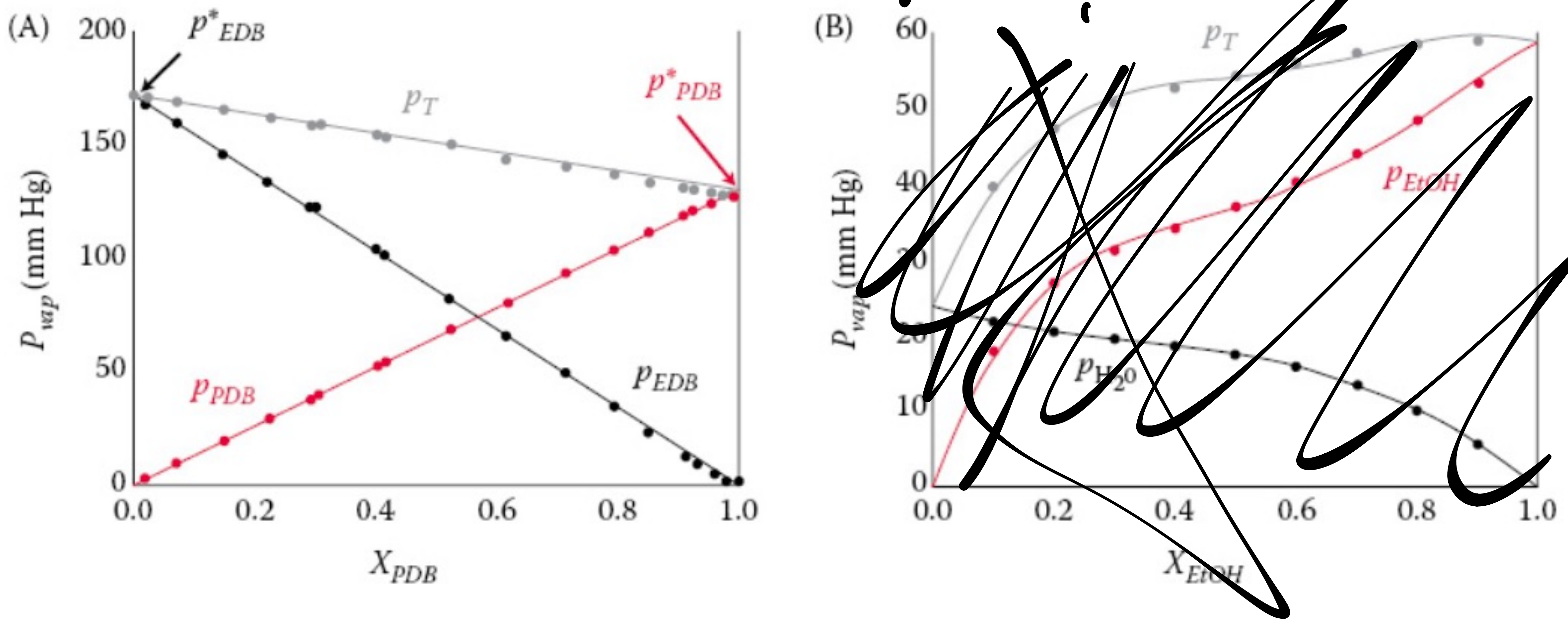
