CHAPTER 2 – SOLUTIONS

Introduction

Solutions are all around us. Our atmosphere is a solution of gases in gases, carbonated beverages are solutions of gases in liquids, sweetened drinks are solutions of solids in liquids, and solder is a solution of solids in solids. Reactions are normally carried out in solutions of gases or liquids because the particles in these solutions are free to move and to collide. In this chapter, we define several terms relevant to the study of solutions and discuss some solution properties.

2.1. Concentration Units

Introduction

The properties of a solution depend upon the relative amounts of solvent and solute(s), which is given by the solute concentration in the solution. A concentrated solution is one in which the concentration of a solute is relatively large, while a dilute solution is one in which the solute concentrations are relatively low. However, the terms 'concentrated' and 'dilute' used in this manner are not quantitative. In this section, we present several different ways of reporting the concentrations of solutions in a quantitative manner.

Objectives

- Determine the concentration of a solution from the amount of solute and the amount of solution or solvent.
- Use the definition of a concentration unit to convert between the amount of solute and the amount of solution or solvent.
- Prepare a solution of known molarity.
- Use and understand the meaning of the prefixes m (milli), μ (micro) and n (nano).

2.1-1. Definitions

A solution consists of a solvent and one or more solutes.

Before we start into the quantitative aspects of solutions, we review some of the terms introduced in Section 10.1 of Chemistry – A Molecular Science (Chapter 10).

- A **solution** is a homogeneous mixture consisting of a solvent and one or more solutes. A homogeneous mixture is one whose composition is the same throughout. For example, sugar dissolves in water to make a homogeneous mixture in which the sugar concentration (sweetness) is the same throughout, so the mixture is a solution. Mixing water and oil forms a mixture whose composition varies from pure water to pure oil, so this mixture is heterogeneous and not a solution.
- The **solvent** is that substance that dictates the phase of the solution. If a liquid is present, it is usually the solvent. This course focuses on **aqueous solutions**, which are solutions in which water serves as the solvent.
- A **solute** is one of the substances that is dissolved in the solvent. Solutes of aqueous solutions can be solid (a sugar solution), liquid (alcoholic beverages contain liquid ethanol in water), and/or gas (carbonated beverages contain CO_2 in water).

When ionic substances dissolve in water, they break up into their component ions, i.e., they ionize or dissociate in water. A substance that ionizes or dissociates completely in water is said to be a strong **electrolyte**. Ionic compounds are *strong electrolytes*. NaCl dissociates completely into Na^{1+} and Cl^{1-} ions in water, so it is a strong electrolyte. Molecular substances do not dissociate when in water and are classified as *nonelectrolytes*. Sugar dissolves in water as sugar molecules ($C_{12}H_{22}O_{11}$), so sugar is a nonelectrolyte. Acids and bases react with water to produce ions, so they too are electrolytes. Strong acids and bases react completely with water and are strong electrolytes, but weak acids and bases react only partially with water and are classified as *weak electrolytes*.
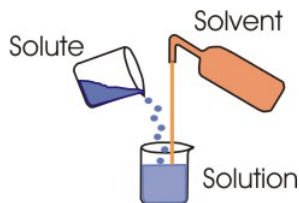
Figure 2.1: Components of a Solution A solution consists of a solvent and at least one solute. Almost all of the solutions considered in this course are aqueous solutions, which are solutions in which water is the solvent.

2.1-2. Molarity (M)

The **molarity** (M) of a solute is the number of moles of the solute in one liter of solution or the number of millimoles of solute in one milliliter of solution.

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{n}{V} = \frac{\text{mmoles of solute}}{\text{mL of solution}} \qquad \text{Molarity } (M) \qquad (2.1)$$
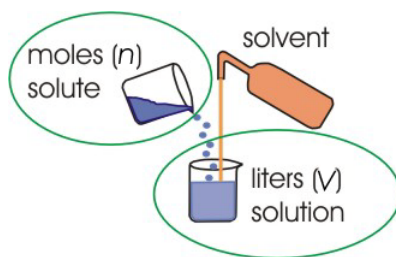

Figure 2.2: Molarity Molarity relates moles of solute to the volume of solution.

The molarity of a solute allows us to convert between the number of moles (or millimoles) of that **solute** and the number of liters (or milliliters) of **solution**.

To determine the number of moles of solute in a given volume of solution, we solve Equation 2.1 for n, the number of moles:

$$n = MV$$

Alternatively, we can use the units of molarity and the factor-label method to determine the number of moles.

$$\frac{M \text{mol solute}}{1 \text{ L solution}} \times V \text{ L of solution} = MV \text{ mol solute}$$

If V is given in milliliters, then MV is millimoles of solute. **We will frequently use millimoles because volumes in a chemistry laboratory are most often given in milliliters.**

We can also solve Equation 2.1 for the volume of solution to determine what volume of solution contains a given number of moles of solute:

$$V = \frac{n}{M}$$

Or, using the factor-label method,

$$n \text{ mol solute} \frac{1 \text{ L solution}}{M \text{ mol solute}} = \frac{n}{M} \text{ L solution}$$

2.1-3. Preparing a Solution of Known Molarity

The denominator of molarity is the volume of the solution, not the volume of solvent. Thus, a solution of known molarity must be made by adjusting the volume after the solute and solvent have been thoroughly mixed. This is done with a volumetric flask of the appropriate volume (Figure 2.3) as follows.
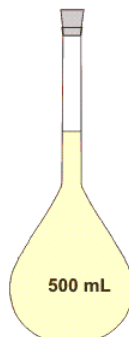

Figure 2.3: A 500-mL Volumetric Flask

1 Select a volumetric flask of the appropriate volume and determine the amount of solute that will be required. The flask in Figure 2.3 would be used to prepare 500 mL of solution.

2 Add solvent to the volumetric flask until it is about half full.

3 Add the required amount of solute and swirl the mixture until the solute has dissolved

4 Add solvent to the flask up to the fill line of the flask.

5 Invert the flask several times to assure homogeneity.

2.1-4. Preparing a Solution Exercise

EXERCISE 2.1:

How many mmoles of K_2HPO_4 are required to prepare 350. mL of 0.0865 M K_2HPO_4?

_____ mmol

How many grams of K_2HPO_4 (M_m = 174.17 g/mol) must be dissolved to make the solution?

_____ g

Molarity is the number of moles of solute per liter of **solution** not solvent, so the K_2HPO_4 would be dissolved in less than 350 mL of water ($\sim$250 mL). Water would then be added to adjust the volume of the resulting solution to 350 mL.

