CHAPTER 13

Chemical Mixtures: Solutions and Other Mixtures

Chapter Contents:

I. Introduction and Solubility Units
II. Inherent Control of Solubility
III. External Control of Solubility
IV. Colligative Properties
V. Other Important Types of Mixtures

I. Introduction

Examine the photograph here of a typical office. How many pure elements can you identify? How many pure chemical compounds? Not many, to be sure. Most rooms contain pure aluminum; often we find fairly pure water; and that’s about it. The reality is that our world is composed of mixtures. The air is a mixture of gaseous nitrogen, oxygen, argon, water vapor, carbon dioxide, and solids like dust and pesky flying insects.

As chemists we think about mixtures in two ways:

1. We want to understand the ways in which different chemical entities mix and properties that those mixtures exhibit.

    and

2. We often want to know how to separate mixtures into pure components.

An entire area of chemistry exists to develop ways of separating mixtures into individual pure components.

Review and Definitions

We have talked before about chemical mixtures and defined pure elements and compounds, homogeneous and heterogeneous mixtures, and solutions, which are a type of homogeneous mixture.
Pure Element: A sample that contains atoms of only one element.

Pure Compound: A sample that has a fixed chemical composition.

Homogeneous Mixture: A mixture in which the composition is uniform.

Heterogeneous Mixture: A mixture in which the composition is not uniform.

Solution: A homogeneous mixture in which one substance is dissolved in another.

Solute: The substance that is dissolved into a solvent to form a solution. A solid can be a solid, a liquid or a gas.

Solvent: The substance into which a solute is dissolved. A solvent is most often a liquid, but can also be a gas or a solid.

Solubility: The extent to which a solute will dissolve in a particular solvent. This can be defined quantitatively in units such as grams solute per 100 grams solvent, or more often qualitatively, where a solute that dissolves to an appreciable extent in a solvent is said to be soluble. One that does not is said to be insoluble.

Miscible: The ability of two different liquids to intermix, essentially saying that one liquid is soluble in another. They form a homogeneous solution.

Immiscible: the inability of two different liquids to intermix. They form a heterogeneous mixture, often in layers with the more dense liquid on the bottom.

Figure 13.1: A flow chart of these relationships is reproduced from Chapter 1 below.
We have, in addition, described the general trends in solubility of ionic compounds in the solvent water. The solubility rules chart is reproduced here, showing, for example, that all sodium salts are soluble in water, while most phosphate salts are not.

**Figure 13.2. Solubility rules for ionic compounds.**

### Soluble and Insoluble Compounds

<table>
<thead>
<tr>
<th>SOLUBLE COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almost all salts of Na⁺, K⁺, NH₄⁺</td>
</tr>
<tr>
<td>Salts of nitrate, NO₃⁻</td>
</tr>
<tr>
<td>chloride, Cl⁻</td>
</tr>
<tr>
<td>perchlorate, ClO₄⁻</td>
</tr>
<tr>
<td>acetate, CH₃CO₂⁻</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EXCEPTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halides of Ag⁺, Hg⁺²⁺, Pb²⁺</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INSOLUBLE COMPOUNDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most salts of carbonate, CO₃²⁻</td>
</tr>
<tr>
<td>phosphate, PO₄³⁻</td>
</tr>
<tr>
<td>oxalate, C₂O₄²⁻</td>
</tr>
<tr>
<td>chromate, CrO₄²⁻</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EXCEPTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salts of NH₄⁺ and the alkali metal cations</td>
</tr>
</tbody>
</table>

| Most metal sulfides, S²⁻ |

| Most metal hydroxides and oxides |
| Ba (OH)₂ is soluble |

### Units of Concentration

The amount of solute dissolved in a particular amount of solvent or solution is called the solution concentration. There are a number of ways of expressing a solution’s concentration and they are described here. For each of these, an example is shown for a solution that contains 26.0 g NaCl (0.445 mol) dissolved in 100.0 g of water to form a solution with a volume of 121 mL.
Weight percent

\[
\text{weight percent} = \frac{\text{mass } A}{\text{total mass}} \times 100\%
\]

For our sample solution, the weight percent of NaCl is given by,

\[
\% \text{NaCl} = \frac{26.0 \text{ g NaCl}}{26.0 \text{ g NaCl} + 100.0 \text{ g H}_2\text{O}} \times 100\% = 20.6\%
\]

Molarity

\[
\text{molarity} = \frac{\text{moles solute}}{\text{liters solution}}
\]

For our sample solution, the molarity of NaCl is given by,

\[
[\text{NaCl}] = \frac{0.445 \text{ mol NaCl}}{0.121 \text{ L}} = 3.68 \text{ mol/L} = 3.68 \text{ M}
\]

Molality

\[
\text{molality} = \frac{\text{moles solute}}{\text{kilograms solvent}}
\]

For our sample solution, the molality of NaCl is given by,

\[
\text{molality NaCl} = \frac{0.445 \text{ mol NaCl}}{0.100 \text{ kg solvent}} = 4.45 \text{ mol/kg solvent} = 4.45 \text{ m}
\]

Mole fraction

\[
\text{mole fraction} = \frac{\text{moles } A}{\text{total moles}}
\]

For our sample solution, the mole fraction of NaCl is given by,

\[
\text{mole fraction NaCl} = X_{\text{NaCl}} = \frac{0.445 \text{ mol NaCl}}{0.445 \text{ mol NaCl} + 5.55 \text{ mol H}_2\text{O}} = 0.0742
\]

The sum of the mole fractions of all components of a mixture must add to exactly 1. So, for our sample solution, \(X_{\text{H}_2\text{O}} = 1.0000 - 0.0742 = 0.9258\).

ppm and ppb

\[
\text{ppm} = \text{parts per million} = \frac{\text{grams solute}}{1 \times 10^6 \text{ grams solution}} = \frac{\text{milligrams solute}}{\text{kilograms solution}}
\]

\[
\text{ppb} = \text{parts per billion} = \frac{\text{grams solute}}{1 \times 10^9 \text{ grams solution}} = \frac{\text{micrograms solute}}{\text{kilograms solution}}
\]
The units ppm and ppb are generally used for very dilute solution, so for these we will use a sample solution that contains 0.000258 g NaCl dissolved to form exactly 100 g of solution.

\[
\text{ppm NaCl} = \frac{0.258 \text{ mg NaCl}}{0.100 \text{ kg solution}} = 2.58 \text{ ppm}
\]

\[
\text{ppb NaCl} = \frac{258 \mu \text{g NaCl}}{0.100 \text{ kg solution}} = 2,580 \text{ ppb}
\]

II. Inherent Control of Solubility

Why do some chemical species mix together to form homogenous solutions but others do not? Why do water and alcohol mix, but not oil and water? Why does sugar dissolve in water but not sand? For that matter, why doesn’t glass or cement dissolve? A major aspect of this depends on intermolecular forces, but we also need to introduce another concept: Entropy.

