Lecture 14

Tuesday, October 31, 2023 11:26

Topic 5A Simple Mixtures (cont'd)

always negative

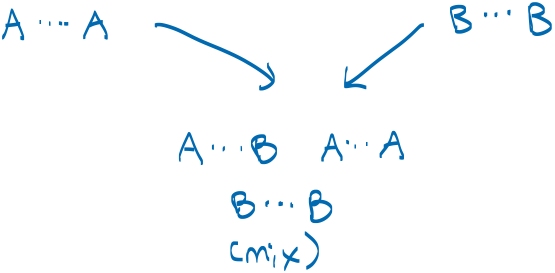
$$\Delta_{mix} G = nRT\,(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} S = -\left(\frac{\partial \Delta_{mix} G}{\partial T}\right)_p$$

always positive

$$= -nR\,(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} H = 0$$



Ideal Solutions

- liquid, with solute

μ_A^* ← pure liquid chemical potential

vapour
liquid

$\mu(\text{vapour}) = \mu(\text{liquid})$

at equilibrium

$$\mu_A^*(g) = \mu_A^\ominus(g) + RT\ln \frac{p_A^*}{\underbrace{p^\ominus}_{1\text{ bar}}}$$

simplify

$$\mu_A^*(g) = \mu_A^\ominus(g) + RT\ln p_A^*$$

$$\mu_A^*(l) = \boxed{\mu_A^\ominus(g)} + RT\ln \boxed{p_A^*}$$

solve for $\mu_A^\ominus(g)$

partial vapour pressure of the pure liquid

vapour
solution
solute

$\mu_A(l) = \mu_A(g)$

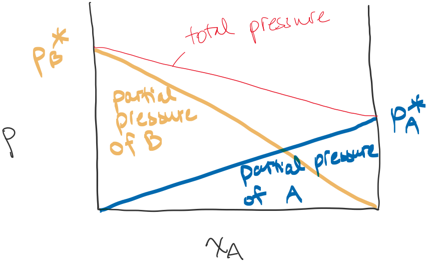
at equilibrium

$$\mu_A(l) = \underbrace{\mu_A^\ominus(g)}_{\text{how to cancel?}} + RT\ln p_A$$

$$\mu_A^\ominus(g) = \overbrace{\mu_A^*(l) - RT\ln p_A^*}$$

$$\mu_A(l) = \mu_A^*(l) - RT\ln p_A^* + RT\ln p_A$$

$$\mu_A(l) = \mu_A^*(l) + RT\ln \frac{p_A}{p_A^*}$$



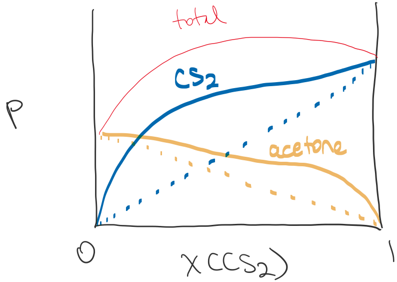
$$\boxed{p_A = x_A p_A^*}$$

Raoult's Law (ideal solution)

$$x_A = \frac{p_A}{p_A^*}$$

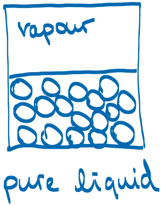
$$\boxed{\mu_A(l) = \mu_A^*(l) + RT\ln x_A}$$

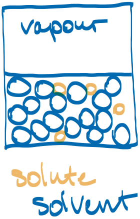
chemical potential (ideal solution)



mixture of acetone and carbon disulfide

C_3H_6O





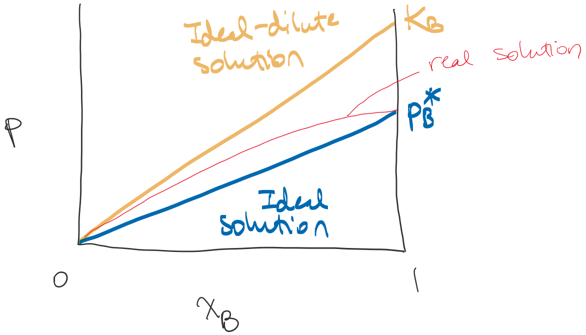
$S(\text{pure liquid}) < S(\text{solution})$

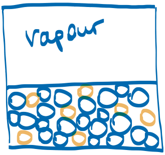
more tendency for molecules to remain in the condensed phase in the mixture → decreased vapour pressure compared to the liquid

Ideal-Dilute Solutions

Raoult's Law : applies to solvent and solute for ideal solutions

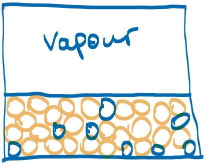
Henry's Law : $\boxed{p_B = x_B K_B}$





solute (minority component)

dissimilar to pure liquid B



solvent (majority component)

similar to pure liquid B

Quick note from Topic 5B : Properties of Solutions

$$\Delta_{mix} G = nRT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} S = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} H = 0$$

ideal solution

pure A

A ⋯ A

pure B

B ⋯ B

→ mixture ↙

A ⋯ A   B ⋯ B

A ⋯ B

A ⋯ A = B ⋯ B = 0 ↙

$\Delta_{mix} H = 0$ perfect gas

$\Delta_{mix} H = 0$ ideal solution

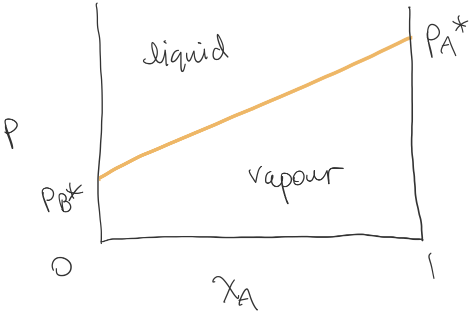
↖ A ⋯ A = B ⋯ B ≠ 0

(skip rest of 5B)

