The thermodynamics of mixing

2 perfect gases:

- Gibbs energy: $\Delta_{mix} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$

$$= nRT(X_A \ln X_A + X_B \ln X_B)$$

- Entropy: $\Delta_{mix} S = -\frac{\partial \Delta_{mix} G}{\partial T} = -nR(X_A \ln X_A + X_B \ln X_B)$

Since $\ln X < 0 \Rightarrow \Delta_{mix} S > 0$

$\Rightarrow \Delta_{mix} H = 0$ no interaction between molecules

$\Rightarrow$ driving force of mixing is entropy!

ideal solutions:

$$\underset{\text{eiquil}}{\mu_A^{*}} \overset{\leftarrow \text{pure}}{=} \mu_A^{0} + RT \ln \overset{\downarrow \text{vapour}}{p_A/p^0}$$
$$= p_A^*$$

+ another substance dissolved:

$$\mu_A = \mu_A^0 + RT \ln p_A$$

$$\Rightarrow \mu_A = \mu_A^* + RT \ln p_A/p_A^*$$

Raoult's law : $p_A = X_A p_A^*$ $\Leftrightarrow$ ideal solution

$$\boxed{\mu_A = \mu_A^* + RT \ln X_A}$$

molecular interpretation:

rate of vaporization $= k\, X_A$
rate of condensation $= k'\, p_A$

equilib.: $\quad k' p_A = k\, X_A$

$$p_A = \frac{k}{k'} X_A \qquad \text{pure liquid } p_A^* = \frac{k}{k'}$$

$$\Rightarrow p_A = p_A^* X$$

- ideal solutions applies for very similar liquids
- $\mu_A = \mu_A^* + RT \ln X_A$ also applies to very dilute solutions where Raoult's law does not apply
  it is replaced by Henry's law: $p_B = X_B K_B$
  empirical constant

dilute $\Rightarrow$ ~~solute~~ solvent behaves like a slightly modified pure liquid
solute sees predominantly solvent molecules $\Rightarrow$ very different

Henry's law ($p_B = \chi_B K_B$)
$\Rightarrow$ solubility of O_2-gas in blood decreases with decreased pressure $\Rightarrow$ problems at high altitude or sku diving

<u>liquid mixtures:</u>

<u>ideal</u>:

$$\Delta_{mix} G = nRT \{ \chi_A \ln \chi_A + \chi_B \ln \chi_B \}$$

$$\Delta_{mix} S = -nR \{ \chi_A \ln \chi_A + \chi_B \ln \chi_B \}$$

rarely found!

<u>regular solution</u>

excess functions describe difference

$$S^{EX} = \Delta_{mix} S - \Delta_{mix} S^{ideal}$$

regular: $H^{EX} \neq 0 \quad S^{EX} = 0$

$$H^{EX} = n \beta RT \chi_A \chi_B \qquad \beta = w/RT$$

$$w \sim |2 \varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}|$$

$\beta < 0 \Rightarrow$ mixing favourable since exothermic
$\beta > 0 \Rightarrow$ endothermic

$$\Delta_{mix} G = nRT \{ \chi_A \ln \chi_A + \chi_B \ln \chi_B + \beta \chi_A \chi_B \}$$

Colligative properties

- depend only on the number of solute particles present, not their identity
- for: solute not volatile, solute does not dissolve in solid solvent
- always a reduction of chemical potential

$$\mu_A = \mu_A^* + RT \underbrace{\ln X_A}_{<1}$$

$\Rightarrow$ liquid-vapour equilib. occurs at a higher temp. and the solid-liquid equili. occurs at a lower temp.

