2.0 INTRODUCTION

A solution is a homogeneous mixture of at least two chemical substances: a single solvent in which at least one solute has been dissolved. The maximum concentration that a solute can attain in a given solvent at some temperature is known as the solubility of the solute in that solvent at that temperature. A solution is said to be saturated if the concentration of the solute equals its solubility.

There are no restrictions on the nature of the solvent, but the solute particles are considered to be dispersed in the solvent, so if there is a liquid present, it is considered the solvent. If more than one liquid is present, the liquid present in the greater amount is considered to be the solvent, but water is such a common solvent that it is usually considered to be the solvent if it is present in a substantial amount even if it is not present in the greatest amount.

Solutions in which water is the solvent are called aqueous solutions. Solutes in aqueous solutions can be classified as either electrolytes or nonelectrolytes. Electrolytes are species that produce ions in solution. They can be further classified as weak or strong. Substances that exist in water exclusively as ions are called strong electrolytes. Ionic substances and strong acids and bases are strong electrolytes. Weak electrolytes exist predominantly in the molecular form in water, but a small fraction also exists as ions. Weak acids and weak bases are weak electrolytes. Nonelectrolytes produce no ions when they dissolve in water. Sugars and alcohols are examples of nonelectrolytes.

While liquid solutions are most common, solutions of solids and gases are also abundant. For example, our atmosphere is a solution of gases (N₂, O₂, Ar, and others). Stainless steel is a solid solution of iron with small amounts of manganese and carbon dissolved in it. The resulting solid solution is stronger and more corrosion resistant than the iron (solvent) alone. Solder is a solid solution of tin and lead with a melting point that is much lower than that of either metal.
THE OBJECTIVES OF THIS CHAPTER ARE TO SHOW YOU HOW TO:

- determine and express the concentration of a solution in common concentration units;
- calculate the amount of solute present in a given volume of sample of known concentration;
- prepare solutions of known concentrations;
- convert from one unit of concentration into another;
- calculate a solution's vapor pressure, boiling and freezing points, and osmotic pressure; and
- apply volume and concentration data to solution stoichiometry.

2.1  CONCENTRATION UNITS

The concentration of a solute, which is the ratio of amount of solute to the amount of solvent or solution, dictates many of the properties of a solution because it is a measure of the relative number of solvent-solvent and solvent-solute interactions. If the ratio is small, the solution is said to be *dilute*, and its properties are similar to those of the solvent because the solution is dominated by solvent-solvent interactions. However, if the ratio is high, the solution is *concentrated*, and the properties can deviate substantially from those of the solvent as the number of solute-solvent interactions becomes important. Dilute solutions may have properties similar to those of the solvent, but the solutes can still have profound effects. Consider that drinking water can provide protection from tooth decay with fluoride ion concentrations of only a few ions for every million water molecules, and it can retard the mental development of children with lead ion concentrations of only a few lead ions in a billion water molecules.

There are many ways of expressing concentration because there are many ways in which it can be determined and used. In this section, we define some of the most common concentration units and give examples of their use.

**MOLARITY (M)**

As shown in Equation 2.1, **molarity** is the number of moles of solute per liter of solution.

\[
M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{n}{V} = \frac{\text{mmoles of solute}}{\text{mL of solution}} \quad \text{Eq. 2.1}
\]

The concentration unit is pronounced ‘molar’ and abbreviated as M. The molar concentration of a substance is normally abbreviated by writing the formula of the substance in square brackets. Thus, \([\text{Cl}^-]\) = 1 M is read “the chloride ion concentration is one molar.” **Molarity is the best unit for concentration for solutions that will be used to deliver a required number of moles of solute.**
It is often more convenient to express the volume in milliliters rather than liters. If the volume in Equation 2.1 is expressed in milliliters, then \( n \) in Equation 2.1 must be in millimoles (mmol).* This is equivalent to multiplying the numerator and the denominator by 1000, an operation that does not change the value of the ratio. Thus, the molarity of a solution is also the number of millimoles of solute per milliliter of solution.

