Last time

Characterize a mixture by μ vapor

$$\mu_i^{liq} = \mu_i^{gas} = \mu_i^{\circ} + RT\ln(P_i/P_i^{\circ})$$

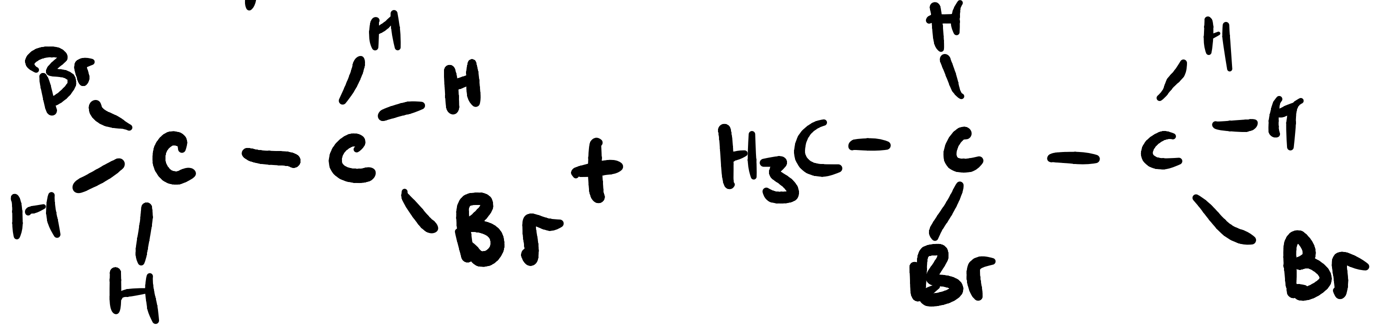
Mix 2 things in solution:

