Lecture 6: Non Electrolyte Solution

Ch 45.5 Exam II
September 1/3 (Multiple Choice/Problem Solving)
Coverage:

Second/Third Laws of Thermodynamics
Nonelectrolyte Solution
Electrolyte Solutions
Phase Equilibria

Exam III October 6 and 7
Chemical Equilibria, Electrochemistry
NONELECTROLYTE SOLUTIONS

SOLUTIONS – single phase homogeneous mixture of two or more components

NONELECTROLYTES – do not contain ionic species.

CONCENTRATION UNITS

percent by weight = \( \frac{\text{wt. of solute}}{\text{wt. of solvent} + \text{wt. of solute}} \times 100\% \)

\[ = \frac{\text{wt of solute}}{\text{wt. of solution}} \times 100\% \]

mole fraction \( (x_i) = \frac{\text{no. of moles of component } i}{\text{no. of moles of all components}} \)
CONCENTRATION UNITS

\[
Molarity (M) = \frac{\text{no. of moles of solute}}{\text{L of solution}}
\]

\[
Molality (m) = \frac{\text{no. of moles of solute}}{\text{wt. of solvent in kg}}
\]

PARTIAL MOLAR VOLUME

Imagine a huge volume of pure water at 25 °C. If we add 1 mol \( H_2O \), the volume increases 18 cm\(^3\) (or 18 mL).

So, 18 cm\(^3\) mol\(^{-1}\) is the molar volume of pure water.
PARTIAL MOLAR VOLUME

Now imagine a huge volume of pure ethanol and add 1 mol of pure H₂O it. How much does the total volume increase by?

PARTIAL MOLAR VOLUME

• When 1 mol H₂O is added to a large volume of pure ethanol, the total volume only increases by ~ 14 mL.

• The packing of water in pure water ethanol (i.e. the result of H-bonding interactions), results in only an increase of 14 mL.
**PARTIAL MOLAR VOLUME**

- The quantity $14 \text{ cm}^3 \text{ mol}^{-1}$ is the **partial molar volume** of water in pure ethanol.
- The partial molar volumes of the components of a mixture vary with composition as the molecular interactions vary as the composition changes from pure A to pure B.

![Graph showing partial molar volume changes](image)
\[
\overline{\Delta V} = \left( \frac{\Delta V}{\Delta n_j} \right)_{p,T,n'}
\]

**PARTIAL MOLAR VOLUME**

When a mixture is changed by \( dn_A \) of A and \( dn_B \) of B, then the total volume changes by:

\[
dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} \, dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} \, dn_B
\]
For a two component system (A, B), the volume of the system at a particular composition is given by:

\[ V = V_A n_A + V_B n_B \]
**PARTIAL MOLAR VOLUME**

- Molar volumes are always positive, but partial molar quantities need not be. The limiting partial molar volume of MgSO$_4$ in water is $-1.4 \text{ cm}^3\text{mol}^{-1}$, which means that the addition of 1 mol of MgSO$_4$ to a large volume of water results in a decrease in volume of 1.4 cm$^3$. 

![Graph of partial molar volume](image)
SAMPLE PROBLEM 5.01

What is the total volume of a mixture of 50.0 g ethanol and 50.0 g of water at 25°C? The partial molar volumes of the 2 substances in mixtures of this compositions are 56.0 ml/mole and 18.0 ml per mole respectively.

SAMPLE PROBLEM 5.02

A commercial rubbing alcohol is 82.5% in ethyl alcohol and 17.5% water. Partial molar volumes of water at this composition is 16.8 ml/mole and 57.4 ml/mole for ethanol. What is the density of the rubbing alcohol?
The concept of partial molar quantities can be extended to any extensive state function.

For a substance in a mixture, the chemical potential, $\mu$, is defined as the partial molar Gibbs energy.

$$\bar{G}_i = \mu_i = \left( \frac{\Delta G}{\Delta n} \right)_{T,P,n}$$
PARTIAL MOLAR GIBBS ENERGIES

- Using the same arguments for the derivation of partial molar volumes,

\[ G = n_A \mu_A + n_B \mu_B \]

- Assumption: Constant pressure and temperature

THERMODYNAMICS OF MIXING

- So we’ve seen how Gibbs energy of a mixture depends on composition.
- We know at constant temperature and pressure systems tend towards lower Gibbs energy.
- When we combine two ideal gases they mix spontaneously, so it must correspond to a decrease in \( G \).
**THERMODYNAMICS OF MIXING**

- The total pressure is the sum of all the partial pressure.

\[ p_j = x_j p \]

\[ p_A + p_B + L = (x_A + x_B + L) p = p \]