**Example 2.1**

**a)** How would 500.* mL of 0.0865 M \( K_2HPO_4 \) solution be prepared?

Solve Equation 2.1 for \( n \), the number of moles of \( K_2HPO_4 \).

\[
\frac{n}{M} = \frac{V}{L}
\]

\( n = M \times V = (0.0865 \text{ mol/L})(0.500 \text{ L}) = 0.04325 \text{ mol } K_2HPO_4 \)

An extra significant digit is carried in the above. 500. mL of solution must contain 0.04325 mol \( K_2HPO_4 \). The mass of \( K_2HPO_4 \) is determined from the number of moles and its molar mass, 174.17 g·mol\(^{-1}\).

\[
0.04325 \text{ mol } K_2HPO_4 \times \frac{174.17 \text{ g } K_2HPO_4}{1 \text{ mol } K_2HPO_4} = 7.53 \text{ g } K_2HPO_4
\]

The solution would be made by dissolving 7.53 g \( K_2HPO_4 \) in about 300 mL of water in a 500 mL volumetric flask such as is represented in Figure 2.1. Water would then be added to bring the solution to the fill line. Finally, the stopper would be placed in the flask and the flask inverted several times to thoroughly mix the solution.

**b)** What volume of 0.0865 M \( K_2HPO_4 \) contains 3.50 mmoles of \( K^{+} \) ions?

Equation 2.1 is rearranged to solve for the volume in terms of the number of moles of solute and the molarity:

\[
V = \frac{n}{M}
\]

where \( n \) and \( M \) are the number of moles (mmoles in this example) and concentration of the same substance. Thus, the given number of mmoles of \( K^{+} \) ions cannot be divided by the molarity of the \( K_2HPO_4 \). Either the mmoles of \( K^{+} \) ions must be converted to the corresponding number of mmoles of \( K_2HPO_4 \) or the concentration of \( K_2HPO_4 \) must be converted into the molarity of \( K^{+} \) ions. We use the latter method here, but either method will work. The chemical equation for dissolving \( K_2HPO_4 \) in water is \( K_2HPO_4(s) \rightarrow 2K^{+} + HPO_4^{2-} \), so the concentration of \( K^{+} \) ions in 0.0865 M \( K_2HPO_4 \) is

\[
[K^{+}] = \frac{0.0865 \text{ mmol } K_2HPO_4}{1 \text{ mL solution}} \times \frac{2 \text{ mmol } K^{+}}{1 \text{ mmol } K_2HPO_4} = 0.173 \text{ M}
\]

The required volume is

\[
3.50 \text{ mmol } K^{+} \times \frac{1 \text{ mL solution}}{0.173 \text{ mmol } K^{+}} = 20.2 \text{ mL solution}
\]

Thus, 20.2 mL of the solution contains 3.50 mmoles of potassium ion.

---

* The same logic applies to \( \mu L \) and \( nL \), in which the numerator would be in \( \mu \text{mol} \) and \( \text{nmol} \), respectively.

---

* The decimal is used to indicate that the zeroes are significant. See Appendix A for more on significant figures.
Example 2.2

Ocean water is typically 0.53 M in chloride ion. What is the mass of the chloride ion contained in 300 mL of ocean water?

The problem gives the concentration of solute and the volume of solution and asks for the mass of solute. We again use Equation 2.1 to solve for the number of moles of chloride ion. 300 mL = 0.300 L, so

\[ n = M \times V = (0.53 \text{ mol L}^{-1})(0.300 \text{ L}) = 0.16 \text{ mol Cl}^{\text{1-}} \]

Moles of chloride ions are converted to mass by multiplying by the molar mass.

\[ (0.16 \text{ mol Cl}^{\text{1-}})(35.5 \text{ g mol}^{-1}) = 5.6 \text{ g Cl}^{\text{1-}} \]

Solutions with concentrations near one molar are considered to be fairly concentrated. While such concentrated solutions are often used in the laboratory, many applications such as biological signaling require only very dilute solutions. Consider that when the concentration of testosterone in the blood reaches 10^{-8} M, it initiates puberty in human males. The following prefixes are typically used to avoid the exponent in expressions for concentration:

- mM (millimolar) \( \equiv 10^{-3} \text{ M} = 1 \text{ mmol L}^{-1} \)
- \( \mu \text{M} \) (micromolar) \( \equiv 10^{-6} \text{ M} = 1 \mu \text{mol L}^{-1} \)
- \( \text{nM} \) (nanomolar) \( \equiv 10^{-9} \text{ M} = 1 \text{ nmol L}^{-1} \)

Thus, male puberty is initiated when the concentration of testosterone reaches 10 nM. Note that a prefix to a concentration unit indicates a change in the numerator of the ratio of Equation 2.1 but not in the denominator.

