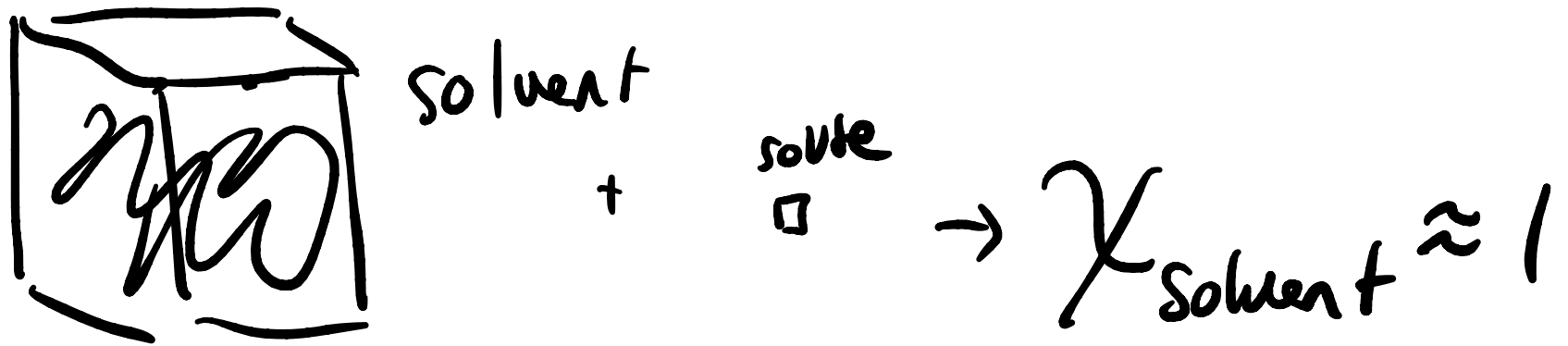


Non ideal mixtures, ctd

Raoult's law limit, for solvent



Then expect $P_{\text{solvent}} \approx X_{\text{solvent}} P_{\text{solvent}}^*$

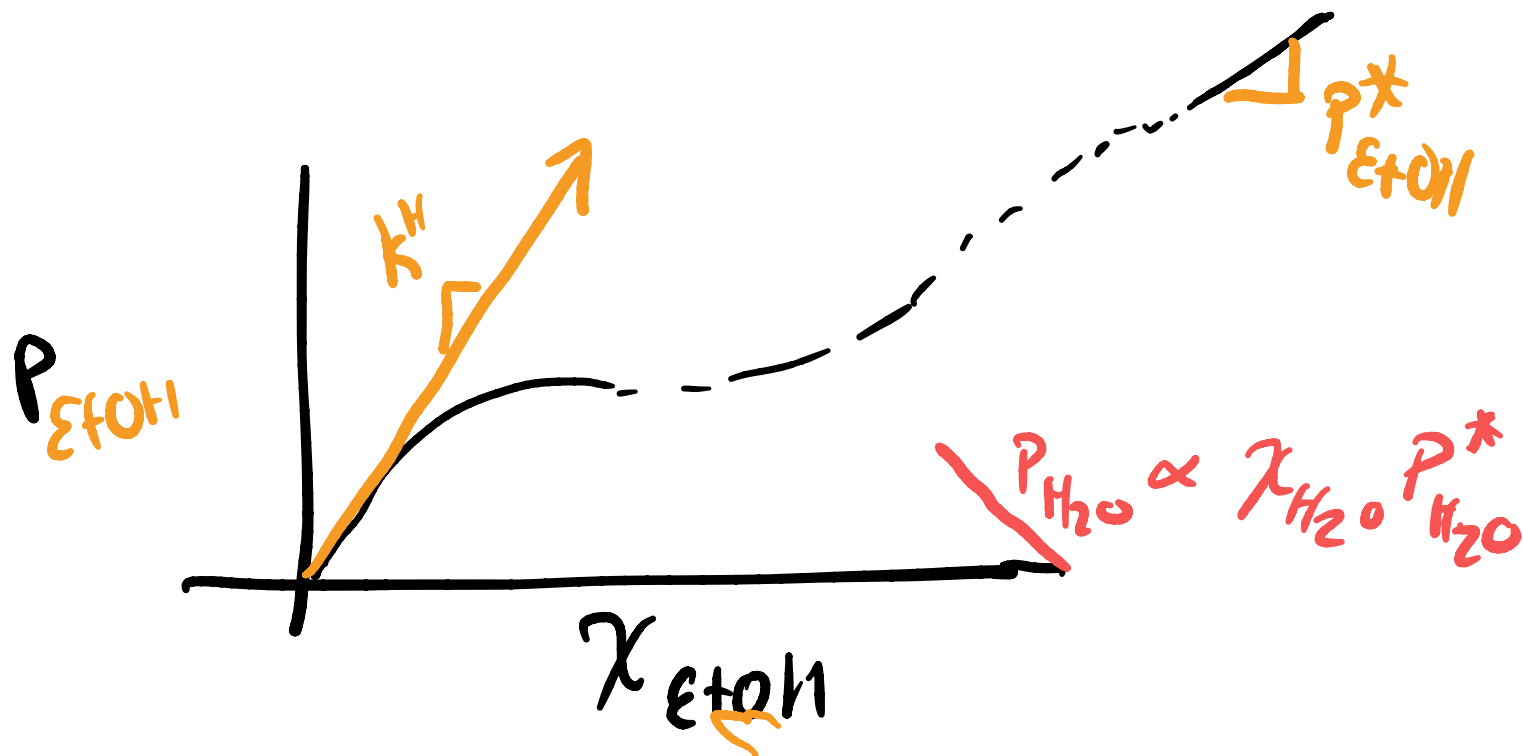
Henry's law

$P_{\text{solute}} \approx K_{\text{solute}}^H X_{\text{solute}}$, usually $K_{\text{solute}}^H \gg P_{\text{solute}}^*$

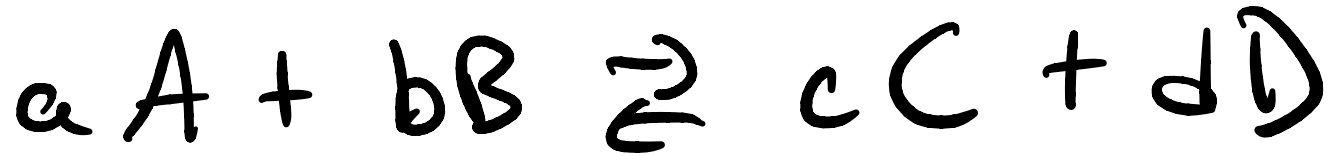
← pressure units

Many/most things are better solvents for themselves than other molecules

Eg EtOH in H_2O
