for solvent $p_i \approx x_i p_i^*$ [mol frac · single comp pressure] Ⓡ

for solute (Henry's law) $p_i \approx x_i K_i^H$

$\mu_{H_2O} = \underline{\mu^{\otimes}_{H_2O}} + RT \ln x_i$

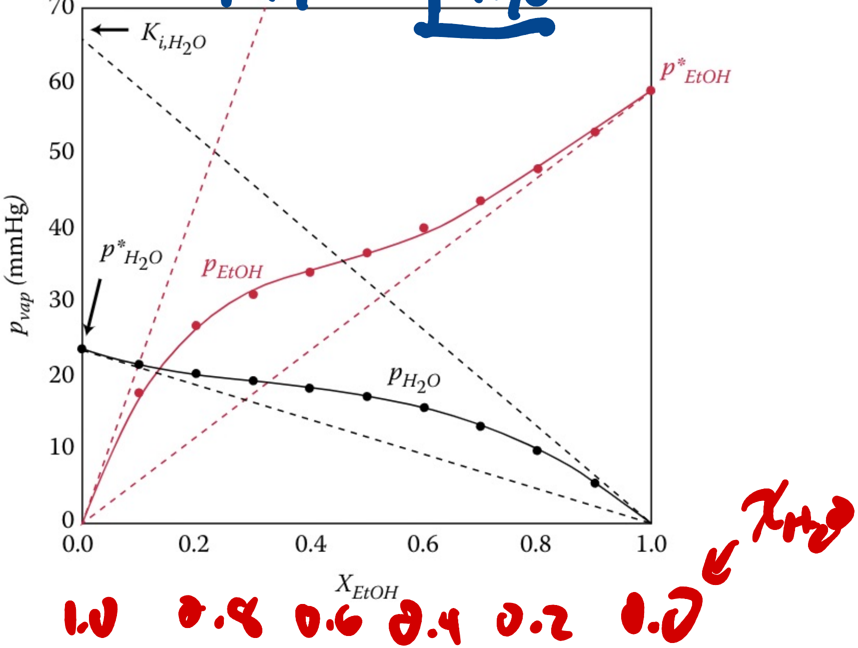


Figure 7.9 Limiting vapor pressures for water and ethanol at high dilution. The data from Figure 7.6 are fitted, and are compared with ideal solution lines (Raoult's law, dashed), and ideal dilute solution lines (Henry's law, dot dashed). For this binary mixture, the Henry's law constants ($K_{H,i}$, corresponding to the slope at $x_i = 0$), are significantly higher than the vapor pressure of the pure species (p_i^*; note the value $K_{H,EtOH}$ lies well off the scale). The Henry's law lines are obtained by taking the slopes (first derivatives in x_i) from evaluated at $x_i = 0$. The Raoult's law lines are drawn to connect p_i^* at $x_i = 1$ to zero pressure at $x_i = 0$.

$K_i^H > p_i^*$ in both cases
for this mixture

⇒ indicates
H_2O is a better solvent for H_2O
than EtOH

EtOH is . - - - -
than H_2O

Chemical Reactions

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

$$\xcancel{\sum \nu_i I} = 0$$

$$cC + dD - bB - aA = 0$$

because of mass balance
there a constraint

$$2H_2O \rightleftharpoons 2H_2 + O_2$$

describe shifts from 1 side to the other with a single #

ξ reaction progress

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$1\,\text{mol} - 2x$ $\quad$ 0 $\quad$ 0

$+x$ $\quad$ $+x$

ξ

$$K_w \sim 10^{-14}$$

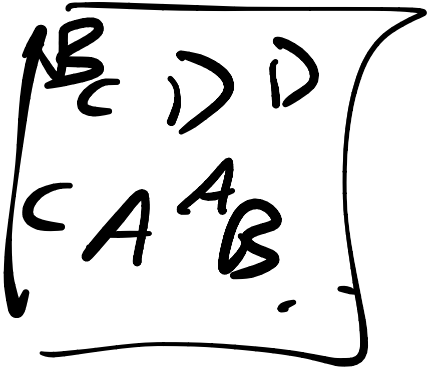
$$K_w = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$10^{-14} = x^2 / (1-2x)^2$$