ideal solution

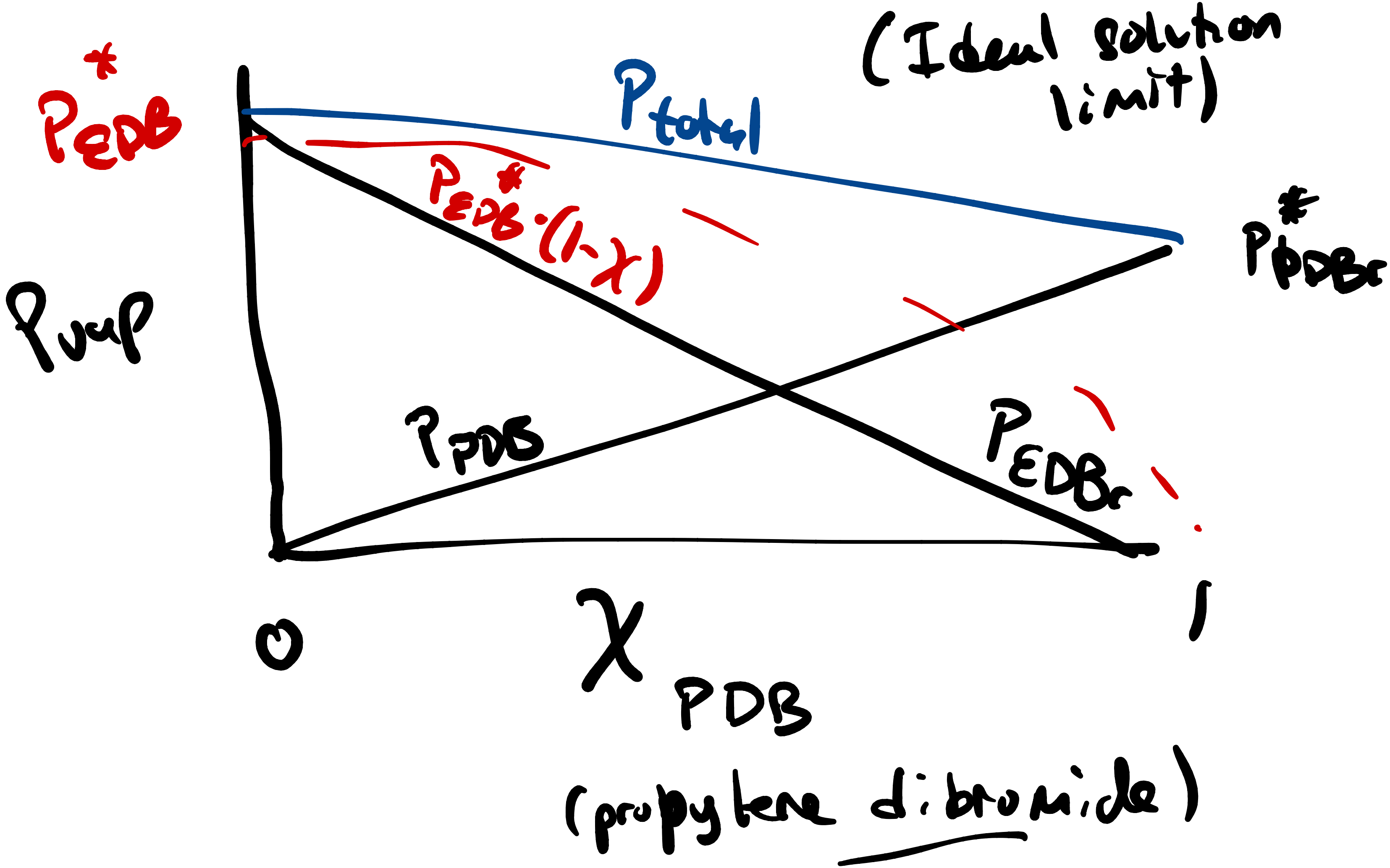
Follow Raoult's Law

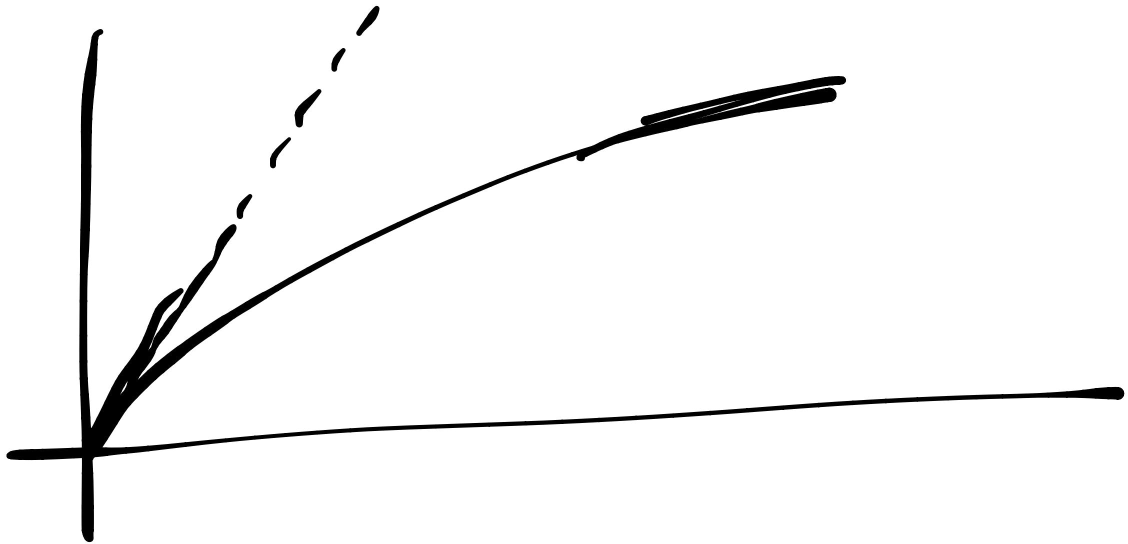
$$p_i = \chi_i \, p_i^*$$

Eg:



A B


(Ideal solution limit)
P^*_{EDB}
P_{total}
$P^*_{EDB} \cdot (1-\chi)$
P_{vap}
P^*_{PDBr}
P_{PDB}
P_{EDBr}
0
1
χ_{PDB}
(propylene dibromide)