IIa. Entropy and Thermodynamic Control of Chemical Processes

Entropy is a measure of the amount of disorder in a system. In a chemical system, it is closely linked to the independent mobility of atoms and molecules. The more mobile, the higher the entropy. Nature favors greater entropy, so any chemical process that increases the free motion of molecules will be favored by entropy.

Recall that nature also favors strong bonds, as represented by low enthalpy. So, any chemical process that increases the overall bonding strength between particles is favored by enthalpy.

When a process is favored by both entropy and enthalpy, it is favored overall. If the process is disfavored by both entropy and enthalpy, it will be disfavored overall, and not occur to any appreciable extent. But, when a process is favored by one and disfavored by the other, then its overall favorability will depend on temperature. These trends are summarized in Figure 13.3.

Figure 13.3: Tabular and Flow Chart Decision Trees for Control of Solubility

<table>
<thead>
<tr>
<th>Positive entropy change: increase in mobility of particles</th>
<th>Positive enthalpy change: reduction in bond strength</th>
<th>Negative enthalpy change: increase in bond strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Favored at higher temperatures</td>
<td>Favored at all temperatures</td>
<td></td>
</tr>
<tr>
<td>Disfavored at all temperatures</td>
<td>Favored at lower temperatures</td>
<td></td>
</tr>
</tbody>
</table>

| Negative entropy change: reduction in mobility of particles | | |
|-------------------------------------------------------------| | |
| Disfavored at all temperatures                               | | Favored at lower temperatures |
Consider a simple example: the vaporization of liquid water. In this process, the water molecules go from being held very close to one another (a highly constrained state) to one in which each molecule moves independently. Therefore, this process is entropy favored. At the same time, the water molecules go from having strong hydrogen bonds with neighboring water molecules. These are broken, leading to a state of weaker bonding. Vaporization of water is disfavored by enthalpy. Figure 13.4 examines these effects.

Figure 13.4. Molecular scale view of evaporation.

Water vaporization is therefore predicted to be favored at higher temperatures and disfavored at lower temperatures. Of course, we already knew that for this case.
In the following sections we will qualitatively examine the manner in which entropy and enthalpy combine to control solubility. In Chapter 20 we will deal with this topic quantitatively.

IIb. Gaseous mixtures.

This one is easy. Mixing of gases increases the disorder of a system, so mixing gases is entropy favored. Because gases have no appreciable intermolecular forces, enthalpy plays no role in mixing gases. Therefore, all gases are expected to mix, and in fact they do, in all proportions. When you mix two or more gases, the result is a completely mixed “solution” of those gases. Any sample taken from the mixture generally has the same proportion of each gas, no matter where in the mixture the sample is taken from. There are some cases where more dense components of mixture sink to the bottom, but in most cases the different gases are very well intermixed. Figure 13.5 shows a box filled with filtered air. The filtration process removes and dust or small droplets of water. All that remains is a mixture of the various gases that make up our atmosphere. This air is 99.9% a mixture of N₂, O₂, and Ar, all fully intermixed.

Figure 13.5: A box of filtered air. Perhaps the most lame text figure ever.

The only time a mixture of gases leads to anything other than a homogeneous mixture is when a chemical reaction occurs to form a product that exists in a different state. This is the case when gaseous ammonia and hydrogen chloride are mixed, as seen in Figure 13.6.
Figure 13.6. An experiment that allows separate gaseous samples of NH₃ and of HCl to come into contact.

Two samples, one containing concentrated ammonia and the other concentrated hydrochloric acid are inserted in the ends of a tube. They give off NH₃ and HCl in the gas phase. When the two gases encounter each other, as shown in the closeup, they undergo an acid-base reaction, forming solid ammonium chloride.

\[
\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)
\]

This is an example of smoke: a dispersed solid floating in a surrounding gas.
IIc. Solubility of Ionic Compounds in Water

Figure 13.7 shows a molecular scale view of what occurs when an ionic compound dissolves.

![Molecular scale view of potassium permanganate dissolution](image)

Figure 13.7: Molecular scale view of the dissolution of potassium permanganate, KMnO₄.

When ions dissolve in water, they form interactions with the water molecules where the polar water molecule is attracted to the ion. This attraction is an ion-dipole intermolecular force. Note on the right side of Figure 13.7 that the (negatively charged) O end of the water molecules are attracted to the K⁺ ion and the (positively charged) H end of the water molecules are attracted to the MnO₄⁻ ion.

Ion-dipole force strength is measured as the hydration enthalpy of an ion. This is the enthalpy change that would occur if one mole of that ion was submerged from the gas phase into water. Relative hydration enthalpy for a series of ions is closely linked to Coulomb’s Law and we see they increase in strength with increasing ion charge and decreasing ion size. Table 13.1 shows the hydration enthalpies for a bunch of cations.

<table>
<thead>
<tr>
<th>Ion</th>
<th>RADIUS</th>
<th>ΔHₜ_{hydr}</th>
<th>Ion</th>
<th>RADIUS</th>
<th>ΔHₜ_{hydr}</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1 Ions</td>
<td></td>
<td></td>
<td>+2 Ions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>181</td>
<td>−263</td>
<td>Ru</td>
<td></td>
<td>−1259</td>
</tr>
<tr>
<td>Rh</td>
<td>166</td>
<td>−296</td>
<td>Ba</td>
<td>149</td>
<td>−1304</td>
</tr>
<tr>
<td>K</td>
<td>152</td>
<td>−321</td>
<td>Sr</td>
<td>132</td>
<td>−1445</td>
</tr>
<tr>
<td>Na</td>
<td>116</td>
<td>−405</td>
<td>NO</td>
<td>124</td>
<td>−1485</td>
</tr>
<tr>
<td>Li</td>
<td>90</td>
<td>−515</td>
<td>Ca</td>
<td>114</td>
<td>−1592</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>−1081</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notice that the greatest hydration enthalpies are for ions with 3+ or 3- charges and that for ions of the same charge, smaller ones have greater hydration enthalpies.

Dissolution of ionic compounds also has an effect on entropy of a system. When ions are released into water, the water molecules surround the ion (via the ion-dipole forces just discussed). These water molecules are thus constrained from free movement by the presence of the ions among them. Ions are the invisible, secret police of the molecule world, silently hindering freedom for all around them. The degree to which this occurs depends on how many water molecules are constrained from moving. This is known as the hydration number and some are given in Table 13.2.
Notice that larger ions (Cs⁺) can have much smaller hydration numbers than smaller ions (Li⁺). This means that entropy effects will be significant for ionic compounds containing small, highly charged ions, and less significant for ionic compounds containing large ions of +1 or -1 charge.

