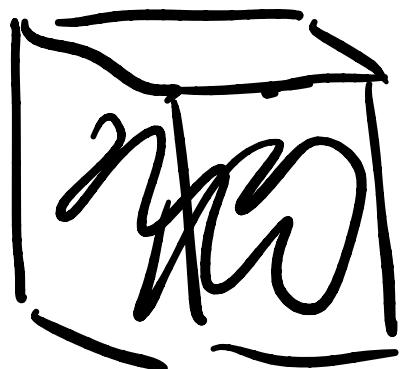


Non ideal mixtures, c+d

Raoult's law limit, for solvent



solvent

+

solute
□

$$\rightarrow \chi_{\text{solvent}} \approx 1$$

Then expect $P_{\text{solvent}} \approx \chi_{\text{solvent}} P^*_{\text{solvent}}$

Henry's law

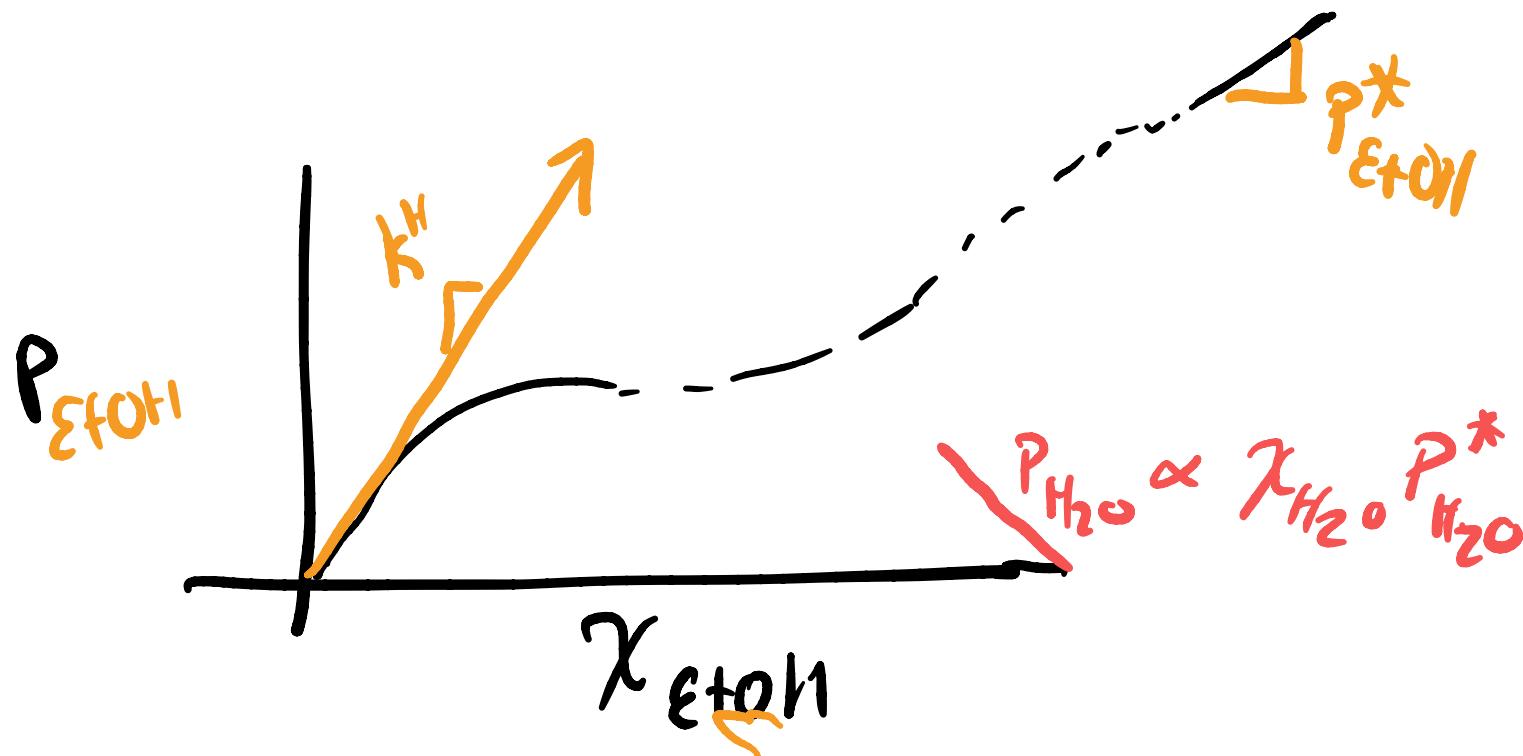
$$P_{\text{solute}} \approx k_{\text{solute}}^H \chi_{\text{solute}}, \text{ usually } k_{\text{solute}}^H \gg P^*_{\text{solute}}$$

