

Colligative Properties

CHEM 361A: Introduction to Physical Chemistry

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Lecture 10

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Learning Objective: Use equilibrium conditions of mixtures to quantify collective properties.

References:

- Atkins and de Paula Focus
- Chang §7.6 - §7.7

Review - Changes in the Chemical Potential

The chemical potential of a component in a mixture changes the same way as previously defined for the Gibbs Free Energy of a single component system:

$$d\mu = dG_m = V_m dp - S_m dT$$

So

- Constant Temperature

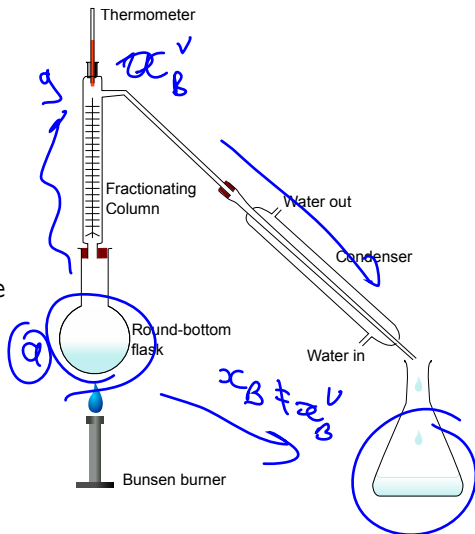
$$d\mu = V_m dp$$

- Constant Pressure

$$d\mu = -S_m dT$$

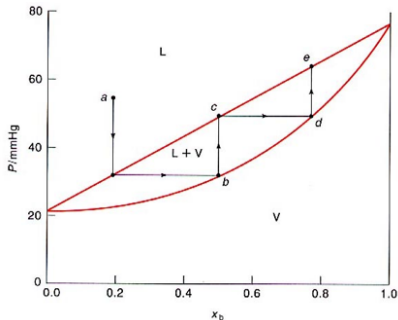
Fractional Distillation

The separation of two volatile liquid components can be accomplished using **fractional distillation**. Typically the components to be separated have boiling points that differ by less than 25°C at 1 atm.



Pressure-Composition Phase Diagram

To understand how this works we will first examine pressure-composition phase diagrams of two component mixtures.



Drawing Pressure-Composition Phase Diagrams

Assuming an ideal mixture (say benzene-toluene) then we can use Raoult's Law:

$$P_b = x_b P_b^* \quad \text{and} \quad P_t = x_t P_t^* \quad (\text{Raoult's Law})$$

- The straight line (liquid/liquid-vapour phase boundary) is found by determining the total pressure as a function of the mole fraction of the liquid:

$$\begin{aligned}
 P &= P_b + P_t && \text{—} \\
 &= x_b P_b^* + x_t P_t^* \\
 &= x_b P_b^* + (1 - x_b) P_t^* \\
 &= P_t^* + (P_b^* - P_t^*) x_b && \text{—}
 \end{aligned}$$

Note that P_t^* and P_b^* are constants so only x_b (mole fraction of benzene in the liquid phase) varies.

Drawing Pressure-Composition Phase Diagrams (cont.)

- ② The curved line (the liquid-vapour/vapour phase boundary) is drawn using the total pressure as a function of the mole fraction of the vapour:

$$\rightarrow x_b^v = \frac{P_b}{P} = \frac{x_b P_b^*}{P_t^* + (P_b^* - P_t^*)x_b}$$

Solving for x_b (the mole fraction of benzene in the liquid phase) gives

$$\rightarrow x_b = \frac{x_b^v P_t^*}{P_b^* - (P_b^* - P_t^*)x_b^v}$$

Drawing Pressure-Composition Phase Diagrams (cont.)

Now that we have this expression for the mole fraction of the liquid we return to Dalton's Law and Raoult's Law to get an expression for total pressure

$$P_b = x_b^v P = x_b P_b^* \quad \rightarrow \quad P = \frac{x_b P_b^*}{x_b^v}$$

Substituting in the previously derived expression for x_b

$$\begin{aligned} P &= \frac{\cancel{x_b^v} P_t^*}{P_b^* - (P_b^* - P_t^*) \cancel{x_b^v}} \frac{P_b^*}{\cancel{x_b^v}} \\ &= \frac{P_t^* P_b^*}{P_b^* - (P_b^* - P_t^*) x_b^v} \end{aligned}$$

