

Introduction

We will now discuss the unique properties of solutions. As you might imagine, a mixture of substances might share some of the properties of the original substances. However, the substances interact when they are mixed, so some of the solution properties are substantially **different** than any of the original substances. We will discuss these so-called **colligative properties** now.

Colligative properties - an overview

Colligative properties are solution properties that depend only on the **amount of solute** dissolved in a solvent and **not on the identity** of that solute. The colligative properties we will discuss are:

1. **Vapor pressure lowering**: The vapor pressure of a solution gets lower as the concentration of solute increases.
2. **Freezing point depression** (the topic of lab 12A): The freezing point of a solution gets lower as the concentration of solute increases.
3. **Boiling point elevation**: The boiling point of a solution gets higher as the concentration of solute increases.
4. **Osmotic pressure** (has to do with osmosis): The osmotic pressure increases as the concentration of solute increases.

Vapor pressure lowering

Remember that **vapor pressure** is the partial pressure of vapor over a liquid phase - in essence, it's how much of the substance present is in the vapor phase. **Vapor pressure lowering**, then, is the change in vapor pressure over a solvent caused by the addition of a nonvolatile solute (that is, a solute that doesn't easily go into the vapor phase itself).

This property can be described with a simple equation called **Raoult's Law**:

$$P_A = P_A^\circ \times X_A \quad (1)$$

P_A = vapor pressure of A in the solution
 P_A° = vapor pressure of pure A
 X_A = the mole fraction of A in the solution

Raoult's Law works best for dilute solutions of similar molecules- in other words, solutions where X_A is close to 1.

For a simple case of **one solute**, you can actually use Raoult's Law directly to find the vapor pressure lowering. How? We'll do a little simple algebra. Assume that the solvent is component "A" and the solute is component "B".

First, realize that vapor pressure lowering, ΔP , can be represented this way:

$$\Delta P = P_A^\circ - P_A \quad (2)$$

If we substitute equation (1) into equation (2), we get:

$$\Delta P = P_A^{\circ} - P_A^{\circ} \times X_A \quad (3)$$

We can collect terms to get:

$$\Delta P = P_A^{\circ} \times (1 - X_A) \quad (4)$$

Remember that all mole fractions must sum to one. Since there are only two components, we know that:

$$X_A + X_B = 1 \quad (5)$$

$$X_B = 1 - X_A \quad (6)$$

Combining equations (6) and (4), we get a simple expression for the vapor pressure lowering of a solution containing only one solute:

$$\Delta P = P_A^{\circ} \times X_B$$

ΔP = vapor pressure lowering

P_A° = vapor pressure of pure solvent

X_B = the mole fraction of solute in the solution

This effect is the basis of **distillation columns** that separate substances based on how volatile they are. In a distillation column, the solute and solvent are both volatile, but one is more volatile than the other. The more volatile component will be present at greater concentrations in the vapor phase.

Freezing point depression and boiling point elevation

We will talk about these two colligative properties together as they are very similar. You're probably familiar - at least in a qualitative sense - with these properties already. When you put an antifreeze such as ethylene glycol in your car, you might notice that the label brags about keeping your radiator from boiling over in the summer and freezing in the winter. What you might not have realized is that the lowering of the freezing point and the raising of the boiling point of the water in your radiator doesn't depend on the kind of antifreeze you put in, merely the **amount**.

You could use anything as antifreeze, as long as it dissolves in water. Sugar, salt, ethylene glycol, etc. All will affect the freezing point and boiling point of water in the same way - assuming they're put in at the same concentration. (Why ethylene glycol? It's not likely to clog the radiator or cause it to rust like sugar or salt would.)

Let's look at the boiling point elevation. Since the boiling point and the vapor pressure

are related (the boiling point is the temperature where the vapor pressure equals atmospheric pressure), if the vapor pressure is lowered by a solvent, the boiling point is increased - it takes a higher temperature to reach the same vapor pressure.

The **boiling point elevation** is the difference between the boiling point of the solution and the boiling point of the pure solvent. Mathematically, this has been found to be

$$\Delta T_b = K_b \times c_m$$

ΔT_b = the boiling point elevation (in °C)
 K_b = the boiling point elevation constant for the **solvent**
 c_m = the **molal** concentration (*m*)

You can look up the boiling point elevation constant for various solvents in books or on the web.

A few notes on the boiling point elevation:

- It's simple to apply - as the concentration goes up, the boiling point goes up.
- It's a colligative property, so the identity of the **solute** doesn't matter - the constant is for the **solvent**.
- The equation uses the **molal** concentration. That's because the molal concentration doesn't depend on temperature like the molar concentration does.

Freezing point depression is treated very similarly to boiling point elevation. Since the freezing process normally depends on the formation of a crystalline solid with the molecules of the substance in fixed positions. Anything that interferes with this process (like, say, the presence of a solute which can get in the way of solvent molecules coming together) will change the freezing point. It will take **more energy loss** to form the solid in the presence of a solute, so the freezing point will be lowered.

The **freezing point depression**, then, is the difference between the freezing point of the pure solvent and the freezing point of the solution. Mathematically, this is:

$$\Delta T_f = K_f \times c_m$$

ΔT_f = the freezing point depression (in °C)
 K_f = the freezing point depression constant for the **solvent**
 c_m = the **molal** concentration (*m*)

As with the boiling point elevation, constant, you can look up the freezing point depression constant for various solvents in books or the web.