Topic 5C: Phase Diagrams of Binary

Systems : Liquids

$p_A = x_A p_A^*$ $p_B = x_B p_B^*$



$$p = p_A + p_B = x_A p_A^* + \overbrace{x_B}^{(1-x_A)} p_B^*$$

$$= x_A p_A^* + p_B^* - x_A p_B^*$$

$$\boxed{p = p_B^* + (p_A^* - p_B^*) x_A}$$

total vapour pressure

Expect mole fractions to be different in the liquid and vapour phases generally

mix water with ethanol

$y_{EtOH} > x_{EtOH}$

↑

more volatile

y_J : mole fraction in the vapour

x_J : mole fraction in the liquid

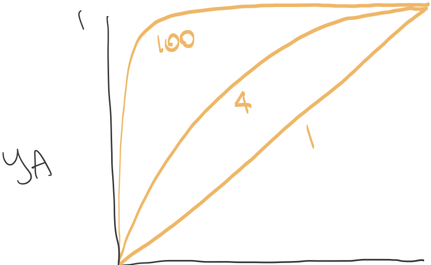
$$y_A = \frac{p_A}{p}, \quad y_B = \frac{p_B}{p}$$

$$y_A = \frac{p_A}{p_B^* + (p_A^* - p_B^*)x_A}$$

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*)x_A}$$

$$y_B = 1 - y_A$$

composition of vapour



various values of p_A^*/p_B^*

0 x_A 1

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A}$$

$$\left[p_B^* + (p_A^* - p_B^*) x_A\right] y_A = x_A p_A^*$$

$$p_B^* y_A + (p_A^* - p_B^*) x_A y_A = x_A p_A^*$$

$$p_B^* y_A = x_A p_A^* - (p_A^* - p_B^*) x_A y_A$$

$$p_B^* y_A = x_A p_A^* + (p_B^* - p_A^*) x_A y_A$$

$$p_B^* y_A = x_A \left[p_A^* + (p_B^* - p_A^*) y_A\right]$$

$$\boxed{x_A = \frac{p_B^* y_A}{p_A^* + (p_B^* - p_A^*) y_A}}$$

$$p = p_B^* + (p_A^* - p_B^*) x_A$$

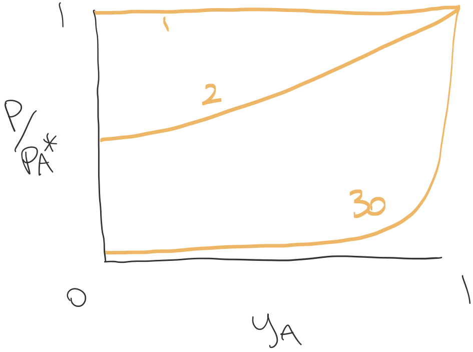
$$p = p_B^* + \frac{(p_A^* - p_B^*)\,p_B^*\,y_A}{p_A^* + (p_B^* - p_A^*)\,y_A}$$

$$p = \frac{p_B^*\left[p_A^* + (p_B^* - p_A^*)\,y_A\right]}{p_A^* + (p_B^* - p_A^*)\,y_A} + \frac{(p_A^* - p_B^*)\,p_B^*\,y_A}{p_A^* + (p_B^* - p_A^*)\,y_A}$$

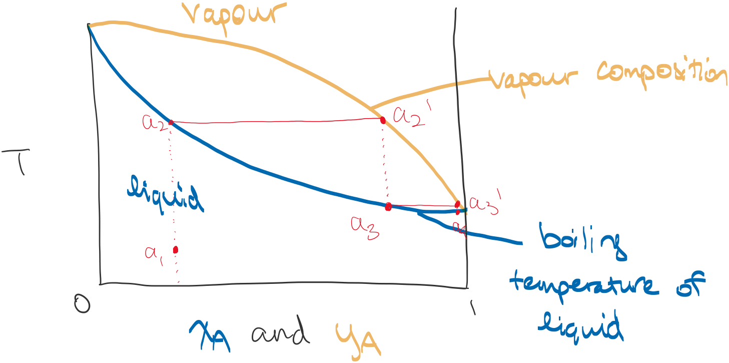
$$p = \frac{p_B^*\,p_A^* - \cancel{(p_A^* - p_B^*)\,y_A\,p_B^*} + \cancel{(p_A^* - p_B^*)\,p_B^*\,y_A}}{p_A^* + (p_B^* - p_A^*)\,y_A}$$

$$\boxed{p = \frac{p_A^*\,p_B^*}{p_A^* + (p_B^* - p_A^*)\,y_A}}$$

total vapour pressure



(still ideal solution)



fractional distillation