Why does this matter? Consider the example of Figure 13.7, the dissolution of KMnO₄. When the solid KMnO₄ dissolves, a number of things happen:

1. The K⁺ and MnO₄⁻ ions are separated from each other. This is enthalpy disfavored.

2. The K⁺ and MnO₄⁻ ions are surrounded by water molecules, forming many ion-dipole IMFs. This is enthalpy favored.

3. The ions change from being constrained near one another, to going their separate ways. This is entropy favored.

4. The water molecules change from being free-moving to being constrained by attractions to the dissolved ions. This is entropy disfavored.

So, the dissolution of KMnO₄ in water is enthalpy favored and disfavored, and it is entropy favored and disfavored. The gain in stability from forming ion-dipole forces is offset by the loss from needing to separate the ions. The gain in entropy from dispersing the ions is offset by the constraining of water molecules to those ions.

How can this be used to predict the solubility of ionic compounds? The answer is that these competing factors always occur and the overall favorability of a dissolution depends on how significant each is. Therefore, this constitutes one area of this course where you can be in position to explain a trend or result, but not necessarily be able to have predicted it.

The difficulty in predicting the relative significance of these effects can be seen in the isolated enthalpy and entropy changes (even in direction, let alone quantitative magnitude) for a series of seemingly similar ionic compounds.
Specific examples to come.

Because there are competing trends governing solubility of ionic compounds, it is generally difficult to predict ionic compound solubility based on structure, but the most general trend is that ionic compounds composed of highly charged ions are insoluble salts. That’s why we use the big chart of ionic compound solubility rules.

Example:

Which of the following ions will have the enthalpy of hydration with the largest magnitude? Which will have the greatest hydration number? Which will be most favored to dissolve in terms of entropy?

ions: $\text{Mg}^{2+}$, $\text{Ca}^{2+}$, $\text{Ba}^{2+}$, $\text{Al}^{3+}$

Solution:

Hydration enthalpy increases in magnitude as the ion charge increases and as radius decreases. Of these ions, $\text{Al}^{3+}$ has both the highest charge and the smallest radius. So, it has the largest magnitude hydration enthalpy. Hydration number also follows the same trends, and $\text{Al}^{3+}$ will have the largest hydration number.

In terms of entropy of dissolution, the smaller the number of water molecules bonding to the dissolved ions, the more favored the dissolution. So, this means the ion with the smallest hydration number. That is, the ion with the lowest charge and the largest radius. Of these, $\text{Ba}^{2+}$ will have the smallest hydration number and will be the most favored to dissolve in terms of entropy.

IId. Mixtures Between Neutral Covalently Bonded Compounds

Theoretical Considerations

When two neutral, covalent molecular compounds are mixed, they undergo the same kinds of energetic changes that occur when ionic compounds dissolve. Figure 13.8 shows a molecular-scale interpretation of what occurs when water and the polar compound methanol are mixed.
The individual molecules of each compound are separated from one another. In this case, energy is needed to break water-water hydrogen bond IMFs and methanol-methanol dipole-dipole IMFs. When the liquids mix, there is formation of new dipole-dipole forces of attraction between the water and acetone molecules. There would seem to be an inherent entropy gain involved in mixing liquids. After all, the liquids go from being pure and separate to being mixed - a clear increase in disorder. However, the changes on the molecular scale often overcome this.

Figure 13.9 shows a molecular scale depiction of a mixture of water and nonpolar carbon tetrachloride.

Figure 13.9: Molecular scale view of a heterogeneous mixture of polar H₂O and nonpolar CCl₄.

When water and a nonpolar compound are mixed, the enthalpy gain (from the water’s point of view) of forming new dipole-induced dipole forces is minimal. So, instead, when water encounters a nonpolar surface, the water molecules adopt a highly specific, constrained arrangement that allows them to break few if any hydrogen bonds to neighboring water molecules. This is enthalpy favored (not breaking stronger bonds) but entropy disfavored. The mixing of water and nonpolar compounds is generally found to have little enthalpy control, but is almost always highly entropy disfavored.

**General Rule**

It is found that polar compounds generally mix well with each other. Likewise, it is generally found that nonpolar molecules mix well with each other. Contrary to this, polar compounds do not mix well with nonpolar compounds. Chemists use the somewhat lame expression “like-dissolves-like” to describe this. For example,
polar water dissolves polar methanol, but not nonpolar iodine. Figure 13.10 shows an experiment where water, carbon tetrachloride and iodine are mixed together.

![Figure 13.10](image)

Figure 13.10. A mixture of polar \(\text{H}_2\text{O}\), nonpolar \(\text{CCl}_4\), and purple nonpolar \(\text{I}_2\). The more dense \(\text{CCl}_4\) layer is on the bottom and contains most of the dissolved \(\text{I}_2\).

We see that the colored iodine dissolves readily into the carbon tetrachloride layer but not so much into the water layer. Moreover, the water and carbon tetrachloride layers remain distinct.

Example:

For each of the following compounds, indicate if it will be more soluble in water, or in carbon tetrachloride.

\[
\text{SiF}_4, \; \text{NH}_3, \; \text{CH}_3\text{CH}_2\text{OH}, \; \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

Solution:

The key here is to match polarities of solutes and solvents. Water is polar, and so polar solutes will dissolve better in water. Carbon tetrachloride is nonpolar, so nonpolar solutes will dissolve better in it. Of the solutes listed, \(\text{NH}_3\) and \(\text{CH}_3\text{CH}_2\text{OH}\) are polar and will dissolve better in water. \(\text{SiF}_4\) and \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\) are nonpolar and will dissolve better in \(\text{CCl}_4\).
III. External Control of Solubility

We have discussed the general principles that govern whether or not a particular solute will be appreciably soluble in a particular solvent. In this section we discuss the effect external conditions and other reactants can have on dissolution processes.

III a. Pressure Effects: Solubility of Gases

Pressure has a large effect on the solubility of gases into liquids, but a negligible effect of the solubility of liquids or solids into a liquid. We will therefore restrict our discussion to the effect of pressure on the solubility of gases.

On the molecular scale, the dissolution of a gas solute into a liquid involves collision of gas phase molecules with the surface of the liquid. Those collisions sometimes result in the solvent molecules surrounding the gas molecules, dissolving it. At the same time, previously dissolved gas solute molecules can sometimes find their way to the surface and, if they have enough energy, escape back into the gas phase. This is described below, and in Figure 13.11.

