Chemistry 2402 - Thermodynamics

Lecture 5: Solubility (cont.)

Lecture 6: Non Ideal Solutions and Activity

Lecture 7: Chemical Equilibria
Chemical Potential and Semi-Permeable Membranes

A membrane that only allow passage of solvent molecules only can result in a cell, when placed in a dilute solution, swelling till it ruptures.

Or, when placed in a concentrated solution, shrinking dramatically
Osmotic Pressure

Consider a solution and the pure solvent, separated by a rigid semi-permeable membranes that permits only the solvent to pass through.

\[ \mu_1^o (liq) + k_B T \ln x_1 + \left( \frac{\partial \mu_1}{\partial P} \right)_T \Delta P = \mu_1^o (liq) \]
Osmotic Pressure (cont.)

\[
\left( \frac{\partial \mu_1}{\partial P} \right)_{T,N} = \frac{\partial}{\partial N_1} \left( \frac{\partial G}{\partial P} \right)_{T,N} = \frac{\partial}{\partial N_1} V = \nu_1
\]

the volume per solvent molecule

So at equilibrium

\[
\mu_1^o (liq) + k_B T \ln x_1 + \nu_1 \Delta P = \mu_1^o (liq)
\]

Or

\[
- \ln x_1 = \nu_1 \Delta P / k_B T
\]

When \( x_1 < 1 \), we need to apply an additional pressure \( \Delta P \) (or \( \Pi \), the osmotic pressure) to establish equilibrium and stop the flow of solvent into the solution. Note that the chemical nature of the solute is irrelevant (again) in the ideal solution.
Example Problem

Calculate the osmotic pressure at 300K of an aqueous sucrose solution at a sucrose mole fraction of $x_{\text{sucrose}} = 0.01$. The volume per molecule of water is $3.0 \times 10^{-29}$ m$^3$.

$$
\Pi = -\frac{k_B T}{v_{\text{water}}} \ln x_{\text{water}}
$$

$k_B = 1.381 \times 10^{-23}$ JK$^{-1}$

$$
\Pi = 1.39 \times 10^3 \text{ kPa} \text{ or } 13.7 \text{ atm} \!
$$
Non-Ideal Solutions

Acetone + Chloroform

(dashed lines indicate Raoult’s Law predictions)

\[ P = P_{\text{acetone}} + P_{\text{chloroform}} \]

- a **negative** deviation from Raoult’s Law
  - the result of additional **attraction** between the different molecules
Introducing the Activity of a Species

For many solutions, \( P_i \neq x_i(\text{liq}) P_i^* \).

To describe these non-ideal solutions while retaining the form of the ideal solution equations, we define a new quantity called the activity \( a_i \) of species \( i \) as

\[
a_i(\text{liq}) = \frac{P_i}{P_i^*} \quad \text{so that} \quad P_i = a_i(\text{liq}) P_i^* \quad \text{is always true (by definition)}.\]

The activity can be thought of as the “effective concentration”.

We define the activity coefficient \( \gamma_i = a_i/x_i \).

For an ideal solution, all \( \gamma_i = 1 \). In a non-ideal solution \( \gamma_i \) maybe greater or less than 1. For the case of acetone + chloroform both \( \gamma_i \)’s are less than 1.
The Chemical Potential for a Non-Ideal Solution

Replacing the mole fraction by the activity, we have

\[ \mu_i(\text{liq}) = \mu_i^0(\text{liq}) + k_B T \ln a_i \]

We can take this, rather than \( a_i = P_i/P_i^* \), as the definition of the activity \( a_i \) but we need to understand that this means the definition of activity depends on our choice of reference state.

For aqueous solutions we need to choose a new reference state because many of the solutes are not liquids at 1 atm in the temperature range for liquid water

\[ \mu_i(\text{liq}) = \mu_i^0(\text{liq}) + k_B T \ln a_i \]

Where the reference state is a 1 molar solution of the solute in water.
Activity Coefficient depends on the Other Molecules Present

The activity coefficient $\gamma_i$ depends on the concentration of species $i$ and what other species are present.

In the case of chloroform, $\gamma_{\text{chloroform}} = 1$ at chloroform mole fractions of 0 and 1 but is less than one in between.

Replace acetone by hexane and the activity coefficient becomes closer to 1 over the whole concentration range.
Phase Diagrams for Non-Ideal Solutions

Acetone + Chloroform

A point where gas and liquid have the same composition is called an azeotrope. Distillation cannot work at such a point.
T-x Phase Diagrams

Azeotropes can arise from positive and negative deviations from Raoult’s Law.