Non-ideal solutions

Strong deviations from ideality are shown by dissimilar substances

Raoult’s law obeyed for a close-to-pure solvent

William Henry (1775-1836) observed Henry’s law (for a dilute solute):

\[ p_B = x_B K_B \] (e.g., gas solubility)
Ideal and real solutions: Activities

From both Raoult’s (solvent) and Henry’s laws (solute) follows:

$$\mu_{solv}(l) = \mu_{solv}(l) + RT \ln x_{solv}$$

$$= \mu_{solv}(l) + RT \ln C_{solv}$$

$$\Rightarrow \mu_J = \mu_J^{\ominus} + RT \ln [J]$$

**BUT:**

\[ \downarrow \]

standard chemical potential @ 1 M

The chemical potential is a measure of the ability of J to bring about physical or chemical change

$$\mu_J = \mu_J^{\ominus} + RT \ln a_J$$

Effective concentration

= activity $a_J = \gamma_J[J]$
Consequences of chemical potential changes in mixtures: Colligative properties

Freezing point depression:
$$\Delta T_f = K_f b_B$$
Cryoscopic constant

Solute is insoluble in solid solvent:
Chemical Potential lowered by solute

Boiling point elevation:
$$\Delta T_B = K_B b_B$$
Ebullioscopic constant

Solute is not volatile:
Chemical Potential lowered by solute
Phase diagrams of binary mixtures

Phase rule: \( F = C - P + 2 \) for binary mixtures = 2

\( p = \text{constant}: \)

Temperature-composition diagram for binary mixture of volatile liquids

- Phase \( \alpha \)
  - \( F' = 2 \)
  - \( F' = 1 \)
- Phase \( \gamma \)
  - \( F = 2 \)
  - \( F' = 0 \)
- Phase \( \beta \)
  - \( F' = 2 \)

Temperature
Composition (mole fraction)

Boiling point of pure B
Composition of vapour
Boiling point of mixture
Boiling point of pure A
Tie line

in equilibrium