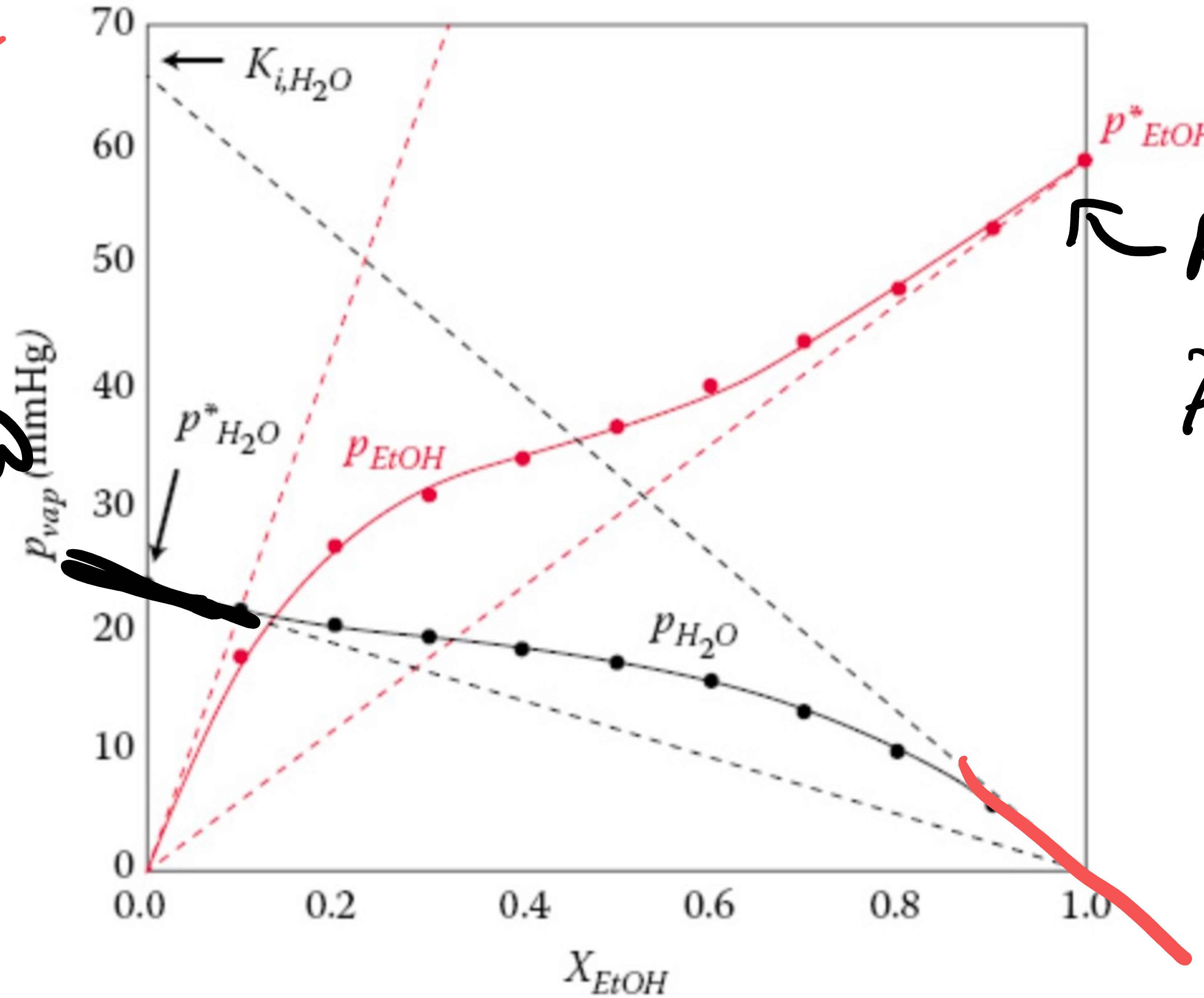