$$P(x) \approx P(x=0) + x\,P(x) + \cdots$$

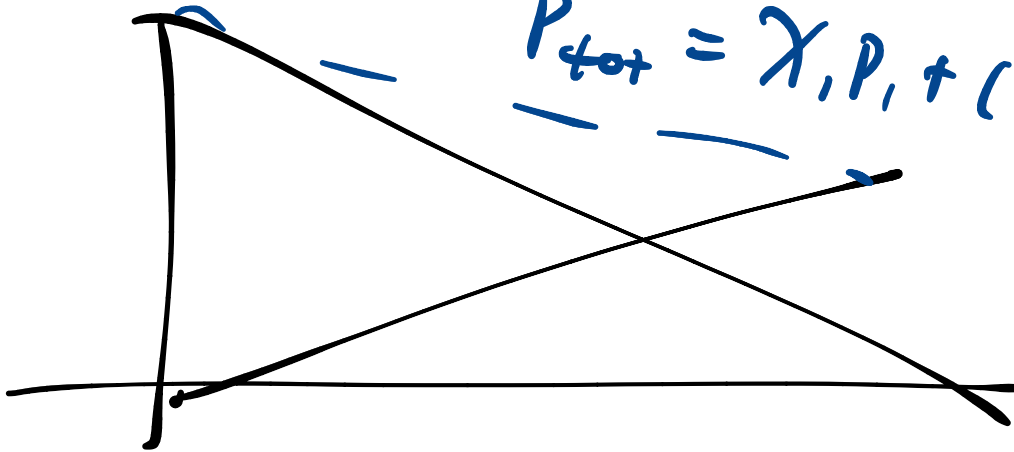
$$\mu_i = \mu_i^{\bullet} + RT \ln\left(P_i / P_i^{\bullet} \right)$$

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

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

$$\mu_i = \mu_i^{*} + RT \ln(x_i)$$

$\mu_i = \mu_i^{*}$ if $x_i = 1$



$$P_{tot} = x_1 P_1 + (1 - x_1) P_2$$

What about non ideal

EtOH + H_2O

Eg 0.001% EtOH
in H_2O

H_2O is solvent
EtOH is solute

for solvent $P_{H_2O} \approx P^*_{H_2O} \chi_{H_2O}$

for solute $P_{EtOH} \approx K^H_{EtOH} \chi_{EtOH}$

"Henry's law", K^H

If both true

"ideally dilute solution"

for this case

$$K_i^H >> p_i^*$$

H_2O & EtOH are better solvents for eachother, than themselves

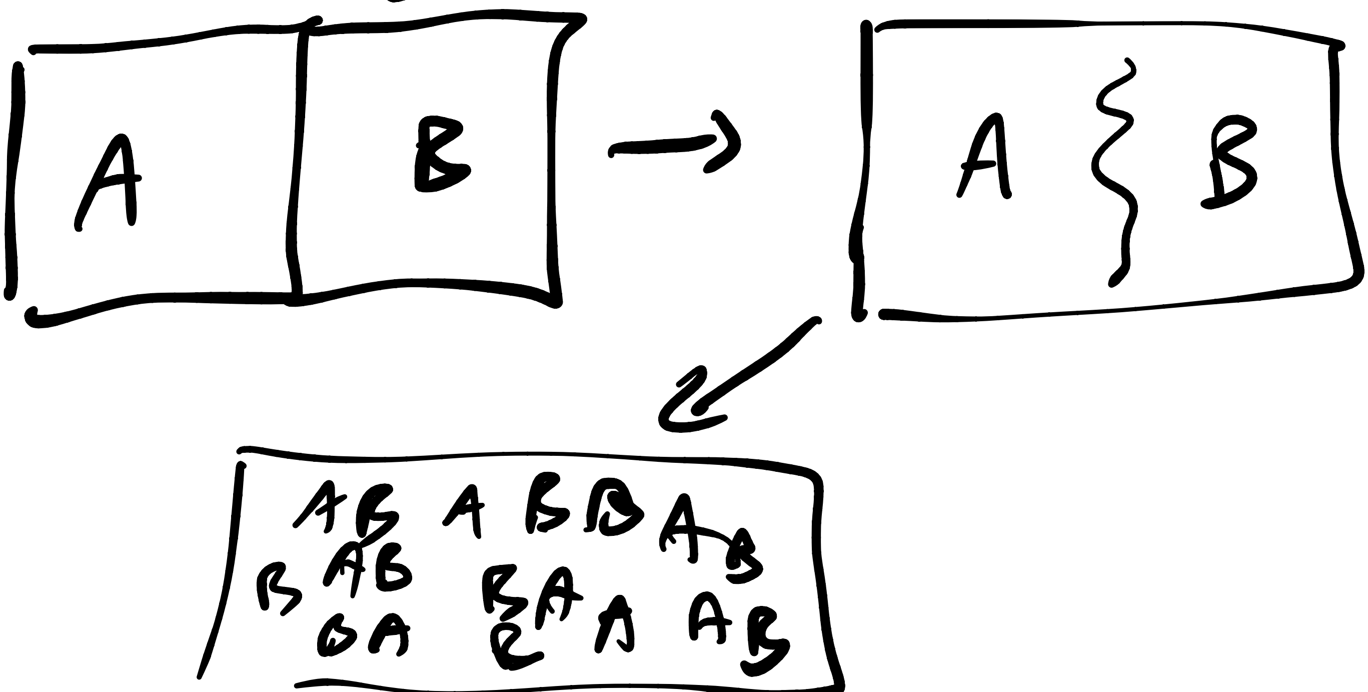
$$\mu_i = \mu_i^{\circ} + RT\ln\left(\frac{K_i^{H} x_i}{P_i^{\circ}}\right)$$