Example 2.3

What total mass of testosterone (C_{19}H_{28}O_{2}, M_m = 288 g mol^{-1}) is in 5.7 liters of blood that has a testosterone concentration of 12.5 nM?

Use Equation 2.1 and the fact that 12.5 nM = 12.5 x 10^{-9} M to solve for the moles of testosterone,

\[ n = M \times V = (12.5 \times 10^{-9} \text{ mol L}^{-1})(5.7 \text{ L}) = 7.1 \times 10^{-8} \text{ mol} \]

which is converted to mass by multiplying by the molar mass.

\[ (7.1 \times 10^{-8} \text{ mol})(288 \text{ g mol}^{-1}) = 2.1 \times 10^{-5} \text{ g} = 21 \mu \text{g testosterone} \]

The number of moles determined in the first step, not the rounded answer, was used to avoid rounding errors (see Appendix A.4).
Example 2.4

Express the following concentrations in units such that the magnitude lies between 1 and 100. See the list of SI prefixes inside the back cover.

a) The concentration of CN⁻ ion in 0.1 M HCN is 2.0 x 10⁻⁵ M
   The closest SI prefix that is smaller than 10⁻⁵ is micro. Multiplying the given cyanide ion concentration by 10⁶, we obtain (2.0 x 10⁻⁵ M)(10⁶) = 20 μM.

b) The concentration of Ag⁺ ion in a saturated AgI solution is 9.1 x 10⁻⁹ M
   10⁻⁹ is nano, so the concentration is 9.1 nM.

c) The hydronium ion concentration is 0.026 M
   Multiply by 1000 to convert to the milli prefix. \([H_3O^+] = (0.026 M)(10^3) = 26 mM\)

MOLE FRACTION (X) AND MASS FRACTION

As expressed in Equation 2.2, the mole fraction of substance A (Xₐ) in a mixture is the number of moles A divided by the total number of moles in the mixture.

\[ X_A = \frac{\text{moles of A in mixture}}{\text{total number of moles in mixture}} \quad \text{Eq. 2.2} \]

The sum of the mole fractions of all of the components in the mixture is 1, so \( X_{\text{solvent}} = 1 - X_{\text{solute}} \) in solutions containing a single solute. Although it can be used for liquid solutions, mole fractions are most commonly used for solutions in which the solvent is not clearly defined. Thus, the concentrations of solutions of gases (Practice Example 2.2) and solids (Example 2.5) are frequently given as mole fractions. Mole fractions are moles divided by moles, so they are unitless. However, when they are used in problems, the substances are specified, which makes the numerator and denominator different. Therefore, units of \((\text{moles of A})/(\text{total moles})\) can be used for \(Xₐ\).

The mass fraction of a solute is the mass of the solute divided by the mass of the mixture.

\[ \text{mass fraction of A} = \frac{\text{mass of A in mixture}}{\text{total mass of mixture}} \quad \text{Eq. 2.3} \]

Mass fractions are also unitless, but units of \((\text{mass of A})/(\text{total mass of mixture})\) can be used in problems. Thus, a mass fraction of 0.2 for A can be expressed as \((0.2 \text{ g A})/(1 \text{ g mixture})\). Like molarity, mass fractions can be very small, but prefixes cannot be used for mass fractions because they are unitless. However, mass fractions are the number of parts of solute present in 1 part (the whole) of mixture, so the number used for the mass fraction
can be increased by simply considering the number of parts present in a larger number of parts of mixture. Consequently, small mass fractions are frequently given as the number of parts of solute in some larger number of parts of solvent. This is done by multiplying the mass fraction by the number of parts required to produce a convenient number. The common multipliers, their names, and the units that can be used in problems are given in Table 2.1. For example, a mass fraction can be expressed as a mass percent by multiplying it by 100, so a mass fraction of 0.2 is a mass percent of 20%, which can be expressed as (20 g A)/(100 g mixture). A mass fraction of 2.3x10^{-5} would ordinarily be expressed as 23 ppm to avoid the negative exponent.