Figure 7.6 Partial pressures of two different two-component liquids. (A) The partial and total vapor pressures of a binary (meaning two-component) mixture of ethylene dibromide (EDB) and propylene dibromide (PDB), two similar components that closely approximate an ideal solution. Vapor pressures were measured at 358 K (Von Zawidzki, Z. Phys. Chem. 35, 129 [1900]). This mixture conforms quite closely to Raoult's law (solid lines) with zero intercepts at xPDB = 0 and 1 for PDB and

ideal dilution limit



Raoult's law

Raoult's law

$P_{CO_2} = P^*_{CO_2} X_{CO_2}$ when $X_{CO_2} \approx 1$

$P_{H_2O} = P^*_{H_2O} X_{H_2O}$ when $X_{H_2O} \approx 1$

H_2O is solute

$P_{H_2O} \propto X_{H_2O}$

$P_{H_2O} = K_H X_{H_2O}$

Figure 7.9 Limiting vapor pressures for water and ethanol at high dilution. The data from Figure 7.6 are fitted, and are compared with ideal solution lines (Raoult's law, dashed), and ideal dilute solution lines (Henry's law, dot dashed). For this binary mixture, the Henry's law constants (KH,i, corresponding to the slope at xi = 0), are significantly

<u>Raoult's law:</u> $P_{solvent} \approx P^*_{solvent}\, \chi_{solvent}$

close to 1

<u>Henry's law</u> $P_{solute} \approx K^H_{\substack{solute \\ in\ solvent}}\, \chi_{solute}$

close to 0

$$K^H_{solute}\, \underbrace{(1-\chi_{solvent})}_{\text{binary mixture}}$$

$$\mu_i^{liq} = \mu_i^{gas} = \mu_i^0 + RT\ln\left(p_i/p_i^0\right)$$

$$\approx \mu_i^0 + RT\ln\left(p_i^* x_i / p_i^0\right)$$

$$= \mu_i^0 + RT\ln\left(\frac{p_i^*}{p_i^0}\right) + RT\ln(x_i)$$

$$\equiv \mu_i^* + RT\ln(x_i)$$

Ref state is pure liquid

$$\mu_i^{liq} \approx \mu_i^{o} + RT\ln\left(\frac{k_i^{H}}{P_i^{o}} x_i\right)$$