![Molecular scale representation of gas solubility](image)

Figure 13.11 shows a molecular scale interpretation of the effect of pressure on the solubility of a gas. The dark spheres are the gaseous solute. The light spheres are the solvent.

In the end, an equilibrium is established where the dissolution and gasification processes attain the same rate and the amount of dissolved gas is constant. (This is somewhat like we discuss when describing vapor pressure, but in that case the liquid molecules were the ones of interest instead of the solute molecules).

Now think what would happen if suddenly there were more molecules of gas in the gas phase. The rate of the dissolution step would increase and more gas would dissolve. This happens and a new equilibrium is established with a greater amount of dissolved gas. The solubility of the gas, therefore, depends on the pressure of the gas.
above the liquid. This is described by Henry’s Law, which states that the solubility of a gas is proportional to the pressure of the gas above the solution.

\[ S = k_H \times P \]

- \( S \) = solubility
- \( k_H \) = Henry’s Law constant for a specific solute, solvent and temperature
- \( P \) = partial pressure of the solute gas

Consider the bottle of soft drink in Figure 13.12.

> Imagine three photographs of a bottle of soda showing it before opening (no bubbles), as it’s bubbling, and after it goes flat (again, no bubbles)

Figure 13.12

The solubility of carbon dioxide is proportional to the pressure of the carbon dioxide above the liquid. In the first frame, the bottle is unopened and the partial pressure of CO\(_2\) is high, greater than 1 atm. The CO\(_2\) is therefore highly soluble and the system is at equilibrium. When the bottle is first opened, the “head gas” at the top of the bottle escapes and the partial pressure of CO\(_2\) drops to almost zero because the ambient atmosphere contains very little CO\(_2\). The CO\(_2\) is now supersaturated because the amount dissolved is greater than the solubility, based on the new, very low pressure of CO\(_2\) in the atmosphere. The CO\(_2\) therefore bubbles out of the soda. After some time, the system reaches equilibrium again with a new, lower solubility of CO\(_2\) in line its new low atmospheric partial pressure. The soda is flat.

Some typical Henry’s Law constants are given in Table 13.3. The magnitude of the constants reflects the relative solubility of each gas. For example, CO\(_2\) is relatively soluble in water when compared with O\(_2\), N\(_2\), or He.

![Henry's Law Constants, 25 °C; Water is the Solvent](image)

<table>
<thead>
<tr>
<th>Gas</th>
<th>( k_H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)</td>
<td>( 8.42 \times 10^{-7} )</td>
</tr>
<tr>
<td>O(_2)</td>
<td>( 1.66 \times 10^{-6} )</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>( 3.4 \times 10^{-2} )</td>
</tr>
<tr>
<td>He</td>
<td>( 3.7 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

Table 13.3. Some Henry’s Law constants. These numbers will differ at different temperatures.
Henry’s law predicts that the solubility of a gas will be proportional to its partial pressure above the solution. This can be viewed graphically for different gases in Figure 13.14. Figure 13.14 shows set of plots of gas solubility vs. pressure of that gas, at a constant temperature. Each line represents the solubility of a different gas as a function of pressure. The slope of each plot is proportional to that gas’s Henry’s Law constant. The steeper the line, the greater the \( k_H \) value. So, gas “a” has the largest \( k_H \) value, and is the most soluble of the three.

![Figure 13.14](image)

Figure 13.14. Plots of solubility vs. pressure for three different gaseous solutes in water at 25 °C.

**Example:**

What is the solubility of oxygen (in units of grams per liter) in water at 25 °C, when the \( \text{O}_2 \) has a partial pressure of 152 mm Hg (typical of oxygen in air under normal conditions)?

**Solution**

The solubility of \( \text{O}_2 \) is given by Henry’s Law: \( S_{\text{O}_2} = k_H(\text{O}_2) \times P_{\text{O}_2} \)

\[
S_{\text{O}_2} = \frac{1.66 \times 10^{-6} \text{ mol}}{\text{L} \cdot \text{mm Hg}} \times 152 \text{ mm Hg} = 2.52 \times 10^{-4} \text{ mol/L}
\]

\[
2.52 \times 10^{-4} \text{ mol/L} \times \frac{32.00 \text{ g O}_2}{\text{mol O}_2} = 8.07 \times 10^{-3} \text{ g/L}
\]
III b. Effects of Temperature on Solubility

Your gut feel is probably that things are more soluble in hot liquids than in cold ones. This is often true, but it is also often false. In common experience, you know that, for example, sugar is easier to dissolve in hot water than in cold water. When you see this, however, you are not observing how soluble the sugar is, but how fast it dissolves. In order to probe its solubility, you would need to add enough sugar to form a saturated solution. We don’t advise it.

As we discussed earlier, it is difficult to predict whether a dissolution process will be endothermic or exothermic. There are competing trends in breaking and forming intermolecular forces that belie constructing any useful rules-of-thumb. However, it is relatively easy to measure the enthalpy change for a dissolution process and the result of that measurement can give a key as to how changes in temperature will affect solubility.

Consider the dissolution of ammonium nitrate, which is highly endothermic.

\[
\text{NH}_4\text{NO}_3(s) \rightarrow \text{NH}_4\text{NO}_3(aq) \quad \Delta H^\circ = +\text{a lot kJ/mol}
\]

This can be written as,

\[
\text{NH}_4\text{NO}_3(s) + \text{a lot kJ} \rightarrow \text{NH}_4\text{NO}_3(aq)
\]

As this solid dissolves, it absorbs heat energy from the solvent. According to LeChatelier’s Principle, perturbing a system results in a shift in the equilibrium that offsets that perturbation. If the temperature of the water in this case is raised, the system will shift so as offset that increase in temperature. This means the system will act to absorb some of that heat, which is a shift in the forward direction: the additional heat energy that comes about from raising the temperature results in more NH4NO3 dissolving. Therefore, the solubility of NH4NO3 increases with increasing temperature.

Now consider the solubility of a gas. When a gas dissolves, new IMFs are formed but none need to be broken. Therefore, all gas dissolution processes are exothermic.

\[
\text{O}_2(g) \rightarrow \text{O}_2(aq) + \text{some kJ}
\]

In this case, raising the temperature results in an opposite shift. Figure 13.15 shows a plot of the solubility of O2 in water as a function of temperature. Notice that the solubility decreases markedly as the temperature increases.
In order to offset the increase in thermal energy, the system shifts to the left, absorbing heat by degassing some of the dissolved O$_2$. The solubility of all gases decrease with increasing temperature.