or H_2O in EtOH



Chemical Reactions



Rxn is a mathematical constraint
on # moles of all species
(conservation of mass)

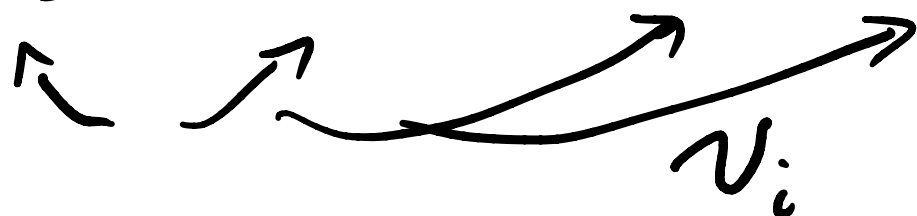
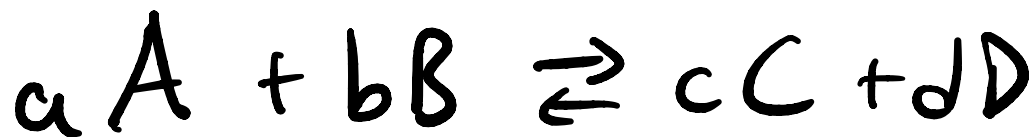
$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D$$

what if #s change

$$dG = \sum \mu_i da_i$$



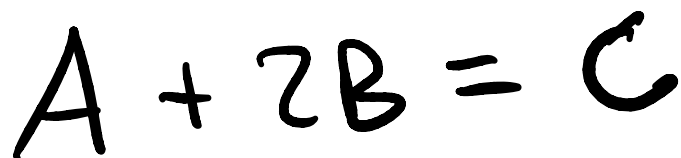
$$dn_A = -dn_B$$



$\xi \leftarrow$ progress

$$dN_A = -\nu_A d\xi \quad dN_B = -\nu_B d\xi \quad dN_C = \nu_C d\xi \quad dN_D = \nu_D d\xi$$