$$= \underbrace{\mu_i^{\circ} + RT\ln\left(K_i^{H}/P_i^{\circ}\right)}_{\mu_i^{\otimes}} + RT\ln x_i$$

$\leftarrow$ chemical potential in infinite dilution limit

Why do (non-ideal) solutions mix

Main driving force is entropy



Const T & P, ΔG to go down

$$\Delta G_{mix} = G_{mix} - G_{unmix}$$

$$= (n_A \mu_A + n_B \mu_B)_{mix}$$

$$- (n_A \mu_A + n_B \mu_B)_{unmix}$$

Consider first, ideal mixture

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

$$G_{mix} = n_A(\mu_A^* + RT\ln X_A) + n_B(\mu_B^* + RT\ln X_B)$$

$$\frac{\Delta G_{mix}}{n_A+n_B} = \frac{n_A RT\ln X_A + n_B RT\ln X_B}{n_A+n_B}$$

$$\overline{\Delta G}_{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta\bar{G}_{mix} = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta\bar{G}_{mix} = \underbrace{\Delta\bar{H}_{mix}}_{0?} - T\Delta\bar{S}_{mix}$$

$$\Delta\bar{S}_{mix} = \left(-\partial\bar{G}/\partial T\right)_p = -R(x_A \ln x_A + x_B \ln x_B)$$

$$-T\Delta\bar{S}_{mix} = RT(x_A \ln x_A + x_B \ln x_B)$$

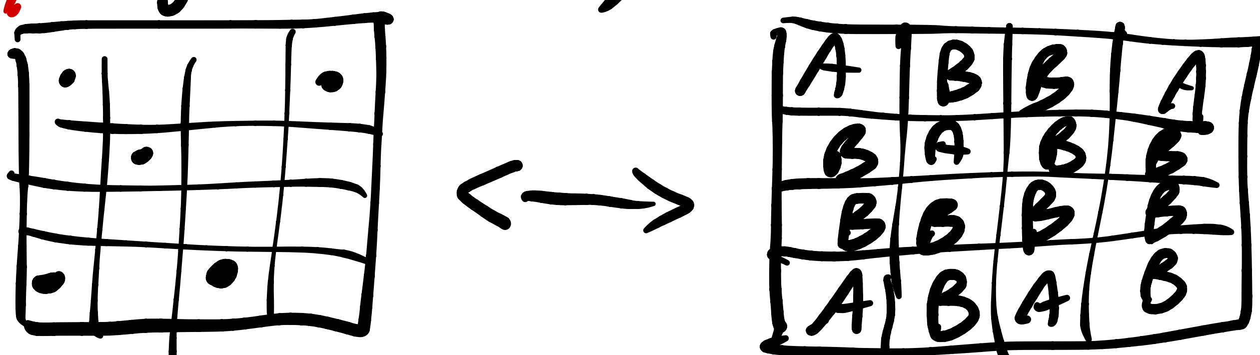
$$= \Delta\bar{G}_{mix} \Rightarrow \Delta\bar{H} = 0$$