**DALTON’S LAW**

- The total pressure is the sum of all the partial pressure.
THERMODYNAMICS OF MIXING

\[ G_m = G_m^\theta + RT \ln \frac{P}{P^\theta} \]

\[ \mu = \mu^\theta + RT \ln \frac{P}{P^\theta} \]

\[ \mu = \mu^\theta + RT \ln p \]

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

\[ n = \text{total number of moles} \]

\[ x_A, x_B \text{ are mole fractions of components } A, B, \text{respectively} \]

\[
\begin{align*}
\mu &= \mu^\theta + RT \ln p \\
G_i &= n_A (\mu_A^\theta + RT \ln p_A) + n_B (\mu_B^\theta + RT \ln p_B) \\
G_f &= n_A (\mu_A^\theta + RT \ln p_A) + n_B (\mu_B^\theta + RT \ln p_B) \\
\Delta_{mix} G &= n_A RT \ln \frac{P_A}{P} + n_B RT \ln \frac{P_B}{P}
\end{align*}
\]
THERMODYNAMICS OF MIXING

\[ \Delta_{\text{mix}} G = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p} \]

\[ \frac{p_A}{p} = x_A \quad \frac{p_B}{p} = x_B \]

\[ \Delta_{\text{mix}} G = n_A RT \ln x_A + n_B RT \ln x_B \]

\[ x_A n = n_A \quad x_B n = n_B \]

\[ \Delta_{\text{mix}} G = nRT( x_A \ln x_A + x_B \ln x_B ) \]

\[ \Delta_{\text{mix}} G < 0 \]
A container is divided into two equal compartments. One contains 3.0 mol H\textsubscript{2}(g) at 25 °C; the other contains 1.0 mol N\textsubscript{2}(g) at 25 °C. Calculate the Gibbs energy of mixing when the partition is removed.

\[
\Delta_{\text{mix}} G = nRT (x_A \ln x_A + x_B \ln x_B)
\]

\[
\Delta_{\text{mix}} G = 3.0(\frac{3}{4} R T \ln \frac{3}{4}) + 1.0(\frac{1}{4} R T \ln \frac{1}{4})
\]

\[
\Delta_{\text{mix}} G = -2.14 \text{ kJ} - 3.43 \text{ kJ}
\]

\[
\Delta_{\text{mix}} G = -5.6 \text{ kJ}
\]
ENTHALPY, ENTROPY OF MIXING

\[ \Delta_{\text{mix}} G = \Delta H_{\text{mix}} - T \Delta_{\text{mix}} S \]

for ideal solutions, \( \Delta H = 0 \)

\[ \frac{\Delta_{\text{mix}} G}{T} = -\Delta_{\text{mix}} S \]

\[ \Delta_{\text{mix}} S = -nR(x_A \ln x_B + x_B \ln x_B) \]

Figure 5-9
Atkins Physical Chemistry, Eighth Edition
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**OTHER MIXING FUNCTIONS**

\[
\Delta_{\text{mix}} G = nRT \left( x_A \ln x_A + x_B \ln x_B \right)
\]

\[
\Delta_{\text{mix}} S = -nR \left( x_A \ln x_A + x_B \ln x_B \right)
\]

\[
\Delta G = \Delta H - T \Delta S
\]

\[
\Delta H = 0 \quad (\text{constant} \ p \ \text{and} \ T)
\]

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**SAMPLE PROBLEM 5.03**

Calculate the Gibbs Energy and entropy of mixing 1.6 moles of Argon at 1.0 atm with 2.6 moles of Nitrogen at 1.0 atm and 25°C. Assume ideal behavior.
To discuss the equilibrium properties of liquid mixtures we need to know how the Gibbs energy of a liquid varies with composition.

We use the fact that, at equilibrium, the chemical potential of a substance present as a vapor must be equal to its chemical potential in the liquid.

**IDEAL SOLUTIONS**

- Chemical potential of vapor equals the chemical potential of the liquid at equilibrium.

\[ \mu_A^* = \mu_A^0 + RT \ln p_A^* \]  

*denotes pure substance

- If another substance is added to the pure liquid, the chemical potential of A will change.

\[ \mu_A = \mu_A^0 + RT \ln p_A \]

\[ \mu_A^0 \text{ is the standard chemical potential at } p = 1 \text{ bar} \]
**IDEAL SOLUTIONS**

\[
\mu_A^* = \mu_A^0 + RT \ln p_A^* \\
\mu_A^0 = \mu_A^* - RT \ln p_A^* \\
\mu_A = \mu_A^0 + RT \ln p_A \\
\mu_A = \mu_A^* - RT \ln p_A^* + RT \ln p_A \\
\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}
\]

**RAOUHLT’S LAW**

\[
p_A = x_A p_A^*
\]

The vapor pressure of a component of a solution is equal to the product of its mole fraction and the vapor pressure of the pure liquid.
Liquids A and B form an ideal solution. At 45°C, the vapor pressure of pure A and pure B are 66 torr and 88 torr, respectively. Calculate the composition of the vapor in equilibrium with a solution containing 36 mole percent A at this temperature.