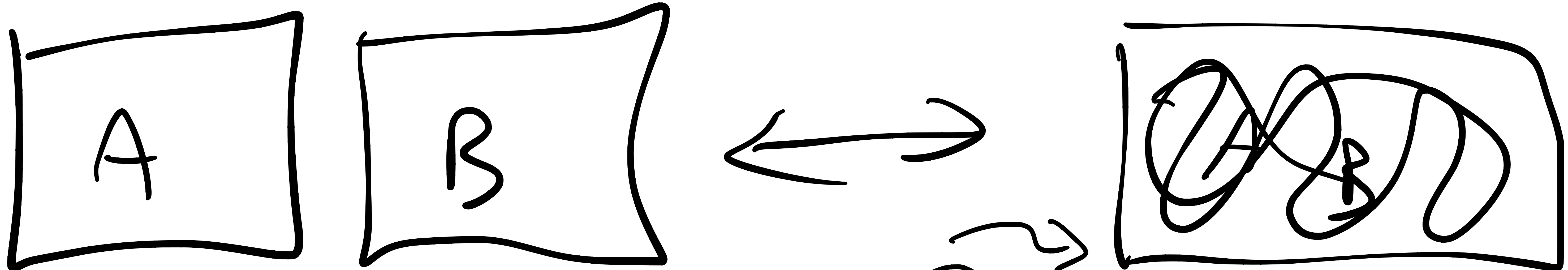
solute

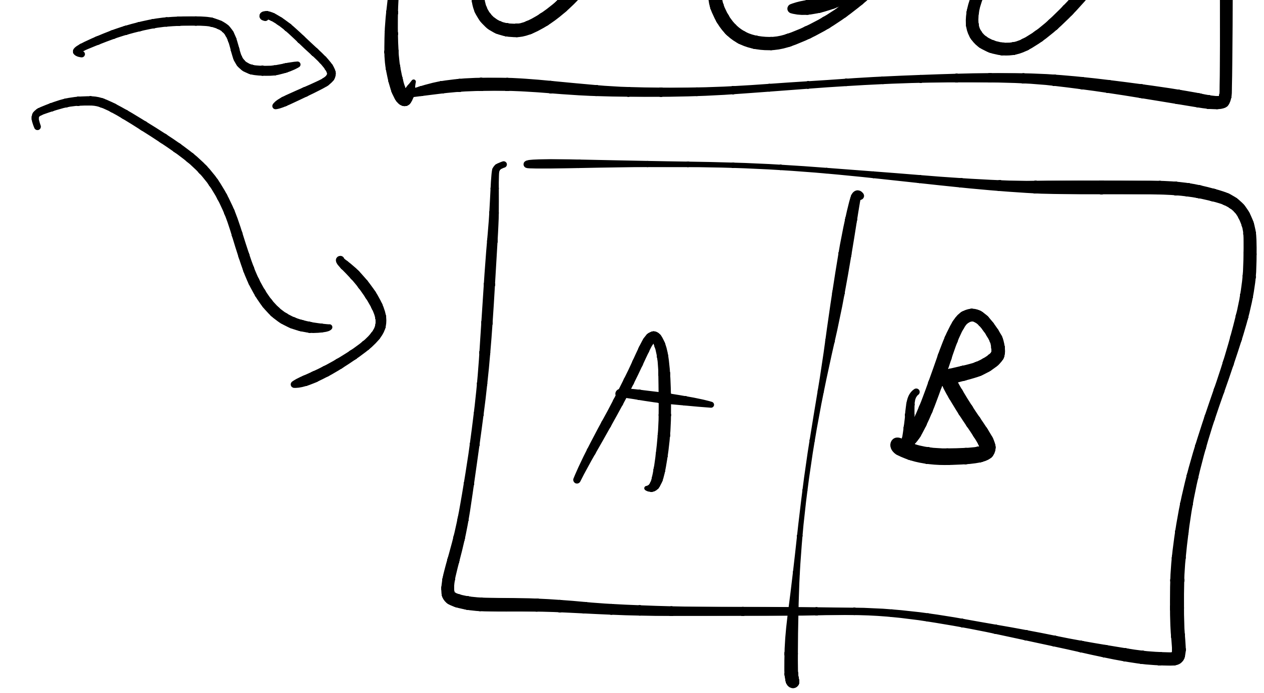
Henry's law

$$= \mu_i^{o} + RT\ln\left(\frac{k_i^{H}}{P_i^{o}}\right) + RT\ln x_i$$

$$\equiv \mu_i^{\otimes} + RT\ln(x_i)$$

chemical potential of ideally dilute system





Will it mix?

$$\Delta G_{mix} = G_{mixed} - G_{unmixed}$$