In general, if the dissolution reaction is,

- **endothermic** \( \Delta H_{\text{dissolution}} > 0 \) solubility increases as temperature increases
- **exothermic** \( \Delta H_{\text{dissolution}} < 0 \) solubility increases as temperature increases

Figure 13.16 shows the solubility of some ionic compounds in water over a wide range of temperatures.
Need to add in enthalpy of dissolution values, but those that slope down have exothermic dissolutions, and those that slope upwards have endothermic dissolutions.

Example:

For each of the following, indicate if the solute will become more soluble or less soluble as temperature increases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enthalpy of Dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>+25.69 kJ/mol</td>
</tr>
<tr>
<td>LiOH</td>
<td>-23.55 kJ/mol</td>
</tr>
<tr>
<td>Ar gas</td>
<td>not given</td>
</tr>
</tbody>
</table>

Solution:

Solubility will increase with temperatures for compounds that have endothermic enthalpies of dissolution. This is the case for NH₄NO₃. LiOH has a negative enthalpy of dissolution, and will become...
less soluble as temperature increases. Ar gas, like all gases, has an negative (exothermic) enthalpy of dissolution and its solubility will also decrease with temperature.

III c. Using Chemical Reactions to Drive Solubility of Ionic Compounds in Water

Suppose your goal is to dissolve an ionic solid in water but you are not concerned with the chemical state of the solute after it dissolves. There are many cases where chemical reactions between an externally added reagent and one of the solute’s constituent ions will serve to effect this dissolution.

Using Acids to Dissolve Ionic Compounds Containing Basic Anions

The first we have seen before: reaction of acids with ionic compounds containing basic anions. Consider the reaction between aqueous hydrochloric acid and normally insoluble calcium carbonate.

\[
2 \text{HCl}(aq) + \text{CaCO}_3(s) \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

The net ionic equation is,

\[
2 \text{H}^+(aq) + \text{CaCO}_3(s) \rightarrow \text{Ca}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)
\]

The key to using this technique is that the ionic compound must contain an anion that is a weak base. Examples of anions that often are amenable to this technique are: \(\text{PO}_4^{3-}\), \(\text{SO}_3^{2-}\), \(\text{CO}_3^{2-}\). Because the behavior of weak bases are well understood and very predictable, acid-driven dissolution reactions are easy to predict.

Using Complexing Agents to React with Metal Ions

Another type of reaction that can sometimes effect a dissolution is a complexation reaction. This type of reaction involves the bonding of one or more complexing agents to a metal ion. There are a wide variety of complexing agents, but the most common contain O or N atoms that have lone pairs. Consider the reaction of insoluble silver chloride with aqueous ammonia.

\[
\text{AgCl}(s) + 2 \text{NH}_3(aq) \rightarrow \text{Ag(NH}_3)_2^+(aq) + \text{Cl}^-(aq)
\]

In this reaction, two \(\text{NH}_3\) molecules attack the \(\text{Ag}^+\) ions in the solid \(\text{AgCl}\), pulling them off to form the soluble complex ion, \(\text{Ag(NH}_3)_2^+\). Unlike acid-driven dissolution, at this stage of your chemical knowledge complexation dissolution reactions are not easy to predict. You should be able to recognize one when you see it, but not necessarily have predicted it would have occurred.

III d. Using Surfactants to Codissolve Polar and Nonpolar Compounds

A surfactant is a molecule that helps nonpolar and polar substances to intermix. These are used as soaps, detergents, and other cleaners where there is a need to dissolve oily substances in water. The molecular structure of all surfactants contain a long, nonpolar hydrocarbon “tail” and a polar or charged “head group.” Many of these work by forming spherical structures called micelles. A micelle has a structure where the surfactant molecules all point there nonpolar tails in towards the center, presenting their polar head groups to the outside where they are exposed to water. The center of the micelle is therefore a little region of nonpolar...
solvent in a sea of water. Figure 13.17 shows the manner in which a micelle can surround a nonpolar oil droplet, dissolving it in water.

![Figure 13.17](image)

Figure 13.17. A molecular scale view of the action of a micelle dissolving an oil droplet.

IV. Colligative Properties

IV a. Introduction

Up to this point, we have discussed the ability or lack thereof of one substance (the solute) to dissolve in another (the solvent). We now turn to how the presence of a dissolved solute affects the properties of the solvent. When a solute is introduced into a solvent, the properties of the solvent that are affected are called colligative properties. The colligative properties we will study here are osmotic pressure, vapor pressure, boiling point and melting point. In each case, the presence of the solute has the same general effect on the solvent: When a solute is in solution, it tends to block solvent molecules from leaving the solution.

Consider the two-compartment thing shown in Figure 13.18.

![Figure 13.18](image)

Figure 13.18 Two pairs of liquid samples separated by a semipermeable membrane. In a., the two samples are both composed of pure water. In b., one of the samples is pure water while the other is a solution.
In this situation, water molecules can move from one side to the other, but the solute molecules cannot. Consider the left image, 13.18 a. With no solute molecules present the rate of solvent molecule movement from left-to-right will equal that of movement from right-to-left. That is, the chances of a water molecule hitting and passing through one of the pores in the membrane is the same on both sides. Now consider the right image, 13.18 b. In this case the left sample is composed of pure water while the right sample is a solution of water and a solute. Only the water molecules can pass through the membrane. Water molecules in the left compartment are unimpeded and can pass into the right compartment. However, in the right compartment, some of the membrane pores are blocked by the solute particles. This decreases the flow of water molecules from right-to-left. This leads to an imbalance: water molecules flow more readily to the right than to the left.

The general impact of the presence of the solute seen here- keeping solvent molecules in a solution from leaving that solution- is observed in a number of

IV b. Osmotic Pressure

In the example above, the flow of water in one direction results in a pressure between the two compartments on either side of the membrane. This special type of pressure is called osmotic pressure, and results in osmotic flow across the membrane.

Osmotic flow always involves solvent moving from the less concentrated solution to the more concentrated solution.

This pressure can be measured and is found to be proportional to the concentration of solute particles in the solution. Osmotic pressure is represented by a capital Pi, Π, and the mathematical relationship between and concentration is,

\[ Π = MRT \]

Where M is the solution concentration in mol/L, R is the gas constant, 0.0821 L-atm/K-mol, and T is the temperature in Kelvins.

Example:

The nonvolatile, nonelectrolyte TNT (trinitrotoluene), \( C_7H_5N_3O_6 \) (227.10 g/mol), is soluble in benzene \( C_6H_6 \). Calculate the osmotic pressure generated when 14.3 grams of TNT are dissolved in 242 ml of a benzene solution at 298 K.