How many milliliters of the 0.0865 M solution of K_2HPO_4 are required to deliver 3.50 mmoles of K^{1+} ions?

V = _____ mL

2.1-5. Molarity to Solute Mass Exercise

EXERCISE 2.2:

Ocean water is typically 0.53 M in chloride ion. How many grams of chloride ion are contained in 500. mL of ocean water?

mass = _____ g Cl^{1-}

2.1-6. Molarity of Ions Exercise

EXERCISE 2.3:

$Ba(OH)_2$ is a strong electrolyte. What are the ion concentrations in a solution prepared by dissolving 0.210 g of $Ba(OH)_2$ in enough water to make 450. mL of solution?

The molarity of the $Ba(OH)_2$ solution is: _____ M

The ion concentrations are:

$[OH^{1-}] =$ _____ M

$[Ba^{2+}] =$ _____ M

The number of millimoles of OH^{1-} in 275 mL of solution is: _____ mmol

The number of milliliters of solution required to deliver 0.300 mmol of Ba^{2+} is: _____ mL

2.1-7. Common Prefixes

1 M solutions are considered fairly concentrated, and most of the solutions encountered in the chemistry laboratory are much less concentrated. Indeed, some processes require only very dilute concentrations. For example, the maximum allowed level of mercury in drinking water is 0.000002 M, and a testosterone level of only 0.00000001 M initiates puberty in human males. Prefixes are used to avoid the preceding zeros or exponents when expressing these very dilute solutions.

Unit	Symbol	Value	
millimolar	mM	10^{-3} M	1 mmol·L^{-1}
micromolar	μM	10^{-6} M	1 μmol·L^{-1}
nanomolar	nM	10^{-9} M	1 nmol·L^{-1}

Table 2.1: Common Prefixes

Thus, the maximum allowed level of mercury in drinking water is 2×10^{-6} M = 2 μM, and the testosterone level that initiates puberty is 10×10^{-9} M = 10 nM.

2.1-8. Using Prefixes Exercise

EXERCISE 2.4:

How many micrograms of testosterone ($C_{19}H_{28}O_2$, M_m = 288 g/mol) are in the blood (5.7 liters) of a person if the testosterone concentration is 12.5 nM?

mass = _____ μg testosterone

2.1-9. Mole Fraction (X)

The ***mole fraction*** (X) of a substance in a solution is the number of the moles of that substance divided by the total number of moles of all substances (solutes and solvent) in solution. Because all of the substances comprise the whole mixture, **the sum of all mole fractions (including the solvent) must equal one**; i.e., $\sum_A X_A = 1$.

$$X_A = \frac{n}{n_{\text{tot}}} = \frac{\text{moles of } A \text{ in mixture}}{\text{total moles in mixture}} \qquad \text{Mole Fraction} \qquad (2.2)$$
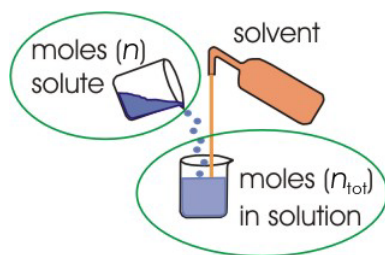

Figure 2.4: Mole Fraction The *mole fraction* of A equals the number of moles of A divided by the total number of moles of substances in the solution.

2.1-10. Mole Fraction Exercise

<u>**EXERCISE 2.5:**</u>

A sample of the alloy known as "yellow brass" is found to be 67.00% Cu and 33.00% Zn by mass. What are the mole fractions of Cu and Zn in the alloy?

Exactly 100 g of alloy contains: The mol fractions are

_____ mol Cu $X_{\text{Cu}} =$ _____

_____ mol Zn $X_{\text{Zn}} =$ _____

_____ mol total in mixture

2.1-11. Mass Fraction (%, ppt, ppm)

The ***mass fraction*** relates the mass of a solute to the mass of the solution. It is commonly used for solutions where the solvent is not clearly defined.

$$\text{mass fraction} = \frac{\text{mass of solute}}{\text{mass of solution}} \qquad \text{Mass Fraction} \qquad (2.3)$$
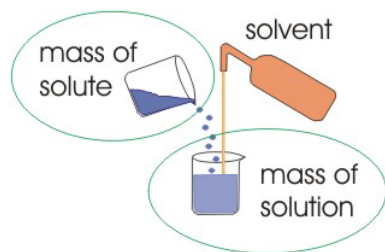

Figure 2.5: Mass Fraction The ***mass fraction*** relates the mass of a solute to the mass of the solution.

2.1-12. Mass Fraction Multipliers

Mass fractions represent a part of the whole, so they are always less than one. Indeed, mass fractions in dilute solutions can be so small that they are multiplied by powers of ten to eliminate the preceding zeros (see Table 2.2). Thus,

- a mass fraction of 0.012 would be reported as $(0.012)(100\%) = 1.2\%$
- a mass fraction of 1.2×10^{-8} would be reported as $(1.2 \times 10^{-8})(10^9 \text{ ppb}) = 12$ ppb.

Name	Multiplier	Useful Units
mass fraction	1	$\dfrac{\text{g } A}{\text{g mixture}}$
mass percent (%)	100	$\dfrac{\text{g } A}{100\text{g mixture}}$
parts per thousand (ppT)	1000	$\dfrac{\text{g } A}{1000\text{g mixture}}$
parts per million (ppm)	10^6	$\dfrac{\text{g } A}{10^6\text{g mixture}}$
parts per billion (ppb)	10^9	$\dfrac{\text{g } A}{10^9\text{g mixture}}$

Table 2.2: Common Multipliers Used with Mass Fraction

2.1-13. Mass Fraction Exercise

EXERCISE 2.6:

A mixture contains 6.0 g N_2, 16.0 g O_2 and 2.0 g He.
What are the mass fraction, mass percent, and mole fraction of each gas?

Mass Fractions

Total mass = _____ g

Mass fraction of N_2 = _____

Mass fraction of O_2 = _____

Mass fraction of He = _____

Mass Percents

Mass percent of N_2 = _____ %

Mass percent of O_2 = _____ %

Mass percent of He = _____ %

Moles

Moles of N_2 = _____ mol

Moles of O_2 = _____ mol

Moles of He = _____ mol

Total moles = _____ mol

Mole Fractions

X_{N_2} = _____

X_{O_2} = _____

X_{He} = _____

2.1-14. Molality (m)

The **molality** (m) of a solute is the number of moles of that solute per kilogram of solvent.