$$= (n_A \mu_A + n_B \mu_B)_{mixed} - (n_A \mu_A + n_B \mu_B)_{unmixed}$$

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

In mixed state (ideal mixture)

$$G = n_A(\mu_A^* + RT\ln \chi_A) + n_B(\mu_B^* + RT\ln \chi_B)$$

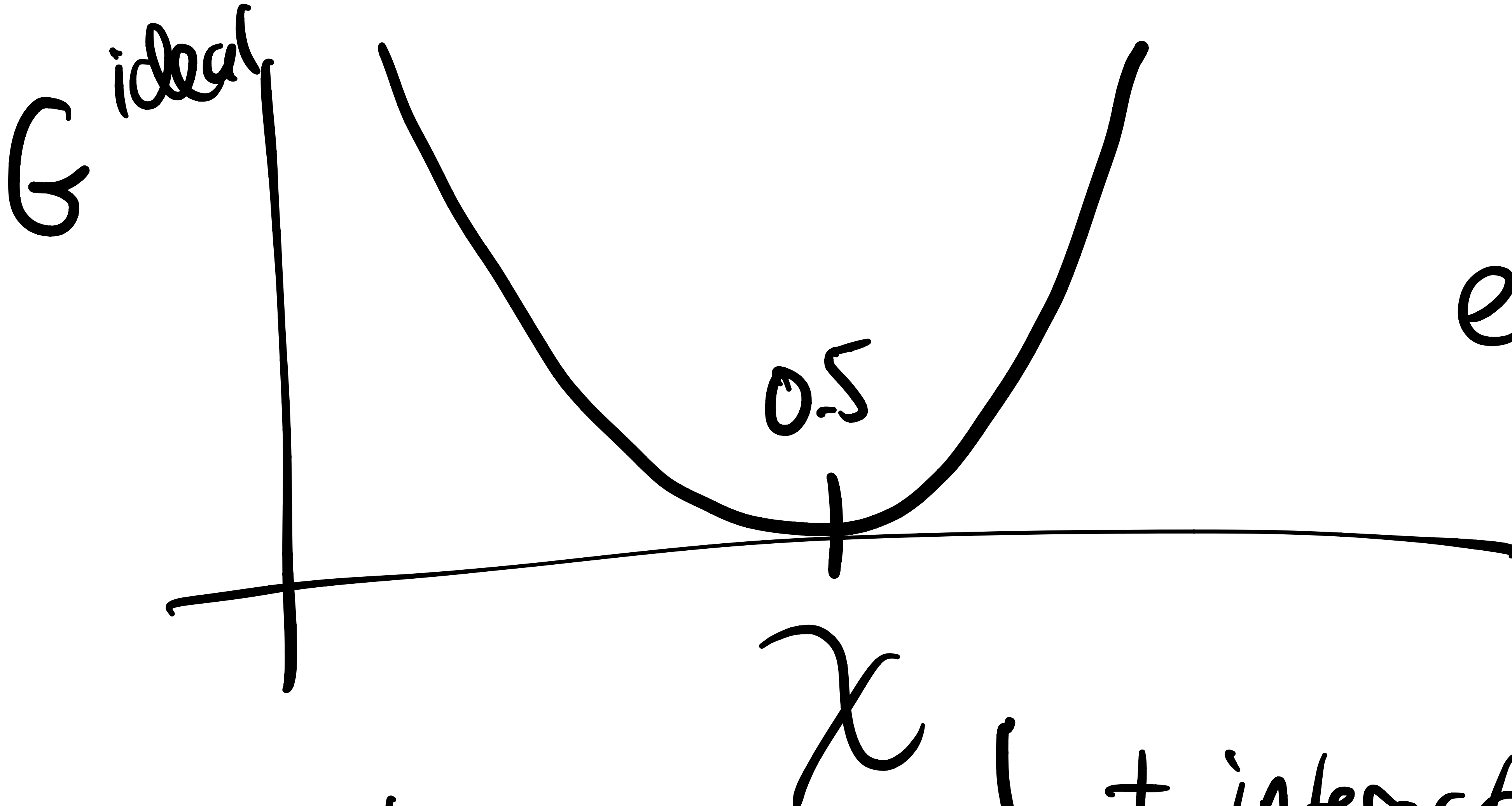
$$\Delta G_{mix}^{ideal} = n_A RT \ln \chi_A + n_B RT \ln \chi_B$$