$$\frac{\Delta \overline{S}_{mix}}{R} = x_A \ln x_A + x_B \ln x_B$$

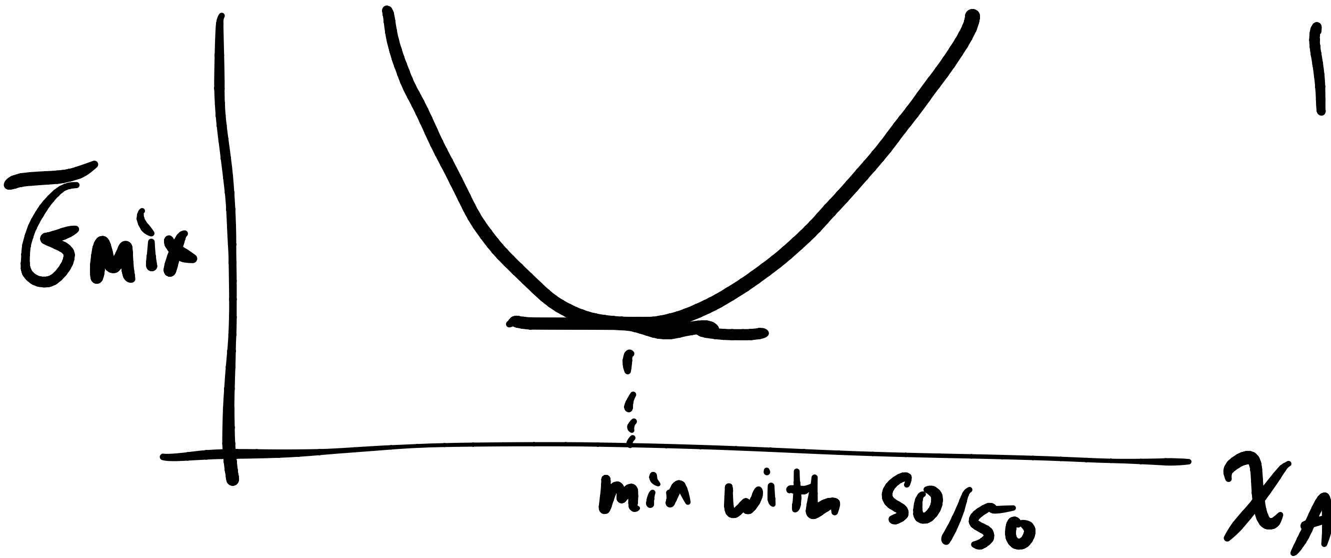
Maximum when $x_A = x_B = 0.5$

M gas molecules, N_c spots

Example?



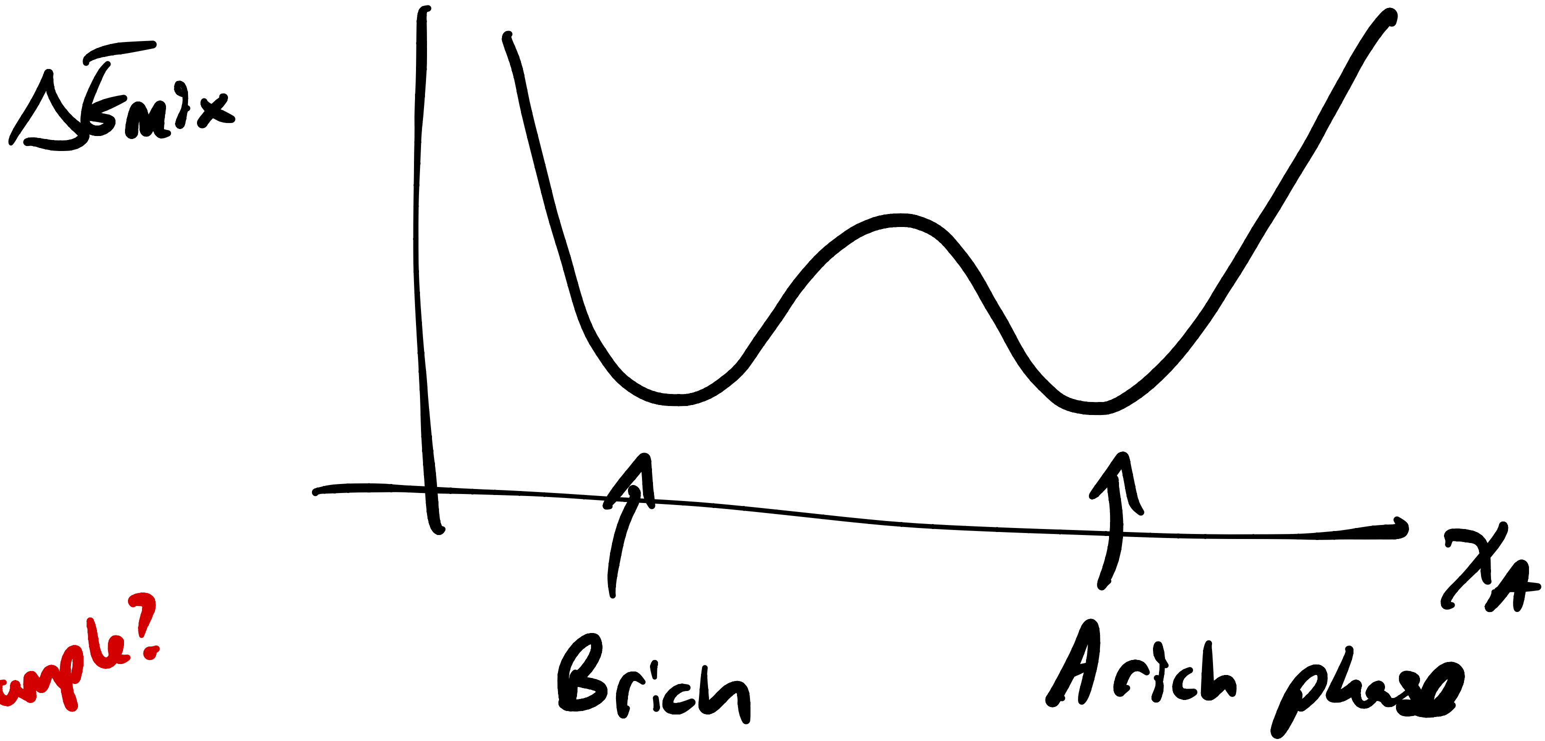
What does G_{mix} look like?