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

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

can be ±



$$G(n_A, n_B, n_C, n_D, \overbrace{P, T}^{\text{const}})$$

$$\rightarrow G(n_A, n_B, n_C, n_D, \overbrace{P, T}^{\text{const}})$$

$$\left(\partial G/\partial n_A\right)_{n_B, n_C, n_D} \qquad \left(\partial G/\partial n_B\right)_{n_A, n_C, n_D}$$

$$\Rightarrow dG = \mu_A \, dn_A + \mu_B \, dn_B$$

$$+ \mu_C \, dn_C + \mu_D \, dn_D$$

$$= \underbrace{\sum \mu_i \, dn_i}_{} \text{ all reaction}$$

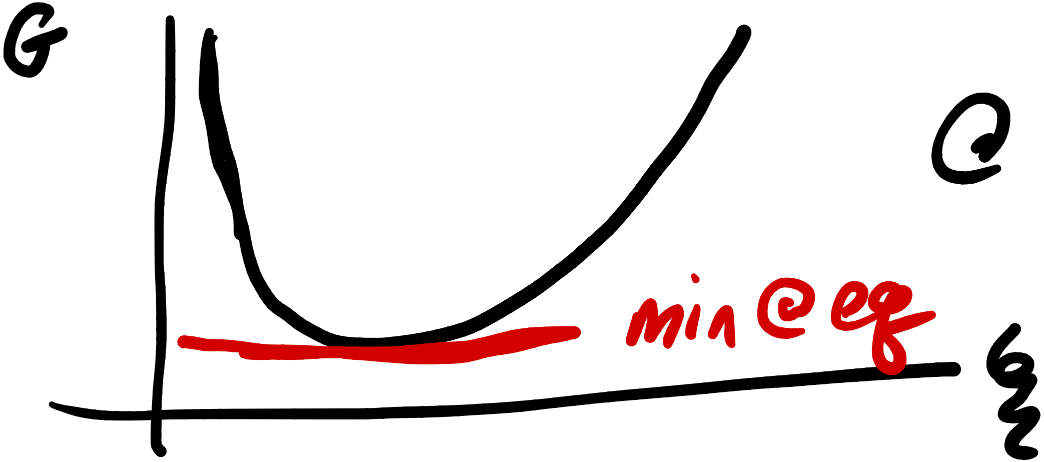
$$dn_A = -a\xi \qquad dn_B = -b\xi \qquad dn_C = c\xi$$

$$dn_D = d\xi$$

ν_i is rxn coefficient

& ν_i is $-$ for reactants

$$dG = \sum \mu_i \nu_i \, d\xi$$



@ const T & P

$$dG = \sum \mu_i \nu_i \, d\xi$$

$$\Leftrightarrow \left(\partial G / \partial \xi\right)_{n_1, n_2, n_3, n_4 \ldots} = \sum \mu_i \nu_i$$

$$\equiv \overline{\Delta G}_{rxn} (n_1, n_2 \ldots, n_m)$$

$$\mu_i = \mu_i^\circ + RT \ln [i] \qquad {}^\circ \Rightarrow [i] = 1M$$

$$\overline{\Delta G}_{rxn} = \underbrace{\sum \mu_i^\circ \nu_i}_{\Delta G^\circ_{rxn}} + \underbrace{\sum_{i=1}^{m} RT \ln [i] \nu_i}$$