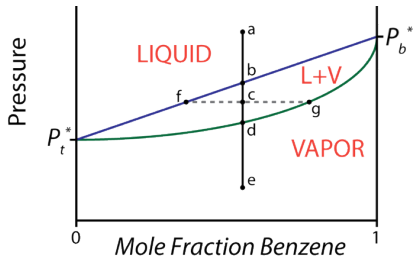
Pressure-Composition Phase Diagram Revisited

1 Blue Line

$$P = P_t^* + (P_b^* - P_t^*)x_b$$

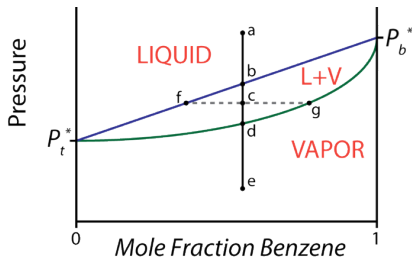
2 Green Line

$$P = \frac{P_t^* P_b^*}{P_b^* - (P_b^* - P_t^*)x_b^V}$$



Pressure-Composition Phase Diagram Revisited

- At 'a' mixture is all liquid
- Lower the pressure to 'b', system at phase boundary where vapour begins to form
- Lower pressure to 'c' where both liquid and vapour exist
 - Composition of vapour given by 'g'
 - Composition of liquid given by 'f'
- Lower pressure to 'd' at second phase boundary
- Lower pressure to 'e' where only vapour phase exists



Pressure-Composition Phase Diagram Problem

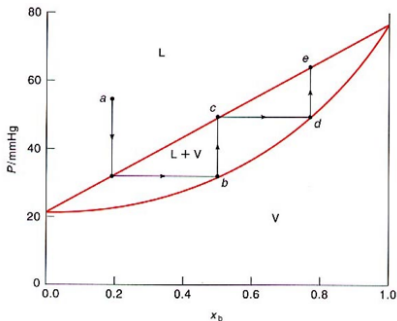
An ideal solution of 5.00 mol of benzene and 3.25 mol of toluene is placed in a piston and cylinder assembly. At 298 K, the vapour pressure of the pure substances are $P_b^* = 12.85$ kPa and $P_t^* = 3.85$ kPa.

- 1 The pressure above this solution is reduced from 101.3 kPa. At what pressure does the vapour phase first appear?
- 2 What is the composition of the vapour under these conditions?

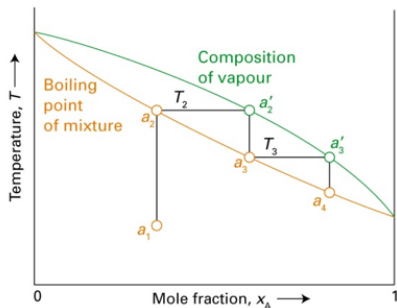
Fractional Distillation

Through a series of Pressure or Temperature changes, one component of the mixture can be separated from the other:

- Constant Temperature

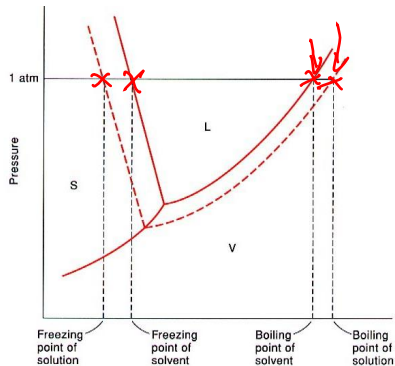


- Constant Pressure



Phase Boundary Changes

By adding a non-volatile solute to a solution (fx. sugar or salt), the freezing point will lower, and the boiling point will increase for the solution. What we will see is that these **colligative properties** only depend on the concentration of the solute.



The Gibbs-Helmholtz Equation

To derive the changes to the phase diagram with respect to the mole fraction of the solute, we need to calculate the **Gibbs-Helmholtz Equation**. We start with applying the product rule to G/T :

$$\begin{aligned}\left(\frac{\partial}{\partial T} \left[\frac{G}{T}\right]\right)_p &= \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p + G \frac{d}{dT} \left[\frac{1}{T}\right] \\ &= \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2}\end{aligned}$$

Recall that $\left(\frac{\partial G}{\partial T}\right)_p = -S$:

$$\left(\frac{\partial}{\partial T} \left[\frac{G}{T}\right]\right)_p = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G + TS}{T^2} = -\frac{H}{T^2}$$

Melting Point Reduction

At the phase boundary

$$\mu_{solid}^* = \mu_{solution} = \mu_{solvent}^* + RT \ln x_{solvent}$$

This expression can be solved for $\ln x_{solvent}$:

$$\ln x_{solvent} = \frac{\mu_{solid}^* - \mu_{solvent}^*}{RT}$$

This difference in chemical potentials $\mu_{solid}^* - \mu_{solvent}^* = -\Delta G_{fusion}$
so

$$\ln x_{solvent} = \frac{-\Delta G_{fusion}}{RT}$$

Where the negative sign comes from the convention that the ΔG_{fusion} records the change in free energy as something goes from solid to liquid.