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} \qquad \text{Molality } (m) \qquad (2.4)$$
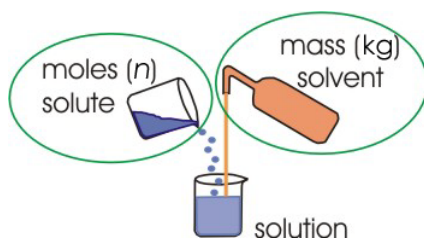

Figure 2.6: Molality Molality relates the moles of solute to the mass of solvent.

The volume of a solution varies with temperature, so the molarity (M) of the solution changes with temperature as well. Thus, molarity (M) is not a good unit of concentration to use in experiments involving temperature change. While volume is temperature dependent, mass is not, so molality (m), which involves no volumes, is commonly used for the concentration of any solution used in experiments that involve measurements resulting from temperature changes.

2.1-15. Molality Exercise

EXERCISE 2.7:

A solution is prepared by mixing 3.75 g of glucose ($C_6H_{12}O_6$, M_m = 180.2 g/mol) and 25.0 g of water. What is the molality of the resulting glucose solution?

moles of glucose in solution

————————— mol $C_6H_{12}O_6$

kilograms of solvent present in solution

————————— kg H_2O

the molality of the solution

————————— m

2.2. Changing Concentrations Units

Introduction

It is sometimes necessary to change the units of concentration. This routine procedure is most often done when the concentration of a stock solution is given in units that are not convenient for a particular experiment. The procedure presented here entails converting the units of the numerator and denominator of the given concentration to those of the desired concentration and then dividing.

Objectives

- Convert between different concentration units.

2.2-1. Converting Concentration Units

To change concentration units, convert the numerator and denominator separately.

All concentrations are ratios of two quantities. The numerator indicates the amount of solute and the denominator the amount of solution or solvent. Use the following steps to convert one concentration unit into another:

1   Convert the given numerator into the numerator of the desired unit.
2   Convert the given denominator into the denominator of the desired unit.
3   Divide the result of step 1 by that of step 2 to obtain the desired concentration unit.

The numerators and denominators of the concentration units that we have dealt with are:

molarity	mass fraction	mole fraction	molality
moles of solute	mass of solute	moles of solute	moles of solute
liters of solution	mass of solution	total moles (all solutes + solvent)	kilograms of **solvent**

To convert between any of the above you need only some combination of the molar masses of solute and/or solvent, and/or the density of the solution.

Conversion	Requires
mol solute $\leftrightarrow$ mass solute	molar mass of the solute
liters solution $\leftrightarrow$ mass solution	density of solution
liters solution $\leftrightarrow$ mol solute + mol solvent	density of solution, molar masses of solute and solvent
liters solution $\leftrightarrow$ kg solvent	solution density, molar mass of solute
mass solution $\leftrightarrow$ mol solute + mol solvent	molar masses of solute and solvent
mass solution $\leftrightarrow$ kg solvent	molar mass of solute
mol solute + mol solvent $\leftrightarrow$ kg solvent	molar masses of solute and solvent

Table 2.3: Converting Concentration Units

2.2-2. Molarity to Mass Percent Exercise

EXERCISE 2.8:

A solution of concentrated sulfuric acid is 18.00 M and has a density of 1.839 g/cm^3. What is the mass percent of H_2SO_4 in the concentrated acid solution? Molar mass of sulfuric acid = 98.08 g/mol.

The given units are molarity, while the desired units are mass fraction, which must be multiplied by 100 to obtain mass percent. Molarity has units of (mol solute)/(L solution), while mass fraction has units of (mass solute)/(mass solution). Thus, we must make the following conversions.
- numerator: 18.00 mol H_2SO_4 yields $\leftrightarrow$ x grams H_2SO_4
- denominator: 1 L solution yields $\leftrightarrow$ y grams solution

Convert the given numerator into the desired numerator.

18.00 mol H_2SO_4 = _____ g H_2SO_4

Convert the denominator of the given concentration units into those of the desired concentration units.

1 L solution = _____ g solution

The mass fraction of H_2SO_4 in the solution = _____

The mass percent of H_2SO_4 in the solution = _____ %

2.2-3. Molarity to Molality Exercise

EXERCISE 2.9:

Concentrated sulfuric acid is 18.00 M and has a density of 1.839 g/cm^3. What is the molality of H_2SO_4 in the concentrated acid solution?

The given units are molarity, while the desired units are molality. Molarity has units of (mol solute)/(L solution), while molality has units of (mol solute)/(kg solvent). Thus, we must make the following conversions:
- numerator: 18.00 mol H_2SO_4 $\rightarrow$ 18.00 mol H_2SO_4
- denominator: 1 L solution $\rightarrow$ y kilograms solvent

The numerators are the same (18.00 mol), so we need only change the denominator and then divide.

1 L solution contains _____ kg solvent

Divide the numerator by the denominator to obtain molality: _____ m

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2.2-4. ppm to Molarity Exercise

EXERCISE 2.10:

What is the molarity of fluoride ion in drinking water that is 7.0 ppm F^{1-}?

The given units are ppm, (grams solute)/(10^6 g solution), while the desired units are molarity, (mol solute)/(L solution). Thus, the following conversions are required.
- numerator: 7.0 g F^{1-} → x mol F^{1-}
- denominator: 10^6 g solution → y liters of solution

Convert the given numerator into the desired numerator.

$$7.0 \text{ g } F^{1-} = \text{_____} \text{ mol } F^{1-}$$

Next, convert the denominator of the given concentration into that of the desired concentration. This solution is very dilute, so you can assume that the density of the solution is the same as the solvent (1.0 g/mL).

$$10^6 \text{ g solution} = \text{_____} \text{ L solution}$$

Finally, divide the two to obtain the desired concentration units.

$$[F^{1-}] = \text{_____} M$$

2.2-5. Mass Percent to Molarity Exercise

EXERCISE 2.11:

What is the molarity of a 30.0% sulfuric acid solution if its density is 1.218 g/mL?
- numerator: 30.0 g H_2SO_4 → x mol H_2SO_4
- denominator: 100 g soln → y L soln

Convert the given numerator into the desired numerator.

$$30.0 \text{ g } H_2SO_4 = \text{_____} \text{ mol } H_2SO_4$$

Next, convert the denominator of the given concentration into that of the desired concentration.

$$100 \text{ g solution} = \text{_____} \text{ L solution}$$

Finally, divide the two to obtain the desired concentration units.

$$[H_2SO_4] = \text{_____} M$$

2.3. Dilutions

Introduction

Stock solutions are often fairly concentrated and must be diluted before they are used. In this section, we show how to make a solution of known volume and molarity from a more concentrated stock solution.