$$-aRT\ln[A] + bRT\ln[B]$$

$$aA \rightleftharpoons bB$$

$$\hookrightarrow \Delta G = \Delta G^0 + RT\ln \frac{[B]^b}{[A]^a}$$

$$\overline{\Delta G} = \overline{\Delta G^0} + RT\ln Q$$

$$Q = \prod_{i=1}^{M} [i]^{\nu_i}$$

$$\overline{\Delta G} = \overline{\Delta G^0} + RT\ln Q$$

@ Eq

$$\Rightarrow \quad 0 = \overline{\Delta G^0} + RT\ln K_{eq}$$

$$\overline{\Delta G^0} = -RT\ln K_{eq}$$

$$K_{eq} = \prod_{i=1}^{n} [i]_{eq}^{\nu_i}$$

$$\sum \mu_i^0 \nu_i$$

What happens if we change T or P to eq

Temp

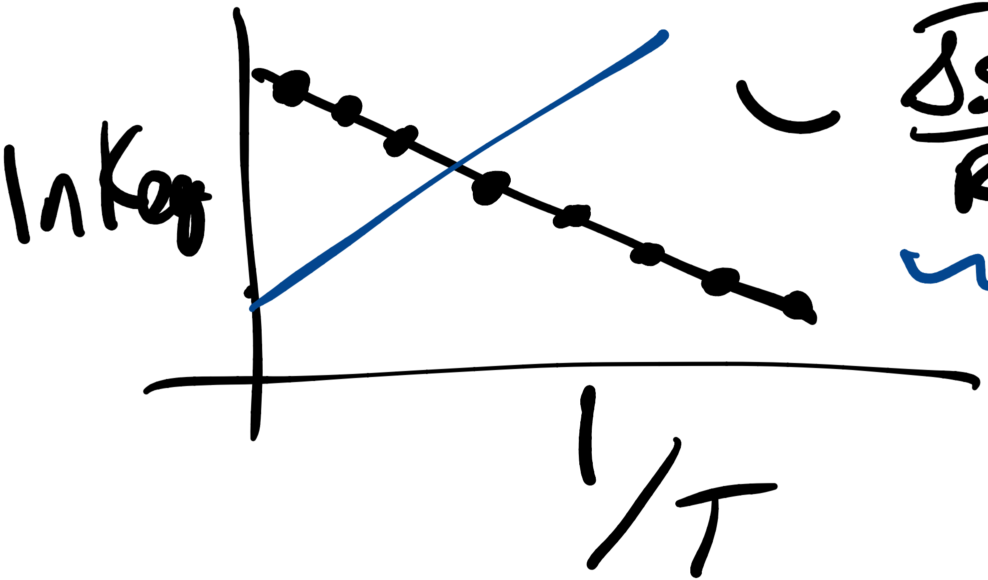
$$\Delta \bar{G}^{\circ} = \Delta \bar{H}^{\circ} - T \Delta \bar{S}^{\circ}$$

$$\parallel$$

$$-RT \ln K_{eq}$$

"Van't Hoff eqn"

$$\ln K_{eq} = -\frac{\Delta \bar{H}^{\circ}}{RT} + \frac{1}{R} \Delta \bar{S}^{\circ}$$



$$= \underbrace{\frac{\Delta S^\circ}{R}}_{\text{intercept}} - \underbrace{\frac{\Delta H^\circ}{R}}_{\text{slope}} \cdot \frac{1}{T}$$