Melting Point Reduction (cont.)

Since we are interested in melting point reduction as a function of the mole fraction of the solvent at constant pressure $((\partial T/\partial x_{\text{solvent}})_p)$ then we will differentiate with respect to mole fraction:

$$\frac{\partial}{\partial x_{\text{solvent}}} [\ln x_{\text{solvent}}] = \frac{\partial}{\partial x_{\text{solvent}}} \left[\frac{-\Delta G_{\text{fusion}}}{RT} \right]; \quad \text{constant } p$$

$$\frac{1}{x_{\text{solvent}}} = -\frac{1}{R} \left(\frac{\partial \frac{\Delta G_{\text{fusion}}}{T}}{\partial T} \right)_p \left(\frac{\partial T}{\partial x_{\text{solvent}}} \right)_p$$

The first partial derivative on the right can be simplified by the Gibb-Helmholtz equation

$$\frac{1}{x_{\text{solvent}}} = \frac{1}{R} \frac{\Delta H_{\text{fusion}}}{T^2} \left(\frac{\partial T}{\partial x_{\text{solvent}}} \right)_p$$

Melting Point Reduction (cont.)

We can rearrange to give

$$\frac{dx_{\text{solvent}}}{x_{\text{solvent}}} = \frac{1}{R} \frac{\Delta H_{\text{fusion}}}{T^2} dT$$

We will now integrate from the pure solvent ($x_{\text{solvent}} = 1$, T_{fusion}) to the dilute solution:

$$\int_1^{x_{\text{solvent}}} \frac{dx}{x} = \int_{T_{\text{fusion}}}^T \frac{\Delta H_{\text{fusion}}}{R} \frac{dT'}{T'^2}$$

Assuming that x_{solvent} is close to 1, then ΔH_{fusion} is temperature independent so

$$\begin{aligned} \ln x_{\text{solvent}} &= \frac{\Delta H_{\text{fusion}}}{R} \left(\frac{1}{T_{\text{fusion}}} - \frac{1}{T} \right) \\ \frac{1}{T} &= \frac{1}{T_{\text{fusion}}} - \frac{R \ln x_{\text{solvent}}}{\Delta H_{\text{fusion}}} \end{aligned}$$

Melting Point Reduction/Boiling Point Elevation

It is more convenient to state this result with respect to molal concentration of the solute

$$\Delta T_f = -\frac{RM_{\text{solvent}} T_{\text{fusion}}^2}{\Delta H_{\text{fusion}}} m_{\text{solute}} = -K_f m_{\text{solute}}$$

where ' K_f ' is the standard freezing point constant. A similar derivation gives boiling point elevation

$$\Delta T_b = \frac{RM_{\text{solvent}} T_{\text{boiling}}^2}{\Delta H_{\text{vap}}} m_{\text{solute}} = K_b m_{\text{solute}}$$

where K_b is the standard boiling point constant. M_{solvent} is the molar mass of the solvent and m_{solute} is the solute molal concentration

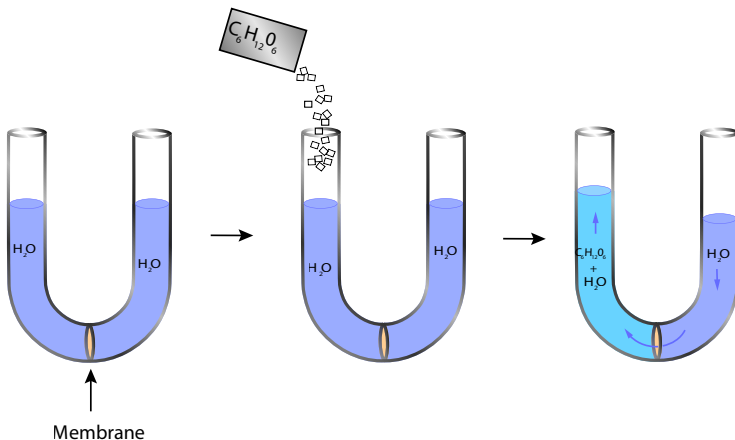
Boiling/Melting Point Change Problem

4.50 g of a substance is dissolved in 125 g of $\text{CCl}_4(\text{l})$. This leads to a boiling point elevation of 0.650 K for $\text{CCl}_4(\text{l})$. Calculate the freezing point depression, and the molar mass of the substance.