Objectives

- Calculate the concentration of a solution after dilution.
- Prepare a dilute solution of known concentration from a more concentrated solution.

2.3-1. Dilution Lecture

A video or simulation is available online.

2.3-2. Equations of Dilution

The amount of solute does not change with the addition of solvent, so we can write the following:

$$C_i \times V_i = C_f \times V_f \qquad \text{Dilution Equation} \qquad (2.5)$$

where C is any concentration that indicates the amount of solute per unit volume of solution. Therefore, C can be molarity or g/mL, but not molality or mass percent. We solve Equation 2.5 for the final concentration, C_f to obtain the following

$$C_f = C_i \times \frac{V_i}{V_f} \qquad \text{Dilution Factor} \qquad (2.6)$$

where the ratio V_i/V_f is called the **dilution factor**. Thus, the final concentration equals the initial concentration times a dilution factor. If a solution is diluted successively several times, then the final concentration equals the initial concentration times the product of all of the successive dilution factors as shown in Equation 2.7.

$$C_f = C_1 \times \frac{V_1}{V_2} \times \frac{V_3}{V_4} \times \frac{V_5}{V_6} \qquad \text{Successive Dilutions} \qquad (2.7)$$

2.3-3. Molarity after Dilution Exercise

EXERCISE 2.12:

What is the molarity of sulfuric acid in a solution prepared by adding 30.0 mL of 18.0 M H$_2$SO$_4$ to enough water to make 500. mL of solution?

concentration = _____ M H$_2$SO$_4$

2.3-4. Volume Required for Dilution Exercise

EXERCISE 2.13:

How many mL of 18.0 M H$_2$SO$_4$ are required to prepare 300. mL of 1.50 M H$_2$SO$_4$?

volume of 18.0 M H$_2$SO$_4$ = _____ mL H$_2$SO$_4$

2.3-5. Concentration After Successive Dilutions Exercise

EXERCISE 2.14:

Solution A is prepared by diluting 20.0 mL of a stock 0.100 M HCl solution to 50.0 mL. Solution B is prepared by diluting 10.0 mL of solution A to 75.0 mL. Solution C is made by diluting 20.0 mL of solution B to 250.0 mL. What is the concentration of HCl in solution C? Note that the concentration is expressed as millimolar.

[HCl] in solution C = _____ mM

2.3-6. Concentration of Initial Solution Exercise

EXERCISE 2.15:

50.00 mL of an unknown solution A is diluted to 500.00 mL to make solution B. 25.00 mL of solution B is diluted to 750.00 mL to make solution C. 15.00 mL of solution C is diluted to 1000.00 mL. What is the concentration of solution A, if the concentration of the final solution is 1.47 μM?

product of all dilution factors $=$ _____

concentration of solution A $=$ _____ M

2.4. Determining Concentrations

Introduction

Analyzing solutions to determine their concentration is an important part of analytical chemistry. In this section, we discuss two important methods used to carry out such an analysis: spectrometry and titration.

Objectives

- Use a color wheel to determine a complementary color.
- Use Beer's Law to determine the molarity of a solution.
- Determine the volume of one reactant that reacts with another reactant of known volume.
- Determine the limiting reactant from a balanced chemical equation and the concentrations and volumes of the reactants.
- Determine the concentrations of the excess reactants.

2.4-1. Complementary Colors

White light is the result of all visible colors. When white light shines on a colored substance, however, some of the colors are absorbed. Those colors that are not absorbed can be either reflected or transmitted to the eye. We perceive this reflected or transmitted portion as the color of the substance. Consequently, the characteristic color of a material is not the color of light that it absorbs; rather it is the mixture of the remaining, unabsorbed colors that are observed. In other words, it appears as its complementary color. The approximate relationship between observed and absorbed colors is summarized in a color wheel as shown in Figure 2.7. For example, a solution appears orange because it absorbs blue light. Thus, when white light shines on the solution, the blue portion of the spectrum is absorbed by the solution, which leaves only the orange portion to be detected by your eyes.
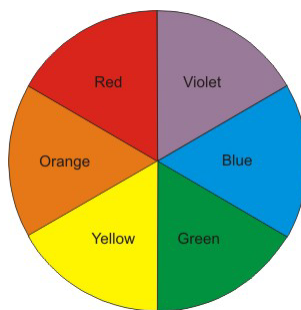

Figure 2.7: Color Wheel Complementary colors are opposite one another in a color wheel, so orange is the complement of blue.

2.4-2. Spectrometry

Spectrometry, measuring the amount of light that a solute absorbs at some wavelength, is a convenient way to determine the concentration of a solute in a solution. The amount of light that is absorbed by the sample is called the **absorbance** (A) of the sample. Consider the experiment shown in Figure 2.8 below. Orange light of intensity I_o

enters the cell, where some of it is absorbed by the blue solution, so the outgoing intensity I, is less than the initial I_o.
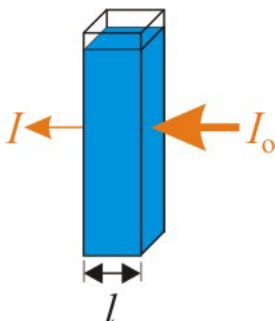

Figure 2.8: Absorbance and Beer's Law Orange light is absorbed by a blue solution. The amount of light that is absorbed by the solution is called the absorbance (A), which is defined as $-\log(I/I_o)$. The absorbance depends upon the concentration of the absorbing substance (c), the distance the light travels through the sample (l), and the molar absorptivity of the solute at the wavelength of the light (ϵ) as given by Beer's law.

The absorbance, which is defined as $A = -\log(I/I_o)$, depends upon three factors:

- how strongly the solute absorbs at the wavelength of light used in the experiment, which is known as the **molar absorptivity** (ϵ, epsilon);
- the concentration of the solute (c); and
- the path length of the light through the solution (l).

The relationship between these factors is given by Beer's Law.

$$A = \epsilon l c \qquad \text{Beer's Law} \tag{2.8}$$

2.4-3. Determining an Unknown Concentration

The following procedure is used to determine an unknown concentration in a solution:

1 Determine a good wavelength of light to use. The light should be absorbed by the solute to be determined, so it should be the complement of the color of the solution. The complement can be found as the color opposite the observed color on a color wheel. The light should not be absorbed by the rest of the solution, but the effect of the rest of the solution can be determined by measuring the absorbance of a blank. The **blank** should mimic the solution to be measured in all aspects except the presence of the solute to be measured. The absorbance of the blank is then subtracted from that of the sample to get a measurement of just the solute's absorbance.