**SAMPLE PROBLEM 5.04**

**IDEAL SOLUTIONS:**

\[ \mu_A = \mu_A^* + RT \ln \frac{P_A}{P_A^*} \]

\[ P_A = x_A P_A^* \]

\[ \mu_A = \mu_A^* + RT \ln x_A \]
NON-IDEAL SOLUTIONS

• Even if there are strong deviations from ideal behaviour, Raoult’s law is obeyed increasingly closely for the component in excess as it approaches purity.
For real solutions at low concentrations, although the vapor pressure of the solute is proportional to its mole fraction, the constant of proportionality is not the vapor pressure of the pure substance.

\[
p_B = x_B K_B
\]

Even if there are strong deviations from ideal behaviour, Raoult's law is obeyed increasingly closely for the component in excess as it approaches purity.
**IDEAL-DILUTE SOLUTIONS**

- Mixtures for which the solute obeys Henry’s Law and the solvent obeys Raoult’s Law are called ideal-dilute solutions.

**PROPERTIES OF SOLUTIONS**

- We’ve looked at the thermodynamics of mixing ideal gases, and properties of ideal and ideal-dilute solutions, now we shall consider mixing ideal solutions, and more importantly the deviations from ideal behavior.
\[ G_i = n_A \mu_A^* + n_B \mu_B^* \]

\[ \mu_A = \mu_A^* + RT \ln x_A \]

\[ G_f = n_A \{ \mu_A^* + RT \ln x_A \} + n_B \{ \mu_B^* + RT \ln x_B \} \]

\[ \Delta_{\text{mix}} G = n_A RT \ln x_A + n_B RT \ln x_B \]

\[ \Delta_{\text{mix}} G = nRT \{ x_A \ln x_A + x_B \ln x_B \} \]

\[ \Delta_{\text{mix}} S = -nR \{ x_A \ln x_A + x_B \ln x_B \} \]

\[ \Delta_{\text{mix}} H = 0 \]
IDEAL SOLUTIONS

\[ \Delta_{\text{mix}} G = nRT \{ x_A RT \ln x_A + x_B RT \ln x_B \} \]

\[ \left( \frac{\partial G}{\partial p} \right)_T = V \]

\[ \left( \frac{\partial \Delta_{\text{mix}} G}{\partial p} \right)_T = \Delta_{\text{mix}} V = 0 \]

REAL SOLUTIONS

- Real solutions are composed of particles for which A-A, A-B and B-B interactions are all different.
- There may be enthalpy and volume changes when liquids mix.
- \( \Delta G = \Delta H - T \Delta S \)
- So if \( \Delta H \) is large and positive or \( \Delta S \) is negative, then \( \Delta G \) may be positive and the liquids may be immiscible.
EXCESS FUNCTIONS

- Thermodynamic properties of real solutions are expressed in terms of excess functions, $X^E$.
- An excess function is the difference between the observed thermodynamic function of mixing and the function for an ideal solution.

REAL SOLUTIONS

\[ S^E = \Delta_{mix} S - \Delta_{mix} S^{\text{ideal}} \]
\[ G^E = \Delta_{mix} G - \Delta_{mix} G^{\text{ideal}} \]
\[ H^E = \Delta_{mix} H - \Delta_{mix} H^{\text{ideal}} = \Delta_{mix} H \]
\[ V^E = \Delta_{mix} V - \Delta_{mix} V^{\text{ideal}} = \Delta_{mix} V \]
A colligative property is a property that depends only on the number of solute particles present, not their identity.

The properties we will look at are: lowering of vapor pressure; the elevation of boiling point, the depression of freezing point, and the osmotic pressure arising from the presence of a solute.

Only applicable to dilute solutions.
COLLIGATIVE PROPERTIES:

- All the colligative properties stem from the reduction of the chemical potential of the liquid solvent as a result of the presence of solute.

\[ \mu_A = \mu_A^* + RT \ln x_A \]

VAPOR PRESSURE LOWERING:

As solute molecules are added to a solution, the solvent become less volatile (decreased vapor pressure).

Solute-solvent interactions contribute to this effect.
Therefore, the vapor pressure of a solution is lower than that of the pure solvent.