Dependence on pressure

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

@ const T

$$d\Delta\bar{G} = \Delta\bar{V}\,dP$$ ↗ $G = \sum G_i$

@standard conditions

$$d\Delta\bar{G}^\circ = \Delta\bar{V}^\circ\,dP$$

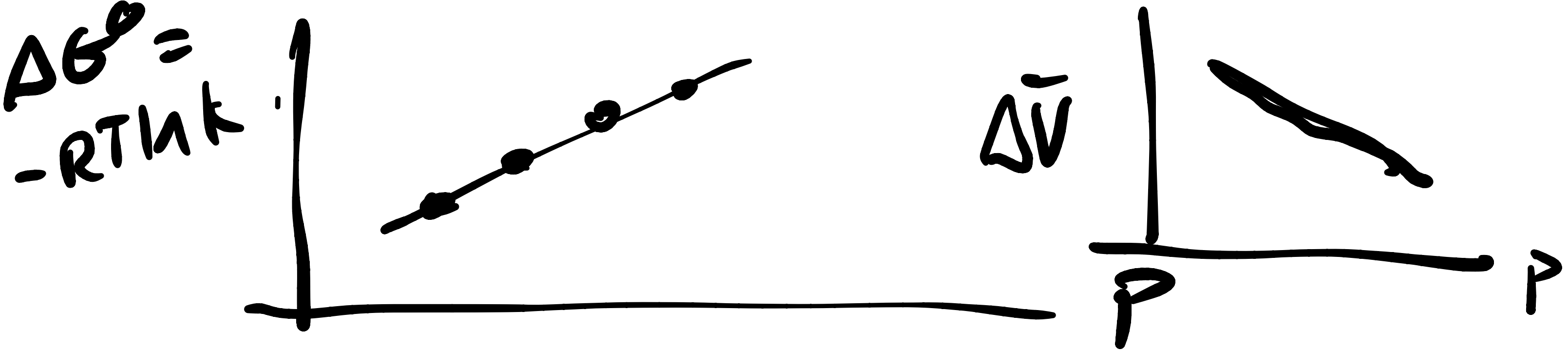
$$C_6H_{12}^{(l)} + 9\,O_2^{(g)} \rightleftharpoons 6\,CO_2^{(g)} + 6\,H_2O$$

$$d\Delta\bar{G}^\circ = \Delta\bar{V}^\circ \, dP$$

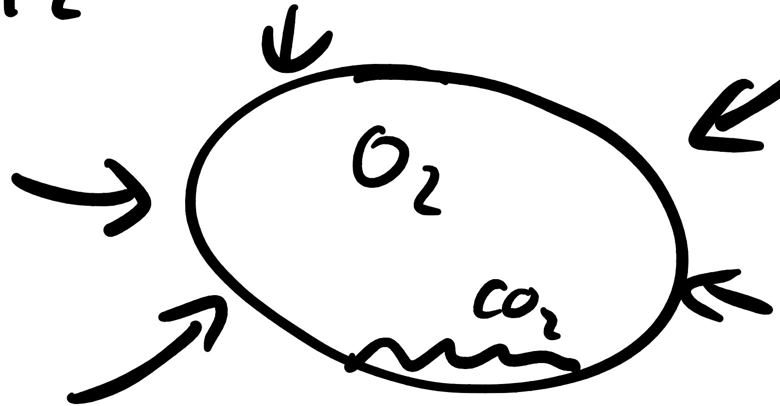
-RT ln K

$$\Delta\bar{V}^\circ = \left(\partial \Delta\bar{G}^\circ / \partial P \right)_T$$

@ standard conditions



$$C_6H_{12}^{(l)} + 9\,O_2^{(g)} \rightleftharpoons 6\,CO_2^{(g)} + 6\,H_2O$$



"Le Chatelier's principle"

$$d\Delta\bar{G}^\circ = \Delta\bar{V}^\circ dP$$

"1st order"

approx

$$\Delta\bar{G}^\circ(p) = \Delta\bar{G}^\circ(p_{ref}) + \Delta\bar{V}^\circ(P - p_{ref})$$