2 Measure the absorbance of a **standard solution**, which is simply a solution in which the concentration of the solute being measured is accurately known. The molar absorptivity of the solute can be determined from the measured absorbance, the known concentration, and the path length of the cell.

3 Measure the absorbance of the sample. The unknown concentration can be determined from the measured absorbance, the molar absorptivity determined in step 2, and the known path length of the cell.

Many solutes absorb very strongly, and the prepared solutions frequently absorb so strongly that too little light passes through the cell. In these cases, the solutions must be diluted before they can be measured. Indeed, it is often the case that they must be diluted several times in order to get a good reading of the absorbance. The following exercise takes you through this process except that no blank is used. Follow the above steps and dilute the samples to obtain the good absorbance readings. Don't forget to take into account your dilutions when doing the calculations.

2.4-4. Determining Concentration Exercise

EXERCISE 2.16:

Determine the concentration of an unknown solution.
A video or simulation is available online.

$\epsilon = $ _____ $M^{-1}\cdot cm^{-1}$ $\qquad\qquad$ $[X] = $ _____ M

2.4-5. Titrations

Spectrometry is an easy way to determine an unknown concentration only if the solute absorbs light at a convenient wavelength (usually one in the visible). The concentration of a solute can also be determined by measuring the stoichiometric amount of a solution of known concentration required to react with the unknown solute. This method is called **titration**. The known solution, whose volume is to be determined, is called the **titrant**, while the solute being analyzed is the **analyte**. The point at which the titrant and analyte are in stoichiometric amounts is called the **equivalence point**. The equivalence point is usually approximated by an **end point**, which is the point at which an indicator undergoes a color change.
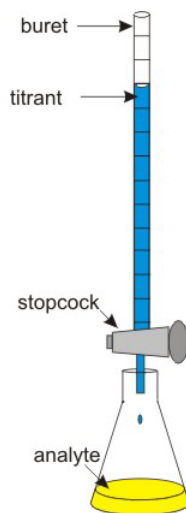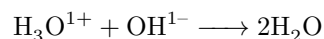

Figure 2.9: Titration Apparatus

2.4-6. Titration Method

Acid-base titrations are very common in the chemistry lab. The net chemical equation for the reaction of a strong acid and a strong base is:

$$H_3O^{1+} + OH^{1-} \longrightarrow 2H_2O$$

The above chemical equation shows that the reactants react in a 1:1 ratio, so the equivalence point is reached when the number of (milli)moles of base added equals the number of (milli)moles of acid present initially. However, the number of (milli)moles of a solute equals the volume of solution in (milli)liters times the molarity of the solute. Thus, the equivalence point in an acid base reaction is that point where

$$M_{acid}V_{acid} = M_{base}V_{base} \qquad \text{Acid Base Equivalence Point} \qquad (2.9)$$

If the acid is the unknown, then a known amount of acid, the analyte, would be added to the flask, so V_{acid} would be known. The concentration of the base (M_{base}), the titrant, would also be known and the volume of base required to reach the equivalence point (V_{base}) would be determined by the titration. M_{acid} would then be determined from Equation 2.9.

2.4-7. Titration Exercise

EXERCISE 2.17:

An indicator that changes color at the equivalence point is added to the analyte solution. The procedure is demonstrated in the following example. The indicator in this example turns a light pink at the equivalence point. When the color forms but then fades, you are close to the equivalence point. If the solution turns a dark red, you have passed the equivalence point. If you pass the equivalence point, you can simply add more acid until the color disappears. Be careful not to drain the buret below the bottom mark.

Determine the concentration of the unknown HCl (analyte) solution by titration with a 0.02597 M solution of NaOH (titrant).

A video or simulation is available online.

The molarity of the unknown acid is _____ M

2.4-8. Precipitation Reactions

Solubility rules can help you determine the precipitate.

The concentration of a solution can also be determined from the amount of precipitate that forms when an excess of another reactant is added. The procedure is the following:

1. Use the solubility rules to decide upon a good reactant.
2. Add an excess of the reactant to a known volume of the solution to be analyzed.
3. Filter the solution to separate the precipitate from the solution. Add more reactant to the remaining solution to be certain no more precipitate forms.
4. Dry and weigh the precipitate then determine the number of moles of precipitate that were produced.
5. Use the results of step 4 to determine the number of moles of the solute that must have reacted.
6. Determine the concentration of the original solution from the number of moles of solute present (step 5) and the original volume.

Rule 1	Compounds of NH_4^{1+} and group 1A metal ions are soluble.
Rule 2	Compounds of NO_3^{1-}, ClO_4^{1-}, ClO_3^{1-} and $C_2H_3O_2^{1-}$ are soluble.
Rule 3	Compounds of Cl^{1-}, Br^{1-}, and I^{1-} are soluble *except* those of Ag^{1+}, Cu^{1+}, Tl^{1+}, Hg_2^{2+},and Pb^{2+}.
Rule 4	Compounds of SO_4^{2-} are soluble *except* those of Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}
Rule 5	*Most* other ionic compounds are insoluble.

Table 2.4: Solubility Rules
Solubility rules for ionic compounds in water.

2.4-9. Precipitation Exercise

EXERCISE 2.18:

What is the concentration of Ag^{1+} ions in a solution if addition of excess PO_4^{3-} ions to 25.00 mL of the solution produced 163.2 mg of Ag_3PO_4 (M_m = 418.6 g/mol)?

The net ionic equation is: $3\ Ag^{1+} + PO_4^{3-} \rightarrow Ag_3PO_4$

The number of millimoles of Ag_3PO_4 produced = _____ mmol

The number of millimoles of Ag^{1+} required = _____ mmol

The concentration of Ag^{1+} in the original solution = _____ M

2.5. Colligative Properties

Introduction

The properties of a solution depend upon the concentrations of the solutes. Indeed, some solution properties depend only upon the concentration of particles in solution and not upon the identity of those particles. These properties are called ***colligative properties***. In this section, we discuss the following colligative properties.
- vapor pressure
- boiling point
- freezing point
- osmotic pressure

Objectives

- Determine the van't Hoff factor (i) for a compound.
- Convert a molarity or molality into a colligative molarity or colligative molality.
- Calculate the boiling point and melting point of a solution given its colligative molality and the boiling elevation and freezing point depression constants.
- Describe the causes of vapor pressure lowering at the molecular level.
- Calculate the vapor pressure of a solution given the mole fraction of the solute and the vapor pressure of the solvent.
- Describe osmosis at the molecular level.
- Determine the osmotic pressure of a solution of known concentration.
- Explain why osmosis is important.