Solution:

Osmotic Pressure is given by \( Π = MRT \)
Where:

\[ \Pi = \text{Osmotic Pressure in atmospheres} \]
\[ M = \text{concentration of solute in moles/Liter} \]
\[ R = \text{Ideal gas constant} = 0.0821 \text{ L atm/mol K} \]
\[ T = \text{Kelvin temperature} = 298 \text{ K} \]

Volume solution = 242 mL = 0.242 L

TNT = \( \text{C}_7\text{H}_5\text{N}_3\text{O}_6 \) = 227.1 g/mol

Mass TNT = 14.3 g

\[
\text{moles TNT} = \frac{1 \text{ mol}}{227.1 \text{ g}} \times 14.3 \text{ g} = 6.30 \times 10^{-2} \text{ mol TNT}
\]

\[
\text{M} = \frac{6.30 \times 10^{-2} \text{ mol TNT}}{0.242 \text{ L}} = 0.260 \text{ M TNT}
\]

\[
\Pi = \frac{0.260 \text{ mol TNT}}{0.0821 \text{ L atm}} \times 298 \text{ K} = 6.37 \text{ atm}
\]

**Applications of Osmotic Pressure**

Osmotic pressure sees a great deal of use in the home, in commerce, and in the laboratory.

Determining Molar Mass of Proteins: Proteins are very large molecules that often have molar masses in the thousands. Such large molecules are difficult to analyze using traditional instrumental methods that work for small molecules. Osmotic pressure is often used to determine the molar mass of proteins.
Example:

In a laboratory experiment, students synthesized a new compound and found that when 11.34 grams of the compound were dissolved to make 229.5 mL of a water solution, the osmotic pressure generated was 6.71 atm at 298 K. The compound was also found to be nonvolatile and a non-electrolyte.

What is the molar mass they determined for this compound?

Solution:

Osmotic Pressure is given by \( \Pi = \frac{MRT}{V} \).

Where:

\( \Pi \) = Osmotic Pressure in atmospheres = 6.71 atm
\( M \) = concentration of solute in moles/Liter
\( R \) = Ideal gas constant = 0.0821 L atm/mol K
\( T \) = Kelvin temperature = 298 K

Volume solution = 229.5 mL = 0.2295 L
Mass unknown = 11.34 g

\[
\text{grams unknown} \quad 11.34 \text{ g} \\
\text{Molar mass of unknown} = \frac{\text{grams unknown}}{\text{moles unknown}} = \frac{11.34 \text{ g}}{0.2743 \text{ mol}}
\]

You need to find the number of moles of the unknown used.

For the calculations below we'll display 4 significant figures in the intermediate steps and round to 3 at the end.

1. First calculate the concentration of the solution:

\[
M = \frac{\Pi}{RT} = \frac{6.7 \text{ atm}}{0.0821 \text{ L atm/mol K} \times 298 \text{ K}} = 0.2743 \text{ mol/L}
\]

2. Use this to calculate the moles of unknown:

\[
? \text{ moles unknown} = \frac{0.2743 \text{ mol unknown}}{0.2295 \text{ L solution}} = 6.294 \times 10^{-2} \text{ mol unknown}
\]
3. Now calculate the molecular weight:

\[
\frac{11.34 \text{ g}}{6.294 \times 10^{-2} \text{ mol}} = \frac{180 \text{ g}}{\text{mol}}
\]

Although you can’t tell just from the osmotic pressure, the compound they synthesized was glucose, \(C_6H_{12}O_6\).

**Preserving meat**: When meat is salted, it tends to not rot. Meat gets rotten through the action of bacteria eating it and producing bad smelling byproducts in the process. When a bacterium lands on a piece of salty meat, there exists a difference in concentration between the solution on the surface of the meat, which is highly concentrated, and that within the bacterium, which is relatively dilute. Because of this difference, water will pass through the bacterial cell membrane to the meat. This loss of water kills the bacterium.

**Isotonic sports drinks**: When you exercise you lose a significant amount of water through sweat. You also lose salts from your system, but not in equal proportion to the water loss. Isotonic sports drinks account for this difference by balancing the concentration of solute particles with that in your system.
**Water softeners** Hard water is water in which a greater concentration of dissolved ions is present. Reverse osmosis is one of the main ways in which the salt content in the water can be reduced. This works by introducing a water needing to be purified to a much more concentrated solution. These systems need to use a great deal of salt, usually employing salt blocks weighing XXX pounds.

*Need a photo and a diagram showing how it works*

**Making Pickles** need stuff here about pickles. Put vegetables in brine (highly concentrated NaCl solution).

**IV c. Vapor Pressure Lowering**

The interface between a liquid and the gas above it is similar to the semipermeable membrane described for osmotic pressure. Figure 13.DD shows a molecular scale view of the effect on vapor pressure of adding a solute to a solvent.

![Molecular Scale View](image)

**Figure 13.20**

On the molecular scale, the presence of solute particles (yellow) block solvent molecules below them from escaping to the vapor phase. They do not block vapor molecules from reentering the liquid phase. This

Figure 13.21 shows two liquid sample in closed containers. In the left case, the liquid is pure solvent. Solvent molecules escape into the gas phase, and gas phase molecules recondense into the liquid. As described in the last chapter, these two processes reach equilibrium and result in an equilibrium vapor pressure.
Figure 13.21

Now consider the image on the right, which represents a solution where the green objects represent solute molecules or ions. Similar to the first case, molecules in the gas phase can recondense onto the surface of the liquid- the rate of this process is unimpeded by the presence of the solute particles. However, many of the molecules near the surface of the liquid are blocked from leaving the liquid by the presence of those solute. This results in a slower rate of movement from the liquid state to the gaseous state. This in turn results in equilibrium being reached with fewer molecules in the gas phase. The solution therefore has a lower vapor pressure than does the pure solvent.

The lowering of a liquid’s vapor pressure by the presence of a solute is called, perhaps surprisingly, as vapor pressure lowering, and mathematically follows Raoult’s Law.

\[ P_{\text{solution}} = P^\circ_{\text{solvent}} \times X_{\text{solvent}} \]

**Example:**

The vapor pressure of hexane (C\textsubscript{6}H\textsubscript{14}) at 50 °C is 399 mm Hg. What will the vapor pressure be of a solution of 70.0 g hexane mixed with 0.100 mol of a nonvolatile solute.