### VAPOR PRESSURE LOWERING: RAOULT’S LAW

\[ P_A = x_A P^\circ_A \]

where
- \( x_A \) is the mole fraction of compound A
- \( P^\circ_A \) is the normal vapor pressure of A at that temperature

**NOTE:** This is one of those times when you want to make sure you have the vapor pressure of the solvent.
SAMPLE PROBLEM:

Glycerin (C$_3$H$_8$O$_3$) is a nonvolatile nonelectrolyte with a density of 1.26 g/mL at 25°C. Calculate the vapor pressure at 25°C of a solution made by adding 50.0 mL of glycerin to 500.0 mL of water. The vapor pressure of pure water at 25°C is 23.8 torr.

PRACTICE EXERCISE

The vapor pressure of pure water at 110°C is 1070 torr. A solution of ethylene glycol and water has a vapor pressure of 1.00 atm at 110°C. Assuming that Raoult’s law is obeyed, what is the mole fraction of ethylene glycol in the solution?
How do we figure out where the new boiling point is when a solute is present? Look for the temperature at which at 1 atm, the vapor of pure solvent vapor has the same chemical potential as the solvent in the solution.

Let’s denote solvent A and solute B. Equilibrium is established when:

\[ \mu_A(g) = \mu_A^*(g) + RT \ln x_A = \mu_A^*(l) + RT \ln x_A \]

\[ \Delta T = Kx_B \]

\[ K = \frac{RT^*}{\Delta_{vap}H} \]
n \Delta T makes no reference to the identity of the solute, only to its mole fraction.

So the elevation of boiling point is a colligative property.

BOILING POINT ELEVATION:

\[ \Delta T = Kx_B \]

\[ K = \frac{RT^*}{\Delta_{vap} H} \]

- \( \Delta T \) makes no reference to the identity of the solute, only to its mole fraction.
- So the elevation of boiling point is a colligative property.
BOILING POINT ELEVATION:

$$\Delta T = K x_B$$

For practical purposes:

$$\Delta T = K_b m \quad K_b = \text{boiling point constant}; \ m = \text{molality}$$
FREEZING POINT DEPRESSION:

- Let’s denote solvent A and solute B.
- Equilibrium is established when:
  \[ \mu_A(s) = \mu_A^*(l) + RT \ln x_A \]
  - Same calculation as before (Justification 5.1)
  \[ \Delta T = K' x_B \quad K' = \frac{RT^*}{\Delta_{fus} H} \]

FREEZING POINT DEPRESSION:

\[ \Delta T = K' x_B \]

For practical purposes:
\[ \Delta T = K_f m \quad K_f = \text{freezing point constant; } m = \text{molality} \]
What will be the freezing point and boiling point of an aqueous solution containing 55.0 g of glycerol, C₃H₅(OH)₃, and 250 g of water? \( K_b(H_2O) = 0.51^\circ C/m \) and \( K_f = 1.86^\circ C/m \).
A solution is prepared from 25.0 g of benzene, C_6H_6, and 2.50 g of an unknown compound. The freezing point of this solution is 4.3 °C. The normal freezing point of benzene is 5.5 °C and the freezing point depression constant for benzene is –5.12 °C/m. Determine the molar mass of the compound.

Cryoscopy

\[ \Delta T = K_f b \]

\[ K_f = \text{freezing point constant; } b = \text{molality} \]

\[ b = \frac{n}{1 \text{ kg solvent}} = \frac{m/M}{1 \text{ kg solvent}} \]
Solubility

• Although solubility is not strictly a colligative property (because solubility varies with the identity of the solute), it may be estimated using the same techniques.

• When a solid solute is left in contact with a solvent, it dissolves until the solution is saturated with the dissolved solute.
Solubility

\[ \mu_B(s) = \mu_B^*(l) + RT \ln x_B \]

- See Justification 5.2

\[ \ln x_B = \frac{\Delta_{fus} H}{R} \left( \frac{1}{T_f} - \frac{1}{T} \right) \]

OSMOSIS:

- Osmosis refers to the spontaneous passage of a pure solvent into a solution separated from it by a semi-permeable membrane.
- In this case, the membrane is permeable to the solvent but not to the solute.
The osmotic pressure, $\pi$, is the pressure that must be applied to the solution to stop the influx of solvent.

Examples of osmosis includes the transport of fluids across cell membranes and dialysis.
OSMOSIS:

\[ \pi = MRT \]
\[ \pi \text{ is the osmotic pressure of the solution} \]
\[ M \text{ is molarity of the solution} \]

or

\[ \frac{\pi}{c_2} = \frac{RT}{M_2} \]
\[ c_2 \text{ is the concentration of the solute in g/L} \]
\[ M_2 \text{ is the molar mass of the solute} \]

SAMPLE PROBLEM:

An aspartic acid solution will produce an osmotic pressure of 1.80 atm measured against pure water at 18.5 °C. How many g of Aspartic Acid(C₄H₇NO₄, M=133.1 g/mol) must be dissolved in a liter of water to produce an isotonic solution?