2.5-1. van't Hoff Factor and Colligative Concentrations

Colligative properties depend upon the concentration of **particles** in solution, which is different than the solute concentration when the solute is ionic and dissociates in water. The solution concentration is converted to a concentration of particles with the ***van't Hoff factor*** (i), which is the number of moles of particles produced when one mole of solute dissolves. For example, $i = 3$ for $CaCl_2$ because dissolving one mole of $CaCl_2$ produces three moles of ions: $CaCl_2 \rightarrow Ca^{2+} + 2\ Cl^{1-}$.

The total particle concentration is called the colligative concentration. It is equal to the solute concentration times its van't Hoff factor. The following equations define the ***colligative molarity*** and ***colligative molality***.

$$\begin{aligned} M_c &= i \times M \\ m_c &= i \times m \end{aligned} \qquad \text{Colligative Concentrations} \qquad (2.10)$$

2.5-2. van't Hoff Exercise

EXERCISE 2.19:

What is the van't Hoff factor for each of the following?

CaSO$_4$: $i =$ _____   Ba(OH)$_2$: $i =$ _____

CH$_3$OH: $i =$ _____   HCl: $i =$ _____

NH$_4$ClO: $i =$ _____   SF$_4$: $i =$ _____

2.5-3. Colligative Molality Exercise

EXERCISE 2.20:

Determine the colligative molarity of each of the following solutions.

Solution	i	M_c
0.080 M K$_3$PO$_4$		
0.042 M C$_6$H$_{12}$O$_6$		

2.5-4. Phase Diagram

Figure 2.10 shows the phase diagrams of a pure substance and of a solution in which the substance is the solvent. The two diagrams are identical except for the region in blue, which is either a solid or gas in the pure substance but is all liquid in the solvent. Thus, the phase diagram of the solvent differs from that of the pure substance in three ways:

- The vapor pressure is lowered by ΔP at every temperature.
- The boiling point is elevated (raised) by ΔT_b.
- The freezing point is depressed (lowered) by ΔT_f.

The impact of these three effects is to increase the temperature-pressure range of the liquid state. The amount by which the liquid state is extended (shown in blue in the figure) depends only on the concentration of the solute particles, so freezing point depression, boiling point elevation, and vapor pressure lowering are all colligative properties, and we now examine the relationship between particle concentrations and their effect on each of these colligative properties. We then define a fourth colligative property, the osmotic pressure.
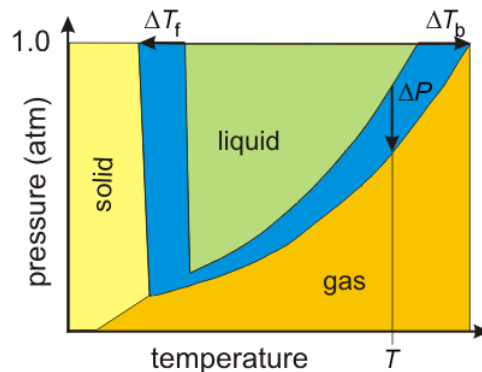

Figure 2.10: Phase diagrams of a solvent and a solution of the solvent. The solvent is liquid only in the green region, while the solution is liquid in both the green and blue regions; i.e., the blue region shows the extent to which the liquid state is expanded due to the presence of the solute particles.

2.5-5. Vapor Pressure Lowering

The vapor pressure of a solution is less than that of the pure solvent.

The liquid $\rightleftharpoons$ vapor equilibrium is a dynamic equilibrium that is established when the rate of evaporation equals the rate of condensation. The pressure of the vapor in equilibrium with the liquid at a given temperature is the vapor pressure of the liquid at that temperature. Evaporation occurs from the surface of the liquid, so the rate of evaporation depends upon the concentration of particles at the surface. Figure 2.11 compares a pure solvent with a solution in which the mole fraction of a nonvolatile solute is 0.2. A solute mole fraction of 0.2 means that 20% of the particles in solution are solute particles, so 20% of the sites on the surface are occupied by nonvolatile solute particles. Consequently, evaporation can occur from only 80% of the surface sites, which results in a 20% reduction in the rate of evaporation, which in turn, causes a 20% reduction in the vapor pressure. We conclude that ΔP, the amount by which the vapor pressure of the solvent at some temperature is lowered by the addition of a solute with a mole fraction of X_{solute}, is

$$\Delta P = X_{\text{solute}} P^{\circ}_{\text{solvent}} \qquad \text{Vapor Pressure Lowering of a Solvent} \qquad (2.11)$$

ΔP is the vapor pressure lowering; it is always positive because the vapor pressure of a solution is always lower than that of the pure solvent. P° is the vapor pressure of the pure solvent at the temperature under consideration. The vapor pressure of the solution is lower than that of the solvent by ΔP, so $P = P^{\circ} - \Delta P = P^{\circ} - X_{\text{solute}} P^{\circ} = (1 - X_{\text{solute}}) P^{\circ}$. However, $1 - X_{\text{solute}} = X_{\text{solvent}}$, so we can rewrite Equation 2.11 as

$$P_{\text{soln}} = X_{\text{solvent}} P^{\circ}_{\text{solvent}} \qquad \text{Vapor Pressure of a Solution} \qquad (2.12)$$

The above indicates that the vapor pressure of a solution is equal to the vapor pressure of the pure solvent times the fraction of the surface sites occupied by the solvent; i.e., the mole fraction of the solvent.
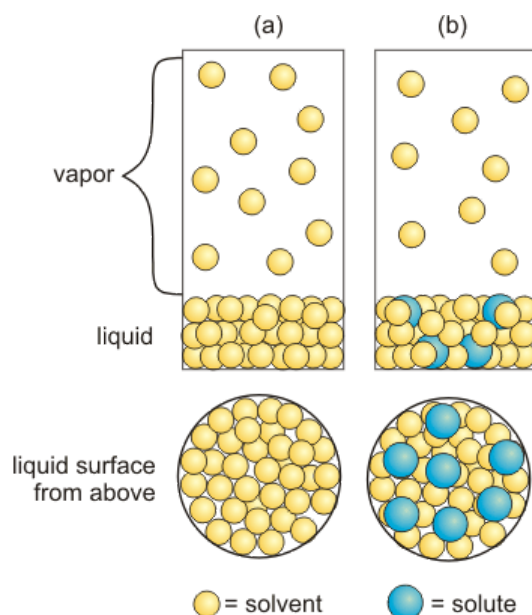

Figure 2.11: Vapor Pressure Lowering (a) Solvent: All of the surface sites are occupied by solvent molecules, which produces ten molecules in the vapor. (b) Solution: The mole fraction of the solute in the solution is ~0.2, so nonvolatile solute particles (blue spheres) occupy ~20% of the surface sites, which reduces the vapor pressure by ~20% as shown by the presence of only eight molecules in the vapor.