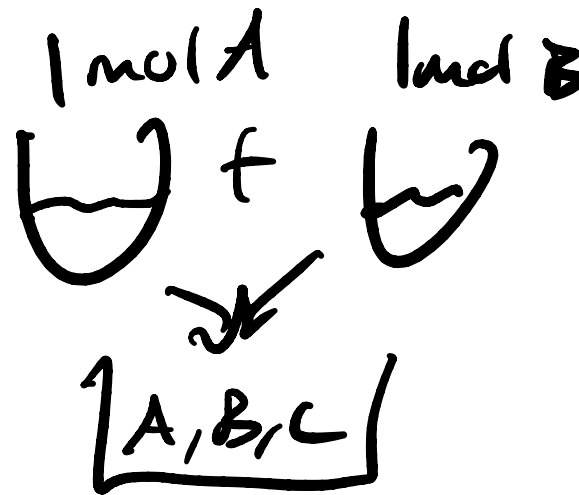
~~$$-\nu_A \xi = -\nu_B \xi = \nu_C \xi = \nu_D \xi$$~~



1 mol A
-x

1 mol B
-2x

0 mol C
+x



$$dG = \sum_i \mu_i \nu_i d\xi$$

ν 's are negative
for reactants

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

$$\frac{\partial G}{\partial \xi} = \sum_i \mu_i \nu_i = 0 \text{ @ equilibrium}$$

$$\Delta G_{\text{rxn}}$$

$$\Delta \mu_{\text{rxn}}$$

b/c G is the thermodynamic
potential for reaction
 $\partial G / \partial \xi = 0 \text{ @ eq}$

$$G(P, T, n_1, n_2, \dots)$$

for fixed P, T, n_1, \dots, n_k

G is minimized

↳ something you can change to
minimize G @ fixed $P \& T$

$$\overline{\Delta G_{rxn}} = \sum_{i=1}^k \nu_i \mu_i \quad \leftarrow \mu_i = \mu_i^\circ + RT \ln [i]$$

$$= \sum_{i=1}^k \nu_i (\mu_i^\circ + RT \ln [i])$$

$$= \left(\sum_{i=1}^k \nu_i \mu_i^\circ \right) + RT \sum_{i=1}^k \nu_i \ln [i]$$

$$+ RT \sum_{i=1}^k \ln [i]^{\nu_i}$$

$$= \sum_{i=1}^k \nu_i \mu_i^\circ + RT \ln \left[\prod_{i=1}^k [i]^{\nu_i} \right]$$

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

Q is reaction quotient
that you are used to

$$Q = \prod_{i=1}^K [i]^{v_i}$$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{for example}$$

↑
b/c v_i are

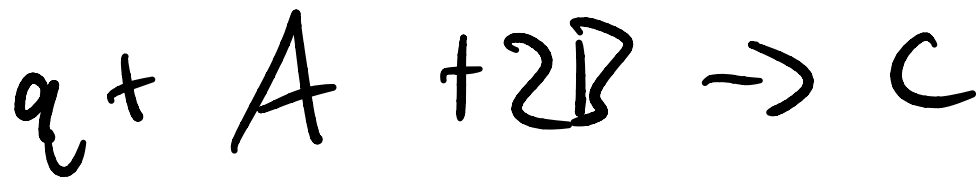
negative

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

@ equilibrium, $\Delta \bar{G}_{rxn} = 0$

$$\Rightarrow \Delta \bar{G}_{rxn}^{\circ} = -RT \ln K_{eq}$$

$$K_{eq} = Q_{eq} = \prod_{i=1}^K [i]_{eq}^{v_i}$$



$$\Delta H_{rxn} = 10 \frac{\text{kJ}}{\text{mol}}$$

What is the dependence on T?

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

$$-RT \ln K_{eq} = \Delta \bar{H}^{\circ} - T \Delta S^{\circ}$$

$$\ln K_{eq} = -\frac{\Delta \bar{H}^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

Van't Hoff Equation

Plot $\ln K_{eq}$ vs $\frac{1}{T}$, intercept $\Delta S^{\circ}/R$
slope $-\Delta H^{\circ}/R$

$$\ln k_{eq} = -\frac{\Delta F^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

$$\ln \frac{k(T_2)}{k(T_1)} = -\frac{\Delta H^{\circ}}{RT_2} + \frac{\Delta H^{\circ}}{RT_1}$$
$$= -\frac{\Delta H^{\circ}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

if ΔS°
doesn't
depend
on T

Dependence on Pressure

$$d\bar{G} = -\bar{S}dT + \bar{V}dP$$

@ const T

$$d\bar{G} = \bar{V}dP$$

$$\begin{aligned} \text{for rxn } d\Delta\bar{G}_{\text{rxn}} &= d\bar{G}_{\text{products}} - d\bar{G}_{\text{reactant}} \\ &= \Delta\bar{V}dP \end{aligned}$$

$P \uparrow$ pushes the reaction to lower volume side