$$= n_{total} RT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$

$$\overline{\Delta G}_{mix} = -T\Delta\overline{S}$$

$$\Delta\overline{H}^{ideal} = 0$$

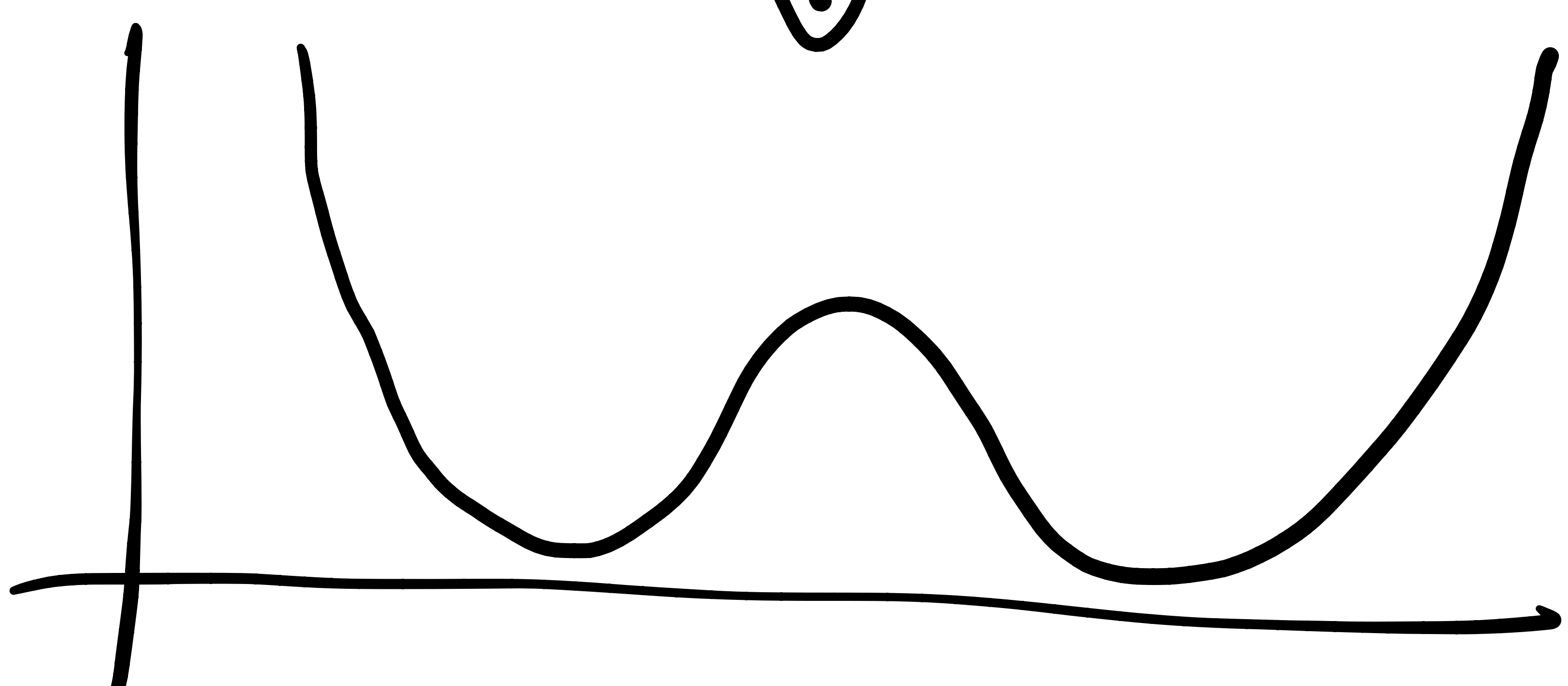
(Check pg 248-252)