2.5-6. Vapor Pressure of Water

We will have made frequent use of the vapor pressure of water. The vapor pressure at 5 °C increments can be found in Table 2.5 and in the Resources.

T (°C)	$P°$ (torr)	T (°C)	$P°$ (torr)
0	4.6	50	92.5
5	6.5	55	118.0
10	9.2	60	149.9
15	12.8	65	187.5
20	17.5	70	233.7
25	23.8	75	289.1
30	31.8	80	355.1
35	41.2	85	433.6
40	55.3	90	525.8
45	71.9	95	633.9

Table 2.5: Vapor Pressure of Water at Selected Temperatures

2.5-7. Vapor Pressure Lowering Exercise

EXERCISE 2.21:

What is the vapor pressure at 25 °C of a solution prepared by dissolving 10.0 g NaCl in 100. g of water?

1. moles of NaCl in solution: _____

2. moles of solute particles in solution: _____

3. moles of solvent particles in solution: _____

4. moles of solute and solvent particles in solution: _____

5. mole fraction of solvent: _____

6. vapor pressure of solvent at 25 °C (see Table 2.5): _____ torr

7. vapor pressure of solution at 25 °C: _____ torr

2.5-8. Boiling Point Elevation

The normal boiling point of a liquid is the temperature at which its vapor pressure is 1 atm. Although this is the definition of the normal boiling point, it is common to refer to it as simply the boiling point. The boiling point of water is 100 °C, so its vapor pressure at 100 °C is 1 atm, but the vapor pressure of an aqueous solution is less than 1 atm at 100 °C due to vapor pressure lowering. Consequently, an aqueous solution must be heated to a higher temperature to achieve a vapor pressure of 1 atm, so the boiling point of an aqueous solution is always higher than that of pure water. This reasoning can be applied to any solution, so we conclude that the boiling point of a solution is always higher than the boiling point of the pure solvent. The amount by which the boiling point of the solvent is increased by the addition of a nonvolatile solute is known as the **boiling point elevation**, ΔT_b, which can be determined from the following equation:

$$\Delta T_b = k_b m_c = i k_b m \qquad \text{Boiling Point Elevation} \qquad (2.13)$$

k_b is the boiling point elevation constant, which has units of °C·m^{-1} and depends on the solvent, and m_c is the colligative molality of the solute. ΔT_b is the amount by which the boiling point of the solvent ($T_b°$) is raised, so the boiling point of the solution (T_b) is given as

$$T_b = T_b° + \Delta T_b$$

2.5-9. Freezing Point Depression

Spreading salt on icy streets and sidewalks melts the ice because solute particles reduce the freezing point of a solvent in much the same way as they reduce its vapor pressure. That is, solute particles block sites on the solid where solvent molecules might otherwise freeze, thereby reducing the rate of freezing. The amount by which the freezing point is lowered is called the ***freezing point depression***, ΔT_f, and is shown in Equation 2.14:

$$\Delta T_f = k_f m_c = i k_f m \qquad \text{Freezing Point Depression} \qquad (2.14)$$

k_f is the freezing point depression constant, which has units of °C·m^{-1} and depends on the solvent, and m_c is the colligative molality of the solute.

ΔT_f is the amount by which the freezing point of the solvent (T_f° is lowered, so the freezing point of the solution (T_f) is given as

$$T_f = \Delta T_f^\circ - \Delta T_f$$

2.5-10. Solvent Constants

The solvent constants relevant for colligative properties are shown in Table 2.6 and in the Resources.

Solvent	Freezing Point (°C)	k_f(°C · m^{-1})	Boiling Point (°C)	k_b(°C · m^{-1})
Acetic acid	16.6	3.90	117.9	3.07
Benzene	5.5	4.90	80.1	2.53
Chloroform	−63.5	4.70	61.7	3.63
Cyclohexane	6.6	20.0	80.7	2.79
Ethanol	−117.3	1.99	78.5	1.22
para-Xylene	11.3	4.30		
Water	0.0	1.86	100.0	0.512

Table 2.6: Freezing Point Depression and Boiling Point Elevation Data for Some Solvents

2.5-11. Antifreeze Exercise

EXERCISE 2.22:

Antifreeze is ethylene glycol ($C_2H_6O_2$, M_m = 62.1 g/mol, d = 1.11 g/mL). What are the boiling and freezing points of an aqueous solution that is 50.% ethylene glycol by volume? Assume a density of 1.0 g/mL for water.

First, we determine the molality of the solution by assuming that water is the solvent and ethylene glycol is the solute. Thus, we need the number of kg of water and the number of moles of $C_2H_6O_2$. To determine the amounts, we must first choose an amount of solution. The easiest amount is exactly 1 L of solution.

The mass of H_2O in 1 L of solution = _____ kg

The number of moles of $C_2H_6O_2$ in 1 L of solution = _____ mol

The molality of $C_2H_6O_2$ = _____ m

The van't Hoff factor for $C_2H_6O_2$ = _____

The colligative molality of the solution = _____ m

Use Table 2.6 to determine the following for water.

    1. freezing point = _____ °C

    2. boiling point = _____ °C

    3. freezing point depression constant = _____ °C/m

    4. boiling point elevation constant = _____ °C/m

The freezing point depression of the solution = _____ °C

The boiling point elevation of the solution = _____ °C

The freezing point of the solution = _____ °C

The boiling point of the solution = _____ °C

2.5-12. Salt Exercise

EXERCISE 2.23:

The salt that is commonly used to melt ice on roads and sidewalks is $CaCl_2$ (M_m = 111 g/mol). Consider a solution prepared by dissolving 62.3 g $CaCl_2$ in 100. g of water.

molality of $CaCl_2$ = _____ m

colligative molality of the solution = _____ m

freezing point of the solution = _____ °C

boiling point of the solution = _____ °C

mole fraction of solvent = _____

vapor pressure of solvent at 20 °C = _____ torr

vapor pressure of solution at 20 °C = _____ torr

2.5-13. Molar Mass from Freezing Point Exercise

EXERCISE 2.24:

A common laboratory in general chemistry is the determination of a molar mass from the freezing point depression that it causes. In this example, we outline the procedure.

