5.60 Thermodynamics & Kinetics
Spring 2008

Two-Component Phase Equilibria III
Ideal and Non-Ideal Solutions

Free energy change ΔG_{mix} in ideal solutions
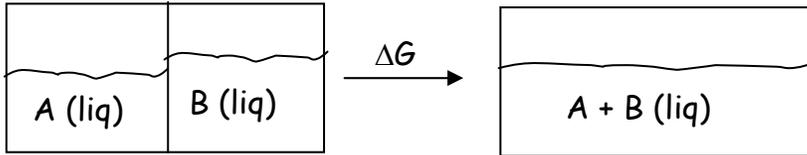
$$G_1(\ell) = n_A x_A \mu_A^*(\ell) + n_B x_B \mu_B^*(\ell) \qquad G_2(\ell) = n_A x_A \mu_A^{mix}(\ell) + n_B x_B \mu_B^{mix}(\ell)$$

$$\Delta G_{mix} = G_2(\ell) - G_1(\ell)$$
$$= n x_A \left[\mu_A^*(\ell) + RT \ln x_A \right] + n x_B \left[\mu_B^*(\ell) + RT \ln x_B \right] - n x_A \mu_A^*(\ell) - n x_B \mu_B^*(\ell)$$

$$\boxed{\Delta G_{mix} = nRT \left(x_A \ln x_A + x_B \ln x_B \right)}$$

Purely <u>entropic</u>, as in gas mixture

$G = Vdp - SdT$

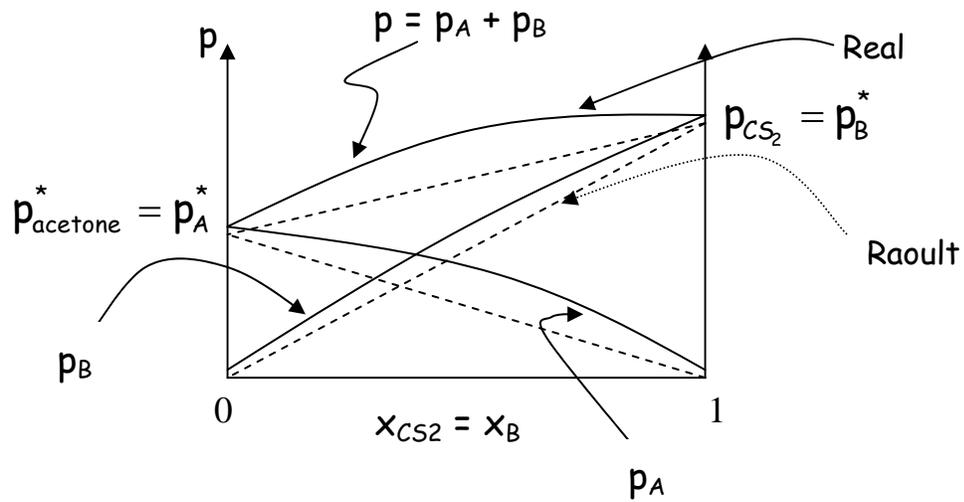$$\Delta S_{mix} = -\left(\frac{\partial \Delta G_{mix}}{\partial T} \right)_p = -nR \left(x_A \ln x_A + x_B \ln x_B \right)$$

$$\boxed{\Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix} = 0}$$

No enthalpy change, all of ΔG is due to entropy of mixing

Change in volume ΔV_{mix}

$$\Delta V_{mix} = \left(\frac{\partial \Delta G_{mix}}{\partial p} \right)_T = 0$$

No volume change, just like ideal gas.

Non-Ideal Solutions:

In reality, molecules interact:

$$u_{AA} < 0 \qquad u_{BB} < 0 \qquad\qquad\qquad u_{AB} \qquad\qquad u_{AB}$$

$$\text{PURE} \qquad\qquad\qquad\qquad\qquad \text{MIXED}$$

$$\Delta u = 2u_{AB} - (u_{AA} + u_{BB})$$

This difference determines how solutions depart from ideality.

    I.   **Positive Deviations**: $\Delta u > 0$ (most common)

Mixing is <u>energetically</u> not favorable in liquid phase.