Hint: for CCl_4 $T_{\text{freezing}} = 250.3 \text{ K}$, $K_f = 30. \text{ K kg mol}^{-1}$,
 $T_{\text{boiling}} = 349.8 \text{ K}$, $K_b = 4.95 \text{ K kg mol}^{-1}$

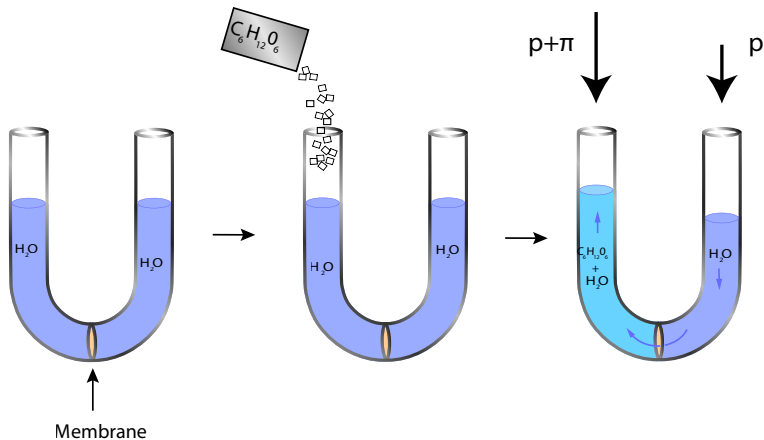
Osmosis

The process by which a solvent passes through a semipermeable membrane and dilutes a solution is known as **osmosis**.



Osmotic Pressure

The amount by which the pressure in the solution is raised is known as the Osmotic Pressure (π)



Deriving the Osmotic Pressure

To derive the added pressure we again start with the equilibrium condition and apply Raoult's Law to express the concentration dependence of $\mu_{solvent}^{solution}$:

$$\begin{aligned}\mu_{solvent}^*(T, p) &= \mu_{solvent}^{solution}(T, p + \pi, x_{solvent}) \\ \mu_{solvent}^*(T, p) &= \mu_{solvent}^*(T, p + \pi) + RT \ln x_{solvent} \\ -RT \ln x_{solvent} &= \mu_{solvent}^*(T, p + \pi) - \mu_{solvent}^*(T, p)\end{aligned}$$

The right hand side is the change in chemical potential as the pressure is raised from p to $p + \pi$. This can be expressed as

$$\begin{aligned}\mu_{solvent}^*(T, p + \pi) - \mu_{solvent}^*(T, p) &= \int_p^{p+\pi} V_m^* dp' \\ &= V_m^* \pi\end{aligned}$$

Assuming that the molar volume of the pure solvent does not change significantly over the pressure difference.

Deriving the Osmotic Pressure (cont.)

This means

$$-RT \ln x_{\text{solvent}} = V_m^* \pi$$

For a dilute solution $n_{\text{solvent}} \gg n_{\text{solute}}$ and using the Taylor Expansion for \ln :

$$\ln x_{\text{solvent}} = \ln(1 - x_{\text{solute}}) \approx -x_{\text{solute}}$$

Expanding on the definition of mole fraction:

$$-x_{\text{solute}} = -\frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} \approx -\frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

Putting this into the top equation (using $V \approx n_{\text{solvent}} V_m^*$):

$$RT \frac{n_{\text{solute}}}{n_{\text{solvent}}} = V_m^* \pi$$

$$\frac{n_{\text{solute}} RT}{V} = \pi; \quad \text{van't Hoff equation}$$

Osmotic Pressure Example

Calculate the osmotic pressure generated at 298 K if a cell with a total solute concentration of 0.500 mol L^{-1} is immersed in pure water. The cell wall is permeable to water molecules, but not to the solute molecules.

Summary

- Using equilibrium conditions of mixtures via the chemical potential, colligative properties of mixtures can be predicted
- Fractional distillation of volatile liquids occurs through cycling pressure or temperature of the mixture and condensing the vapour at each cycle
- The lowering of the freezing point or raising the boiling point in a mixture is found using

$$\Delta T_f = -K_f m_{solute} \quad \text{and} \quad \Delta T_b = K_b m_{solute}$$

- The additional osmotic pressure on the solution side of a semipermeable membrane is predicted using the van't Hoff equation:

$$\pi = \frac{n_{solute}RT}{V}$$