entropy max
at $\chi = 0.5$

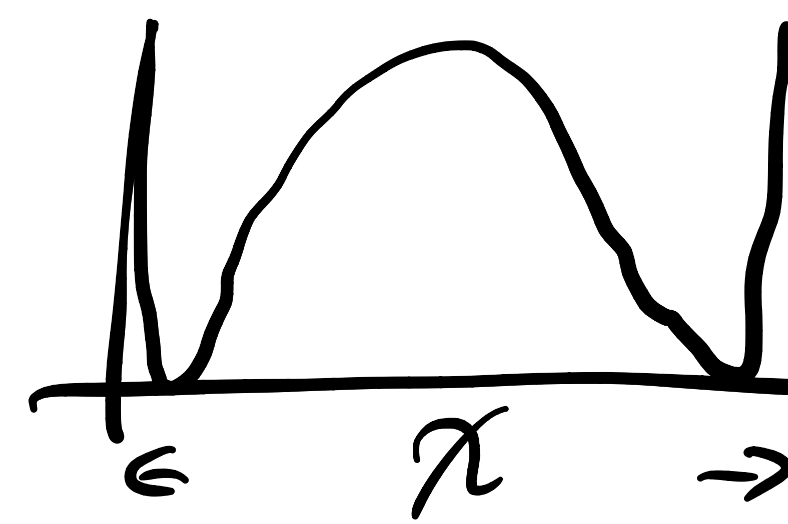
↓ + interactions

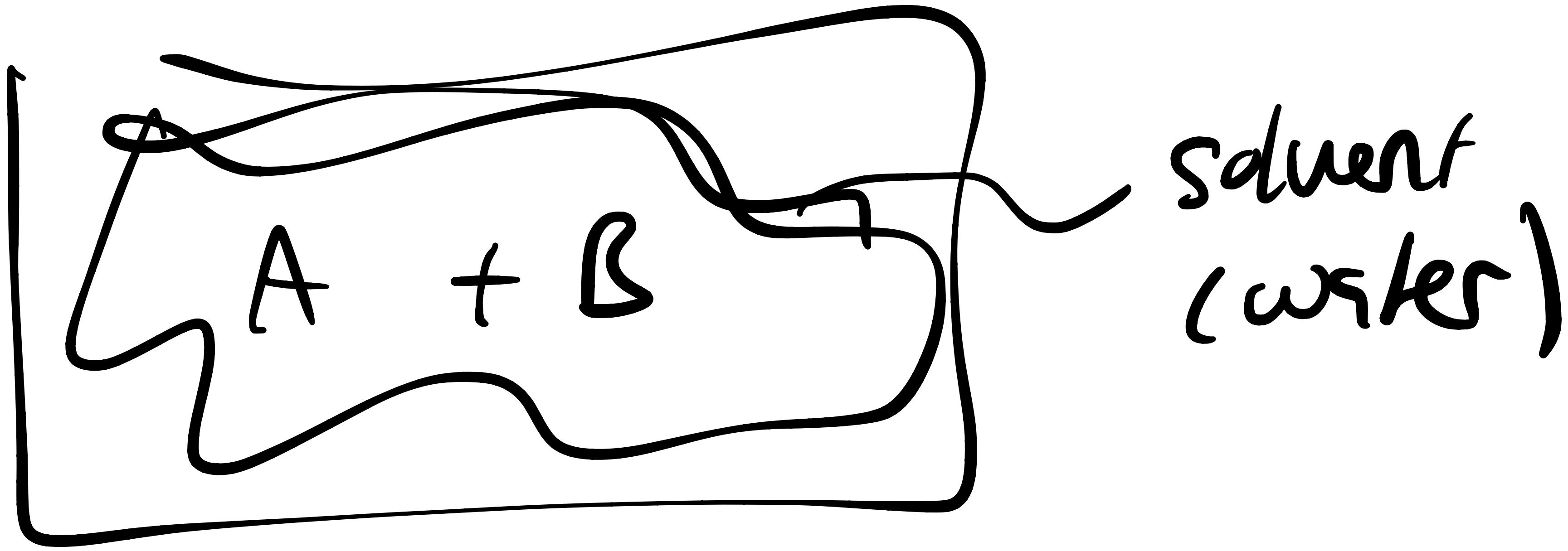
$G^{non\text{-}ideal}$



what if
$\Delta H_{mix} > 0$

oil water





$$[H_2O] \approx 55.5\ M$$

$$\mu_i^{liq} \equiv \mu_i^{0} + RT \ln [i]$$

$$\chi_i = \frac{n_i}{n_T} \approx \frac{n_i}{n_{solvent}}$$

$$V \approx n_s \bar{V}_s^{*}$$

$$[i] = n_i / V = \frac{\chi_i n_s}{n_s \bar{V}_s^{*}} = \chi_i / \bar{V}_s^{*}$$

$$\mu_i^{liq} = \mu_i^{X} + RT \ln \left([i] \cdot \bar{V}_s^{*} \right)$$

Chemical Reactions

ν_i negative for react
positive for products

$$aA + bB \rightleftharpoons cC + dD$$

* Conservation of mass

also $$M + L_6 \rightleftharpoons ML_6$$

$$P + L \rightleftharpoons PL$$

"number of moles reacted" "η" =

$$\Delta G_{rxn} = \eta\left(-a\bar{G}_a - b\bar{G}_b + c\bar{G}_c + d\bar{G}_d\right)$$

$$= \eta \sum \nu_i \mu_i$$

$$\Delta \bar{G} = \frac{\Delta G}{\eta} = \sum_i \nu_i \mu_i$$

$$\Delta \bar{G} = \sum \nu_i \left(\mu_i^\circ + RT\ln[i]\right)$$

$$= \sum \nu_i \mu_i^\circ + \sum_i \nu_i RT\ln[i]$$

$$\text{"} \qquad + RT \sum_i \ln[i]^{\nu_i}$$

$$\text{"} \qquad + RT\ln\Big(\overbrace{\prod_i [i]^{\nu_i}}^{Q}\Big)$$

$$\Delta \bar{G} = \overbrace{\sum_i \mu_i \mu_i^\circ}^{\equiv \Delta \bar{G}^\circ} + RT\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

$$\Delta \bar{G} = \Delta \bar{G}^\circ + RT \ln Q$$

$$Q = \prod_i [i]^{\nu_i}$$

@ Eq $\quad \Delta \bar{G} = 0$

$$\boxed{\Delta \bar{G}^\circ = -RT \ln \underbrace{K_{eq}}_{\text{eq const}}}$$

$$\boxed{\Delta \bar{G} = \Delta \bar{G}^\circ + RT \ln Q}$$