$$\Delta H = \Delta U + \Delta(PV) \approx \Delta U$$

$$\Delta G_{mix} = \frac{n}{4}\Delta u + nRT\left(x_A \ln x_A + x_B \ln x_B\right) > \Delta G_{mix}\text{(ideal)}$$

e.g. acetone & carbon disulphide

$$p_{CS_2} > x_{CS_2}p_{CS_2}^*$$

$$p_{acetone} > x_{acetone}p_{acetone}^*$$

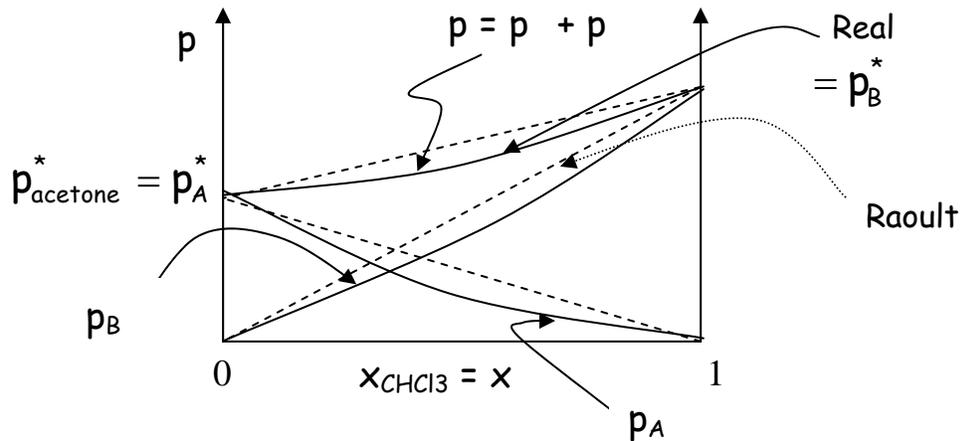$$\Rightarrow \boxed{p_{tot}\left(real\right) > p_{tot}\left(Raoult\right)}$$

$\Rightarrow$ vapor pressure is higher than expected by Raoult's Law

II.   Negative Deviations: $\Delta u < 0$

e.g. acetone & chloroform
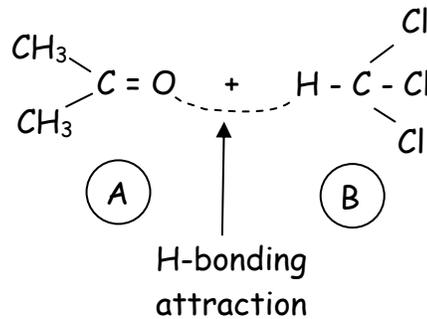
Mixing is energetically favorable in liquid phase.

$$p_{CS_2} < x_{CS_2} p_{CS_2}^*$$

$$p_{CHCl_3} < x_{CHCl_3} p_{CHCl_3}^*$$

$$\Rightarrow \boxed{p_{tot}(real) < p_{tot}(Raoult)}$$

Ideal Dilute Solutions and Henry's Law:

Non-ideal solutions are difficult to describe completely

$\Rightarrow$ Describe limits $x_B \to 1$ and $x_B \to 0$ $\Rightarrow$ <u>"Ideal Dilute Solution"</u>

I. $x_{CS_2} = x_B \to 1$ (B is the "solvent")

Then Raoult's Law applies for CS_2

CS_2 molecules see mostly other CS_2 molecules

$$\boxed{p_{CS_2} = x_{CS_2} p_{CS_2}^*}$$

II. $x_B \rightarrow 0$ (B is the "solute")

Then <u>Henry's Law</u> applies: $p_{CS_2} = x_{CS_2} K_{CS_2}$ $p_B = x_B K_B$
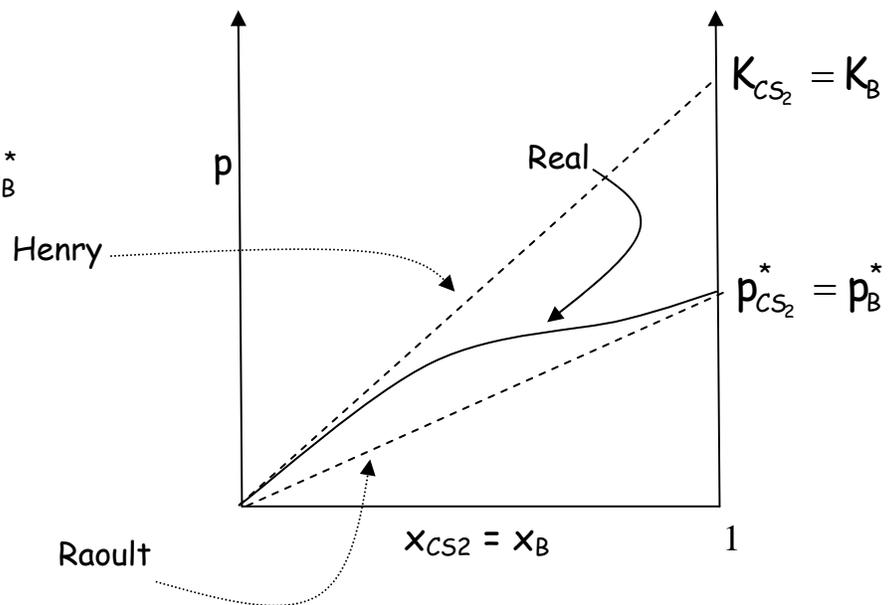
Henry's Law constant

$K_B \equiv$ Henry's Law constant, <u>depends on the solvent/solute mixture and the temperature.</u>

Labeled just K_B, even though it depends on A also.