\nwarrow pressure units

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

Eg EtOH in H₂O

or H₂O in EtOH



Chemical Reactions



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

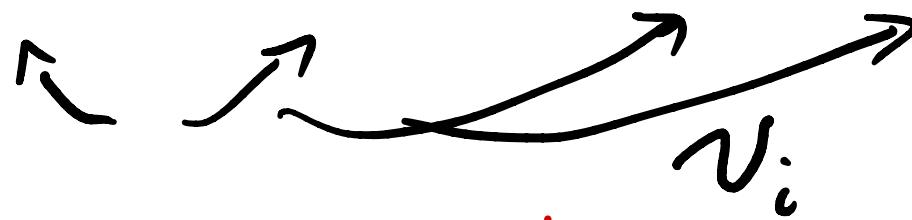
$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D$$

What if #s change

$$dG = \sum \mu_i da_i$$



$$\Delta n_A = -\Delta n_B$$



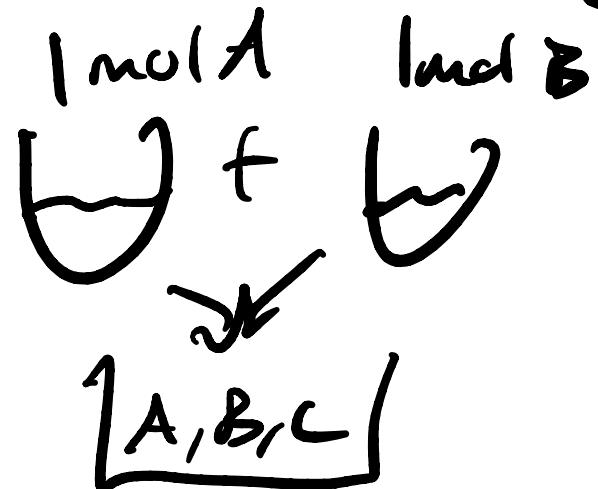
ξ ← progress

$$\Delta n_A = -v_A \Delta \xi \quad \Delta n_B = -v_B \Delta \xi \quad \Delta n_C = v_C \Delta \xi \quad \Delta n_D = v_D \Delta \xi$$

$$-\cancel{v_A} \xi = -v_B \cancel{\xi} = v_C \cancel{\xi} = v_D \cancel{\xi}$$



$$\begin{array}{ccc} 1 \text{ mol } A & 1 \text{ mol } B & 0 \text{ mol } C \\ -x & -2x & +x \end{array}$$



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

v_i 's are negative
for reactants

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

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

$$\Delta \bar{G}_{rxn}$$



$$\Delta \mu_{rxn}$$

b/c β is the thermodynamic potential for reaction

$$\frac{\partial G}{\partial \xi} = 0 @ eq$$

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

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

G is minimized

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

$$\Delta \bar{G}_{rxn} = \sum_{i=1}^k v_i \mu_i \quad \leftarrow \mu_i = \mu_i^{\circ} + RT \ln[i]$$

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

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

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

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

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

Q is reaction quotient
that you are used to

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

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

↑ bottom

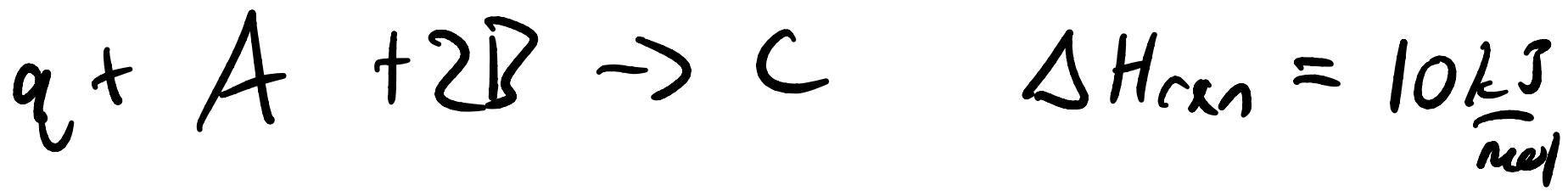
b/c v_i are negative

$$\Delta\bar{G}_m = \Delta\bar{G}_{rm}^0 + RT \ln Q$$

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

$$\Rightarrow \Delta\bar{G}_{rm}^0 = -RT \ln K_{eq}$$

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



What is the dependence on T?

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

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

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

Van't Hoff Equation

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

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

$$\ln \frac{k(T_2)}{k(T_1)} = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta H^\circ}{RT_1}$$

$$= -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

if ΔS°
doesn't
depend
on T

Dependence on Pressure

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

@ const \bar{T}

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

for rxn $d\Delta\bar{G}_{rxn} = d\bar{G}_{products} - d\bar{G}_{reactants}$

$$= \Delta\bar{V}dP$$

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