**Solution:**

The vapor pressure of the solution is given by Raoult’s law.

\[ P_{\text{solution}} = P^\circ_{\text{hexane}} \times X_{\text{hexane}} \]
The number of moles of hexane and the mole fraction of hexane must first be determined.

\[
\text{mol hexane} = \frac{70.0 \text{ g}}{86.18 \text{ g hexane}} \times \frac{1 \text{ mol hexane}}{\text{mol hexane}} = 0.812 \text{ mol}
\]

\[
X_{\text{hexane}} = \frac{\text{mol hexane}}{\text{mol hexane} + \text{mol solute}} = \frac{0.812}{0.812 + 0.100} = 0.891
\]

Then the vapor pressure of the solution can be calculated.

\[
P_{\text{solute}} = 399 \text{ mm Hg} \times 0.891 = 355 \text{ mm Hg}.
\]

**Applications of Vapor Pressure Lowering: Distillation**

An important use of vapor pressure lowering is the process of distillation, whereby a mixture of two liquids of different volatility are either separated or the concentration of one increased at the expense of the other. Consider a mixture of 50 mol percent water and 50 mol percent ethanol, at a temperature of 55 °C. The vapor pressures of the two liquids are: 126 mm Hg and 290 mm Hg. The mole fraction of each compound in the gas phase is proportional to their partial pressures. For each, the partial pressure will be given by their vapor pressure times the mole fraction.

\[
P_{\text{water}} = 126 \text{ mm Hg} \times 0.500 \text{ mol fraction} = 63 \text{ mm Hg}.
\]

\[
P_{\text{ethanol}} = 290 \text{ mm Hg} \times 0.500 \text{ mol fraction} = 145 \text{ mm Hg}.
\]

If the gas mixture is condensed, the mole fraction in the vapor phase will be the mole fraction of the new liquid sample.

\[
X_{\text{water}} = \frac{63 \text{ mm Hg}}{63 \text{ mm Hg} + 145 \text{ mm Hg}} = 0.303
\]

\[
X_{\text{ethanol}} = \frac{145 \text{ mm Hg}}{63 \text{ mm Hg} + 145 \text{ mm Hg}} = 0.697
\]

So, this single distillation step has increased the mole fraction of ethanol from 0.500 to 0.697.

**IV d. Boiling Point Elevation**

A solution at any temperature will have a vapor pressure less than that of the pure solvent. That vapor pressure will still increase with increasing temperature, just like it does for a pure solvent. Figure 13.22 shows the vapor pressure – temperature curves for pure water and a solution of 6 M sugar.
At each temperature, the vapor pressure of the solution is lower than that of pure water. As the temperature increases, the vapor pressure of pure water reaches 1 atm at a temperature of 100 °C, the normal boiling point of pure water. The solution, however, needs to be heated to a higher temperature to get the vapor pressure to increase to 1 atm. The boiling point of the solution is therefore higher than that of pure water. This effect is called boiling point elevation and mathematically follows the relationship,

$$\Delta T_{bp} = K_{bp} \times m_{\text{solute}}$$

$K_{bp}$ is the boiling point elevation constant and is different for each liquid. The larger its value, the more susceptible that particular liquid is to having its boiling point affected by the solute.

$m_{\text{solute}}$ is the molality of the solute, defined as the mol solute/kg solvent

**Example:**

What is the boiling point of a solution containing 40.0 g I$_2$ dissolved in 250 g of a benzene (C$_6$H$_6$)?

**Solution:**

The boiling point will equal the normal boiling point plus the boiling point elevation. Using data from Table 13.5,
\[ BP = 80.1 \, ^\circ C + m_{I_2} \times 2.53 \, ^\circ C/m \]

The molality of \( I_2 \) is given by,

\[ m_{I_2} = \frac{\text{mol} \, I_2}{\text{kg} \, \text{benzene}} = \frac{40.0 \, \text{g} \times \frac{1 \, \text{mol} \, I_2}{253.8 \, \text{g} \, I_2}}{0.250 \, \text{kg} \, \text{benzene}} = 0.630 \, \text{mol/kg} \]

\[ BP = 80.1 \, ^\circ C + 0.630 \times 2.53 \, ^\circ C/m = 81.7 \, ^\circ C. \]

Table 13.5 gives boiling point elevation and freezing point depression values for six solvents. Notice that not all solvents are equally susceptible to changes in boiling or freezing points. Nitrobenzene is about 10 times as sensitive to changes in boiling point that is water.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>bp (pure)</th>
<th>( K_b ) (^{\circ} \text{C/m} )</th>
<th>fp (pure)</th>
<th>( K_f ) (^{\circ} \text{C/m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>100*</td>
<td>0.512</td>
<td>0*</td>
<td>1.86</td>
</tr>
<tr>
<td>benzene</td>
<td>80.1</td>
<td>2.53</td>
<td>5.5</td>
<td>5.12</td>
</tr>
<tr>
<td>acetic acid</td>
<td>118.1</td>
<td>3.07</td>
<td>16.6</td>
<td>3.90</td>
</tr>
<tr>
<td>nitrobenzene</td>
<td>210.9</td>
<td>5.24</td>
<td>5.7</td>
<td>7.00</td>
</tr>
<tr>
<td>phenol</td>
<td>182</td>
<td>3.56</td>
<td>43</td>
<td>7.40</td>
</tr>
<tr>
<td>camphor</td>
<td>207.4</td>
<td>5.61</td>
<td>178.4</td>
<td>40.0</td>
</tr>
</tbody>
</table>

Table 13.5 Boiling Point Elevation and Freezing Point Depression Values

### IV e. Freezing Point Depression

The interface between a solid and a solution is similar to that we have discussed between two solutions or between a solution and the gas above it. When a solution is cooled enough, the molecules of solvent reach a point where their thermal energy cannot overcome the intermolecular forces between them. The solution starts to freeze. Perhaps surprisingly, in most cases only the solvent molecules solidify. The solute molecules or ions remain in solution. So, as the solution is cooled, solvent solidification reduces the volume of solution, which in turn leads to an increase in the concentration of the solute in the remaining solution. Figure 13.5S shows a solution of a dye in water at room temperature and then the same sample after cooling has led most of the liquid water to solidify. Notice that the solid water is colorless, showing that it solidified as pure water with no dye in the solid state. In the solution the dye is now more concentrated and appears darker.

Photo of this experiment
Figure 13.23: The result of freezing a solution of a dye in water.

Figure 13.24: Vapor pressure-temperature curves showing the resulting decrease in freezing point for a solution.

On the molecular scale, the presence of solute particles block some water molecules from moving from the solution to the solid. The ability of molecules on the solid surface to enter the solution is unimpeded. Therefore, the presence of the solute in the solution leads shifts the equilibrium of solvent molecules from the solid to the solution. Therefore, in order to start the solution freezing, the solution must be cooled to temperatures lower
than the normal freezing point. Figure 13. PP shows a phase diagram for pure water and for a solution of 6 M sugar.