Positive deviation $\Rightarrow K_B > p_B^*$

Henry

(Negative deviation would have $K_B < p_B^*$)

Real

$K_{CS_2} = K_B$

p

$p_{CS_2}^* = p_B^*$

Raoult
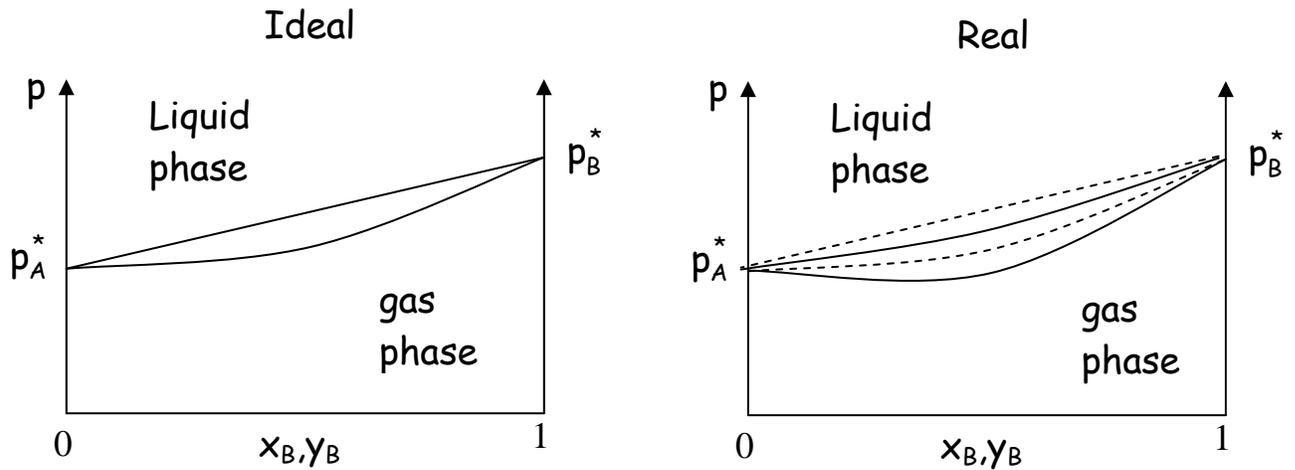
$x_{CS2} = x_B$

1

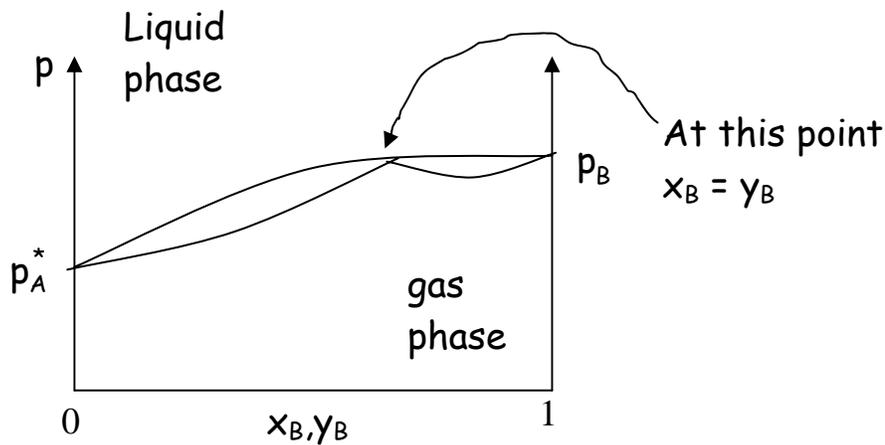Ideal dilute solution:

Solvent, e.g. A: $x_A \sim 1$ $\Rightarrow$ Raoult's Law $p_A = x_A p_A^*$

Solute, e.g. B: $x_B \sim 0$ $\Rightarrow$ Henry's Law $p_B = x_B K_B$

Total phase diagram:

Ideal

p

Liquid
phase

p_B^*

p_A^*

gas
phase

0   x_B, y_B 1

Real

p

Liquid
phase

p_B^*

p_A^*

gas
phase

0   x_B, y_B 1

Stronger non-ideality: Azeotropes

p

Liquid
phase

At this point
$x_B = y_B$

p_B

p_A^*

gas
phase

0   x_B, y_B 1

Similar for constant p phase diagram
Can have positive or negative azeotropes

Cannot distill
past azeotrope
$x_B = y_B$

T

gas
phase

T_A^*

T_B^*

Liquid
phase

0   x_B, y_B 1

T

gas
phase

T_A^*

T_B^*

Liquid
phase

0   x_B, y_B 1