1.00 g of a non-dissociating solute is dissolved in 10.0 g of *para*-xylene. What is the molar mass of the solute, if the freezing point of the solution was 1.95 °C lower than that of the pure solvent? $k_f = 4.30$ °C/m for *para*-xylene.

Use Equation 2.14 to determine the molality of the solution: _____ m

Use the molality and the mass of the solvent to determine the number of moles of solute in the solution: _____ mol

Use the mass and number of moles of the solute to determine its molar mass: _____ g/mol

---

2.5-14. Osmosis

Solvent molecules flow through a semipermeable membrane *from dilute* solutions to concentrated solutions.

A semipermeable membrane allows solvent molecules to pass through but denies passage of solute particles. The rate of passage of solvent molecules through the membrane is proportional to the concentration of the solvent molecules, so the rate is greater for a pure solvent than for a solution. When a solvent and a solution are separated by a semipermeable membrane, more solvent molecules move from the solvent to the solution than in the reverse direction. The net movement of the solvent molecules through the membrane from the solvent or a more dilute solution into a more concentrated one is called ***osmosis***.
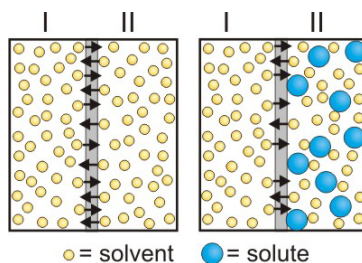

Figure 2.12: Osmosis (a) Rate of movement through the membrane is the same in both directions because the solvent concentration is the same on both sides. (b) A solute is added to side II, so the concentration of solvent is less in side II than in side I. Consequently, the rate of solvent motion I → II is greater than II → I.

2.5-15. Osmotic Pressure

Osmotic pressure depends on colligative *molarity*.

Osmosis of the solvent through the membrane from a solvent to a solution decreases the concentration of particles in the solution, but it also increases its volume while decreasing the volume of the solvent. These volume changes result in a height difference in the two columns as represented by h in Figure 2.13. The height difference results in a pressure differential at the membrane that increases the flow of solvent molecules from the solution side. Eventually, the combination of the increased pressure coupled with the decrease in concentration of the solute particles increases the flow of solvent particles from the solution back into the solvent to the point where the flow of solvent molecules through the membrane is the same in both directions. The pressure at which equilibrium is attained is called the osmotic pressure (Π) of the solution. The osmotic pressure that is developed is given in Equation 2.15

$$\Pi = M_c \times R \times T = i \times M \times R \times T \qquad \text{Osmotic Pressure} \qquad (2.15)$$

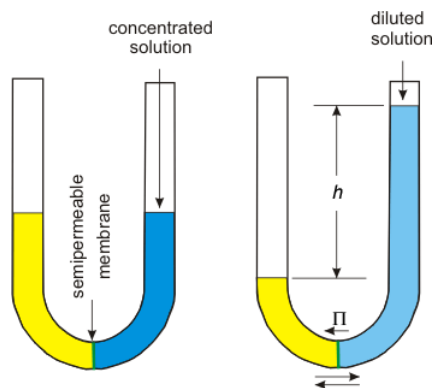where R is the ideal gas law constant ($R = 0.0821$ L·atm/K·mol).

Figure 2.13: Osmotic Pressure Solvent molecules penetrate the semipermeable membrane, but solute molecules do not. Thus, there is a net flow of water molecules into the side with more solute.

A video or simulation is available online.

2.5-16. Osmotic Pressure of Sea Water Exercise

EXERCISE 2.25:

What is the osmotic pressure developed by seawater at 25 °C. Assume that seawater is a 0.53 M solution of NaCl.

$\Pi = $ _____ atm

2.5-17. Molar Mass from Osmotic Pressure Exercise

EXERCISE 2.26:

1.00 L of an aqueous solution containing 0.40 g of a peptide has an osmotic pressure of 3.74 torr at 27 °C. What is the molar mass of the peptide?

$\Pi = $ _____ atm

molar concentration of the peptide $=$ _____ M

number of moles of peptide in the solution $=$ _____ mol

molar mass of peptide $=$ _____ g/mol

2.5-18. Applications of Osmosis

Purification: Solvents can be purified by a process called reverse osmosis. If a pressure that exceeds the osmotic pressure is applied to a solution, solvent can be forced from the solution into the pure solvent. This process has been used to purify seawater in the Middle East. The challenge to purifying seawater lies in finding membranes that can withstand the large pressure (over 26 atm) required.

Biology: Cell membranes are semipermeable. When the solution around a cell has the same colligative concentration as within the cell, the cell maintains its size. However, if the cell is placed in water, water passes into the cell and can rupture it. Placing the cell in a solution with a greater colligative molarity causes water to leave the cell. This is why drinking seawater does not quench your thirst.

Water transport in plants: Water enters a tree through the membranes in the roots, but it evaporates from the leaves resulting in a substantial concentration difference between the roots and leaves. The large concentration difference can develop osmotic pressures of up to ~20 atm in tall trees.

2.6. Colloids

Introduction

Sometimes, rather than dissolving, one material will be suspended as small aggregates in another. Thus, sand will stay suspended in water as long as the water is stirred; but soon after the stirring has stopped, the sand settles to the bottom of the container. Because these mixtures do not meet the rigorous criterion of a solution, they are called dispersions or suspensions.

Objectives

- Identify common colloidal suspensions.

2.6-1. Types of Colloids

Suspensions in which the particle size is very small (1 nm to 1 μm) are called colloidal suspensions or simply **colloids**. White paint is a colloidal suspension of SiO_2 and TiO_2 particles, which are used to make the paint opaque and white, respectively. Colloidal suspensions, which can be stable (will not settle) for years, are classified according to their composition. Whipped cream is a foam: a gas suspended in a liquid. Jellies and starch solutions are **sols**: solids suspended in a liquid. Milk is an **emulsion**: a liquid suspended in a liquid. **Aerosols** can be liquids suspended in a gas (hair sprays) or solids suspended in a gas (smoke). Fog is also an aerosol (water in air) and smog, the combination of smoke and fog, is also a colloidal suspension.

2.7. Exercises and Solutions

Select the links to view either the end-of-chapter exercises or the solutions to the odd exercises.