A few notes on the freezing point elevation:

- Like the boiling point elevation, it's simple to apply - as the concentration goes up, the freezing point goes down.
- It's a colligative property, so the identity of the **solute** doesn't matter - the constant is for the **solvent**.
- The equation uses the **molal** concentration. That's because the molal concentration doesn't depend on temperature like the molar concentration does.
- We use the freezing point depression in one of the lab experiments to find the

molecular weight of an unknown substance. We can do this because the freezing point depression depends on the number of moles of substance present, but **not** what kind of substance the solute is.

Freezing point depression and boiling point elevation are properties that find wide use in the real world. Freezing point depression is used in the kitchen - salt lowers the freezing point when you make ice cream. The same effect is used to remove ice from roads (when the ice melts a bit, salt solution is formed - and the freezing point is lowered). Both freezing point depression and boiling point elevation are used in your car - to keep the coolant in your radiator from freezing in winter or boiling away in summer.

Osmotic pressure

To understand our fourth colligative property, we need to understand first what the phenomenon of **osmosis** is. **Osmosis** is the flow of a solvent through a **semipermeable membrane** to equalize the concentration of a solute on either side of the membrane. The membrane is called "semipermeable" because while **solvent** particles can flow through the membrane, **solute** particles cannot. The situation looks like this:

	<ul style="list-style-type: none"> • The membrane is in the middle of the pictures. It contains holes large enough for one type of particle to pass but not the other.. The membrane divides the system into two parts, left and right. • The solute particles are represented by the large red circles. In this illustration, the left side is more concentrated and the right side is more dilute. • The solvent is represented by the smaller blue circles. The solvent can flow through the membrane, and will flow in the direction of the arrow to equalize the concentration of solute particles on both sides of the membrane.
Illustration 1 - Osmosis	

Osmosis occurs naturally. It can, however, be stopped by the application of pressure to the concentrated solution. The pressure that is needed to just stop osmosis is called the **osmotic pressure**, and **osmotic pressure** is a colligative property. It depends on the concentration of solute particles.

If you have a situation where you have a concentrated solution on one side of the membrane and no solute on the other side, the osmotic pressure can be calculated simply using:

$$\Pi = M \times R \times T$$

Π = osmotic pressure (atm)
 M = the molarity of the solution (M)
 $R = 0.08206 \text{ L-atm/(mol-K)}$. This is the ideal gas constant
 T = the temperature in Kelvin (K) units.

If you apply a pressure **greater** than the osmotic pressure, you can actually make the solvent flow from an area of high concentration to an area of low concentration. This is exactly how water is purified by reverse osmosis - pressure is applied to salt water stored in a setup similar to illustration #1. The water is forced to flow through the membrane by pressure, and you get pure water.

Osmosis is also important in biological systems, since most cells are held together with semipermeable membranes. Osmosis is part of the reason that organisms that thrive in salt water have a tough time living in fresh water.

Colligative properties and ionic substances

Since **ionic solutions** contain solutes that actually break apart into multiple particles (ions) when they dissolve, you might wonder how that affects colligative properties. Colligative properties don't depend on the nature of the particles - only their numbers, so the colligative properties of ionic solutions depend on the amount of **ions** present. If you use a salt like sodium chloride (NaCl), two moles of ions are produced for every mole of salt you dissolve. If you use a salt like lithium carbonate (Li_2CO_3), **three** moles of ions are produced. You can account for this effect by multiplying the concentration of the solute (molar or molal concentration) by the number of ions produced when you dissolve it. Here's a brief example and comparison to a molecular substance (which does **not** ionize)

Let's say we have a 1.00 molal aqueous solution of each of these substances: glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), sodium chloride (NaCl), and lithium carbonate (Li_2CO_3). What are the boiling point elevations of each?

To solve this, we remember that $\Delta T_b = K_b \times c_m$. We have been given the molal concentration of each solution already (1.00 *m*). If we look up water's K_b , we find that it is $0.512 \text{ }^\circ\text{C}/m$. So, all we have to do is plug in, and take into account that the ionic substances break up into ions:

<i>Substance</i>	<i>Expression</i>	ΔT_b
$\text{C}_6\text{H}_{12}\text{O}_6$	$(0.512 \text{ }^\circ\text{C}/m)(1.00 \text{ } m)$	$0.512 \text{ }^\circ\text{C}$
NaCl (2 ions)	$(2)(0.512 \text{ }^\circ\text{C}/m)(1.00 \text{ } m)$	$1.02 \text{ }^\circ\text{C}$
Li_2CO_3 (3 ions)	$(3)(0.512 \text{ }^\circ\text{C}/m)(1.00 \text{ } m)$	$1.54 \text{ }^\circ\text{C}$

So the lithium carbonate raises the boiling point more than the other two solutes at the same nominal concentration. This is because the lithium carbonate forms more actual

particles than the other two. Glucose doesn't ionize at all, and sodium chloride forms only two ions compared to lithium carbonate's three.

[This is an *approximation* for ionic substances - the actual boiling point elevations are a little different due to interactions between ions. It's a good enough approximation for our work.]

Summary

This note pack discussed four colligative properties of solutions - properties based only on the **number** of solute particles dissolved in a solution. You should know what vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure are and how to calculate each. You should also be familiar with real-world applications of colligative properties (can you think of any that aren't listed here in this pack?). Finally, you should understand that ionic substances form multiple ions when they dissolve, so you have to account for those.