low interaction regime

$\approx -T\Delta S$

Strong interactions



Example?

for Eq, can also define

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

comparing to species i being in 1M concentration

Chemical Reactions

$$aA + bB \rightleftharpoons gG + hH$$

ν_i conservation equation $-\nu_i$

$$\overset{2 \to 1}{2H_2O} \rightleftharpoons \overset{1 \to 2}{2H_2} + \overset{1 \to 1.5}{O_2}$$

$4 - 2 - 1 = 1$

$2 - 4 - 1.5$

coeff

$$\sum_i \nu_i I = \text{const}$$

#moles

Eg 2 #moles H_2O

-2 #moles H_2

$-$ #moles O_2 $=$ const

Constraint equation

can describe chemical reaction by one progress variable

η

$$\Delta G_{rxn} = \underbrace{\eta_{rxn}}_{\#\text{moles}} \left(-a\bar{G}_a - b\bar{G}_b + g\bar{G}_g + h\bar{G}_h \right)$$

eg if $\eta = 1$

μ_i

$$\overline{\Delta G_{rxn}} = -a\mu_a - b\mu_b + g\mu_g + h\mu_h$$

$$\Delta \bar{G}_{rxn} = \sum \nu_i \mu_i$$

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

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

$$\ln [A]^{\nu_A} + \ln [B]^{\nu_B} + \dots$$

$$= \ln [A]^{\nu_A} [B]^{\nu_B}$$

$$aA + bB \rightleftharpoons gG + hH$$

$$\Delta \bar{G}_{rxn} = \underbrace{\sum \nu_i \mu_i^\circ}_{= \Delta \bar{G}^\circ} + RT \ln \frac{[G]^g [H]^h}{[A]^a [B]^b}$$

@ eq ΔG_{rxn} has to be 0

$$\Delta G^\circ = -RT \ln(K_{eq}) \qquad K_{eq} = \prod_i [i]_{eq}^{\nu_i}$$

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

$$\mu_A \qquad \mu_B \qquad\qquad \mu_C \qquad \mu_D$$

$$G_{right} = n_C \mu_C + n_D \mu_D$$

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

$$\Delta G = G_{right} - G_{left} = \sum \nu_i \mu_i$$

$$\mu_i = \mu_i^\circ + RT \ln([i])$$

$$\Delta G = \sum \nu_i \mu_i = \sum \nu_i \mu_i^\circ \quad \text{const}$$

$$+ \sum \nu_i RT \ln([i])$$

$$RT \ln Q$$

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