- molecular interpretation
  - entropy of mixing is added and lowers tendency to get into the higher entropic state of a gas
  - also additional molecular randomness ~~or~~ hinders freezing!

boiling point

$$\mu_A^*(g) = \mu_A^*(l) + RT \ln X_A$$

$$\ln(1 - X_B) = \frac{\mu_A^*(g) - \mu_A^*(l)}{RT} = \frac{\Delta_{vap} G}{RT}$$

$$\Delta_{vap} G = \Delta_{vap} H - T \Delta_{vap} S$$

ignore small T-dependence

$$\ln(1 - X_B) = \frac{\Delta_{vap} H}{RT} - \frac{\Delta_{vap} S}{R}$$

$$X_B = 0 \Rightarrow \underbrace{\ln 1}_{=0} = \frac{\Delta_{vap} H}{RT^*} - \frac{\Delta_{vap} S}{R}$$

$$\Rightarrow \ln(1 - X_B) = \frac{\Delta_{vap} H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$X_B << 1 \qquad \ln(1 - X_B) \approx - X_B$$

$$X_B = \frac{\Delta_{vap} H}{R}\left(\frac{1}{T^*} - \frac{1}{T}\right)$$

$$\underset{T \approx T^*}{=} \frac{\Delta_{vap} H}{R} \frac{T - T^*}{TT^*}$$

$$\approx \frac{\Delta T}{T^{*2}}$$

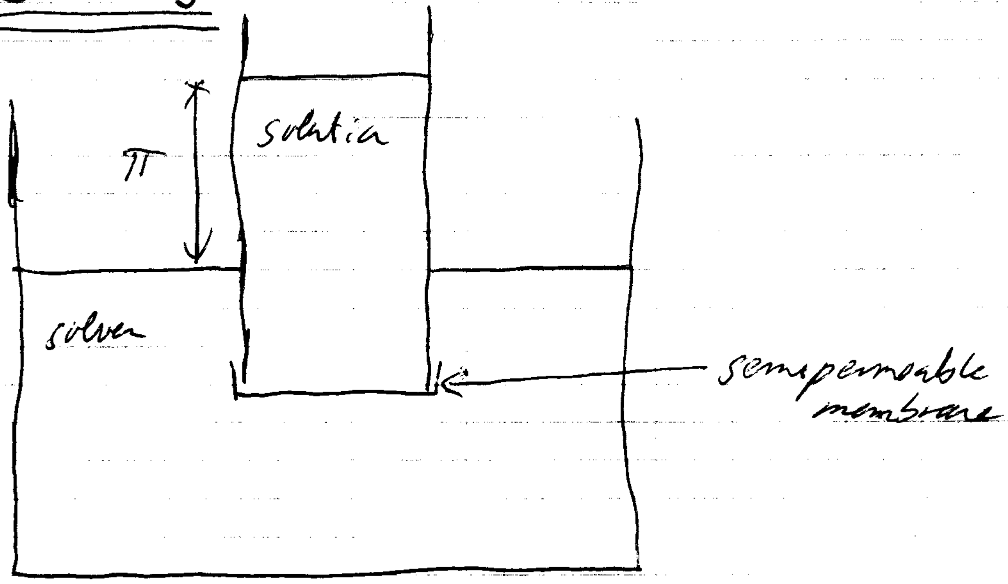
$$\Rightarrow \boxed{\Delta T = K X_B \qquad K = \frac{RT^{*2}}{\Delta_{vap} H}}$$

analog for freezing point

Solubility

$$\ln \chi_B = \frac{\Delta_{fus} H}{R} \left(\frac{1}{T^*} - \frac{1}{T} \right)$$

Osmosis



$$\mu_A^*(p) = \mu_A(\chi_A, p+\pi)$$

$$\mu_A(\chi_A, p+\pi) = \mu_A^*(p+\pi) + RT \ln \chi_A$$

$$\mu_A^*(p+\pi) = \mu_A^*(p) + \int_p^{p+\pi} V_m \, dp$$

$$\Rightarrow \; -RT \underbrace{\ln \chi_A}_{\substack{= \ln(1-\chi_B) \\ \approx -\chi_B \text{ dilute}}} = \int_p^{p+\pi} \underbrace{V_m}_{\approx \text{ const}} \, dp$$

$$\Rightarrow \; RT \chi_B = \pi V_m$$

$$\chi_B \approx \frac{n_B}{n_A} \qquad n_A V_m = V$$

$$\Rightarrow \; \boxed{\pi = \frac{n_B}{V} RT}$$