$$\Delta\bar{G}^\circ = -RT\ln K$$

$$-RT\ln K < 0$$

top of K_{eq} goes up

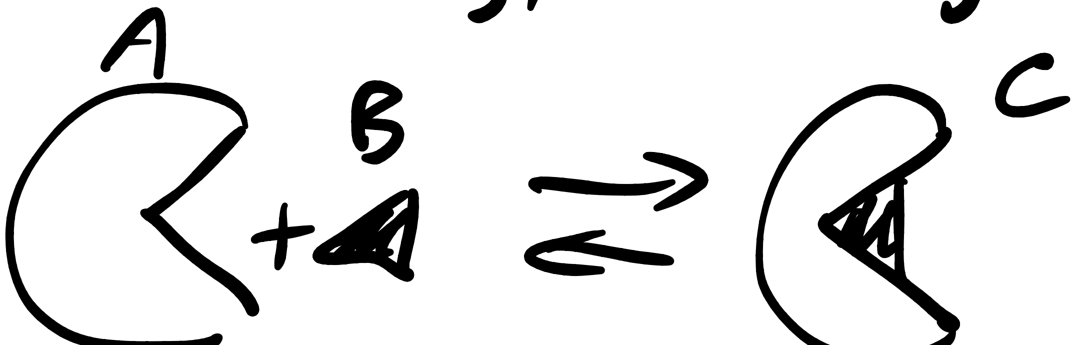
$$\left(\partial \bar{G}^{\circ}/\partial p\right)_T = \Delta \bar{V}^{\circ}$$

$$\Delta \bar{G}^{\circ}(p) \approx \Delta \bar{G}^{\circ}(p_{ref}) + (p - p_{ref})\frac{\partial \bar{G}^{\circ}}{\partial p} + \cancel{\frac{(p-p_{ref})^2}{2}\frac{\partial^2 G}{\partial p^2}}$$

Conformational Equilibrium

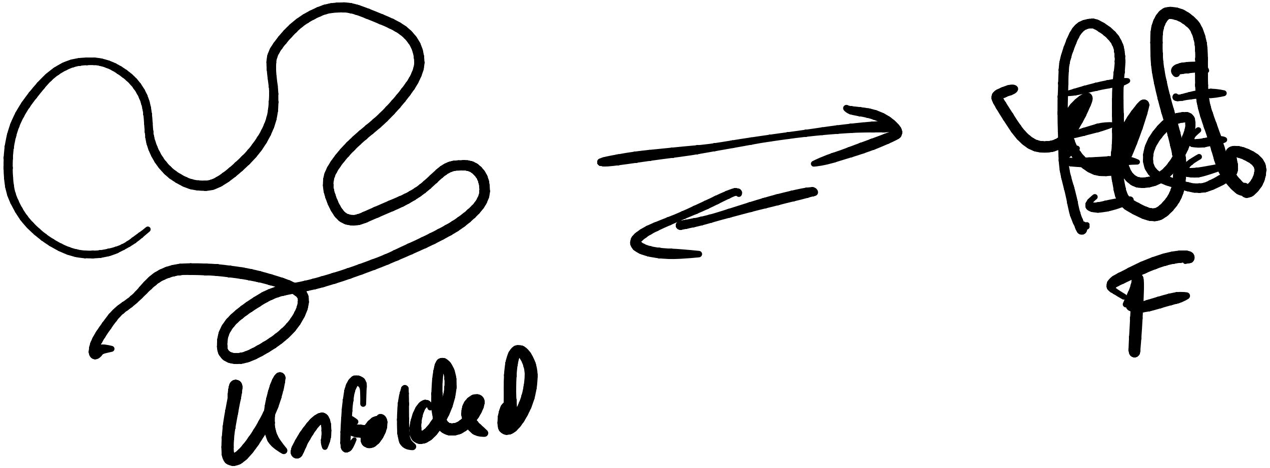
Biomolecular reaction

"binding/unbinding"



$$A + B \rightleftarrows (AB)$$

"reaction" transition between stable states of 1 molecule.



$$U \rightleftharpoons F$$

Folding controlled by

$$\Delta G = \Delta H - T\Delta S$$

$U \rightleftarrows F$

$G_F - G_U$

in general

$\Delta H_{folding} < 0$

$\Delta S_{folding} < 0$ “more ordered”

(consider H_2O, ions)

Competition btwn energy & entropy
& depends on T