Figure 13.25: Phase diagrams for a pure solvent and its solution, showing that the solution has a greater range for the liquid state.

Mathematically, freezing point depression is similar to that describing boiling point elevation. But in the case of freezing point depression, of course, the freezing point of the solution is lower than that of the pure solvent.

\[ \Delta T_{fp} = K_{fp} \times m_{solute} \]

**Example:**

What is the freezing point of a solution of a solution containing 40.0 g I₂ dissolved in 250 g of a benzene (C₆H₆)?

**Solution:**

The freezing point will equal the normal freezing point minus the freezing point depression. Using data from Table 13.5,

\[ FP = 5.5 \, ^\circ C - m_{I_2} \times 5.12 \, ^\circ C/m \]

The molality of I₂ is given by,

\[ m_{I_2} = \frac{\text{mol I}_2}{\text{kg benzene}} = \frac{40.0 \, \text{g}}{253.8 \, \text{g I}_2} \times \frac{1 \, \text{mol I}_2}{0.250 \, \text{kg benzene}} = 0.630 \, \text{mol/kg} \]

\[ FP = 5.5 \, ^\circ C - 0.630 \times 5.12 \, ^\circ C/m = 2.27 \, ^\circ C \]
IV e. Ionic Compounds and Colligative Properties

Consider a 1 m solution of sugar and a 1 m solution of NaCl. Sugar is a neutral, covalently bonded compound, so when it dissolves its molecules stay intact. Each sugar molecule takes up one place on the surface of the solution. Now consider the solution of NaCl. When sodium chloride dissolves the Na\(^+\) and Cl\(^-\) ions separate and go their separate ways. Each ion can take its own place on the surface of the solution. Mole for mole, NaCl has twice the effect on colligative properties as does a nonionic compound like sugar.

The multiplicative factor by which a solute is multiplied is called the van’t Hoff factor. For NaCl, the van’t Hoff factor is expected to be 2 because each mole of NaCl yields 2 moles of ions. The van’t Hoff factor for CaCl\(_2\) is expected to be 3 because CaCl\(_2\) breaks up into 3 ions.

The equations for boiling point elevation and freezing point depression can be rewritten taking this into account.

\[
\Delta T_{bp} = K_{bp} \times i \times m_{solute}
\]

\[
\Delta T_{fp} = K_{fp} \times i \times m_{solute}
\]

where \(i\) = the van’t Hoff factor for the solute. Non-ionic solutes will have \(i = 1\).

Example:

What is the freezing point of a solution of 25.0 g CaCl\(_2\) dissolved in 115 g H\(_2\)O?

Solution:

The freezing point will equal the normal freezing point minus the freezing point depression. Using data from Table 13.5,

\[
FP = 0.0 \degree C - I \times m_{CaCl2} \times 1.86\degree C/m
\]

The molality of CaCl\(_2\) is given by,

\[
m_{CaCl2} = \frac{\text{mol CaCl}_2}{\text{kg H}_2\text{O}} = \frac{25.0 \text{ g} \times \frac{1 \text{ mol CaCl}_2}{110.98 \text{ g CaCl}_2}}{0.115 \text{ kg H}_2\text{O}} = 1.96 \text{ mol/kg}
\]

\[
FP = 0.0 \degree C - 3 \times 1.96 \text{ m} \times 1.86 \degree C/m = -10.9 \degree C
\]

V. Other Important Mixtures
The mixtures we have discussed thus far involve the fairly common case of a solute dissolved in a liquid to form a homogeneous solution. There are, of course, many other types of mixtures of great importance and we discuss some of them here.

Alloys

Alloys are mixtures of different metals, almost always in the solid state. Alloys can be heterogeneous mixtures where small crystalline regions of each metal are intermixed to form the solid. This type of structure can often be seen on old brass door handles. The photo below shows this.

Fully homogeneous alloys also exist, where atoms of the two metals are completely intermixed. Important alloys include brass, bronze, others other people will think of. Amalgams are a special type of alloy where mercury is the “solvent” and other metals serve as the “solute.” Most people live close at hand with amalgams. Amalgams of mercury and other metals have been used for decades because they can be formulated to melt at temperatures not much above body temperature, inserted into cavities in teeth and allowed to cool and solidify there, forming common metallic fillings.

Another important class of alloys is steel. Steel is an alloy of iron with some carbon and often other elements as well. Inclusion of different elements lends different properties to the steel.

Need a table of elements added and the property they give to the steel.

Composites

Composites are heterogeneous mixtures of a continuous phase in which a reinforcing phase is distributed. The continuous phase is often a metal, and the reinforcing phase is often a “whisker” shaped solid of a different substance. The inclusion of the reinforcing phase can have dramatic effects on the strength of the metal.

Need a molecular scale drawing of this, and also some real examples- graphite tennis racket comes to mind.

Colloids

A colloid is a mixture where one substance is distributed evenly throughout another. The two substances are in separate phases when viewed on the microscopic scale, but appear homogeneously mixed on the bulk scale. A variety of colloids exist but the two most important are emulsions and aerosols.

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Liquid in liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol</td>
<td>Solid or liquid in gas</td>
</tr>
</tbody>
</table>

Emulsions
An emulsion is a heterogeneous mixture of two liquids that does not separate into two distinct phases. Consider milk, which consists of a “continuous phase” of water containing “emulsified” globules of nonpolar fat. This is a typical example of an “oil in water” emulsion. Figure 13.UU shows an electron micrograph of such an emulsion.

Figure 13.26: An oil-in-water emulsion.

Emulsions can be formed in the opposite fashion, with a continuous nonpolar oil phase containing globules of water.

Figure 13.27: Process for formation of two main types of emulsions.

Surprisingly, it is possible to have an emulsion that is composed of only 5% continuous phase.
Obviously, water and oil do not normally mix. Forming an emulsion requires an external reagent called an emulsifier. There are thousands of emulsifiers used commercially and they all are similar to the surfactants described in Section 13.3d.

Emulsions are of great importance in commerce. They are used to form:

- Dairy products such as milk and butter
- Cosmetics such as hand lotion and cold cream
- Floor and car oils and “waxes”
- Paint and other pigments (*make sure paint and pigment are both correct here*)
- Delivery systems for pharmaceuticals

**Aerosols**

An aerosol is a mixture of small particles of either liquid or solid in a gas. The term aerosol is often used when referring to “spray cans” in which a liquid is dispersed into the air in tiny droplets. Other aerosols exist in nature. The haze you see on a hazy day is an aerosol of water in the atmosphere. Solid aerosol particles represent a health risk and are regulated... *or are they?*