Percents in solutions prepared from two or more liquids can also refer to volume percent, which is (volume of A)/(total volume of solution) x 100, rather than a mass percent. To distinguish between the mass and volume percents, the percent can be followed by (w/w) for solute weight/solution weight or (v/v) for solute volume/solution volume.

**Example 2.5**

Matrix alloy is 40.8% Bi, 24.5% Pb, 13.1% Sb, and 21.6% Sn by mass. What are the mole fractions of the elements in the alloy?

First determine the number of moles of each element present in a sample. We are given the mass percents, so we assume a 100.0-g sample, in which case the mass percents equal the masses.

\[
\begin{align*}
40.8 \text{ g Bi} & \times \frac{1 \text{ mol Bi}}{209.0 \text{ g Bi}} = 0.195 \text{ mol Bi}; \\
24.5 \text{ g Pb} & \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} = 0.118 \text{ mol Pb}; \\
13.1 \text{ g Sb} & \times \frac{1 \text{ mol Sb}}{121.8 \text{ g Sb}} = 0.108 \text{ mol Sb}; \\
21.6 \text{ g Sn} & \times \frac{1 \text{ mol Sn}}{118.7 \text{ g Sn}} = 0.182 \text{ mol Sn}
\end{align*}
\]

Determine the total number of moles in 100 g of matrix alloy.

\[
0.195 \text{ mol Bi} + 0.118 \text{ mol Pb} + 0.108 \text{ mol Sb} + 0.182 \text{ mol Sn} = 0.603 \text{ mol}
\]

Calculate the mole fractions with Equation 2.2.

\[
\begin{align*}
X_{\text{Bi}} &= \frac{0.195 \text{ mol Bi}}{0.603 \text{ mol}} = 0.323; \\
X_{\text{Pb}} &= \frac{0.118 \text{ mol Pb}}{0.603 \text{ mol}} = 0.196; \\
X_{\text{Sb}} &= \frac{0.108 \text{ mol Sb}}{0.603 \text{ mol}} = 0.179; \\
X_{\text{Sn}} &= \frac{0.182 \text{ mol Sn}}{0.603 \text{ mol}} = 0.302
\end{align*}
\]

Note that the sum of all mole fractions in the mixture is 1.00. Multiplication of each mole fraction by 100 produces the mole percent. Thus, 32.3% of the atoms in the matrix alloy are bismuth atoms.

**Table 2.1 Common multipliers used with mass fractions**

<table>
<thead>
<tr>
<th>Name</th>
<th>Multiplier</th>
<th>Useful Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass fraction</td>
<td>1</td>
<td>g A/g mixture</td>
</tr>
<tr>
<td>mass percent</td>
<td>100</td>
<td>g A/100 g mixture</td>
</tr>
<tr>
<td>parts per million (ppm)</td>
<td>10^6</td>
<td>g A/10^6 g mixture</td>
</tr>
<tr>
<td>parts per billion (ppb)</td>
<td>10^9</td>
<td>g A/10^9 g mixture</td>
</tr>
</tbody>
</table>

**PRACTICE EXAMPLE 2.2**

A mixture contains 6.0 g N₂, 16.0 g O₂ and 2.0 g He. What is the mole fraction of each gas?

\[
\begin{align*}
\text{Moles of N}_2 &= \frac{6.0 \text{ g N}_2}{28.01 \text{ g/mol}} = \text{_______mol} \\
\text{Moles of O}_2 &= \frac{16.0 \text{ g O}_2}{32.00 \text{ g/mol}} = \text{_______mol} \\
\text{Moles of He} &= \frac{2.0 \text{ g He}}{4.00 \text{ g/mol}} = \text{_______mol} \\
\text{Total} &= \text{_______ mol}
\end{align*}
\]

\[
\begin{align*}
X_{\text{N}_2} &= \frac{\text{_______mol}}{\text{_______ mol}} = \text{_______} \\
X_{\text{O}_2} &= \frac{\text{_______mol}}{\text{_______ mol}} = \text{_______} \\
X_{\text{He}} &= \frac{\text{_______mol}}{\text{_______ mol}} = \text{_______}
\end{align*}
\]
EXAMPLE 2.6
What is the mass fraction of sulfate ion in drinking water if 1.24 kg of the water is found to contain 68.6 mg of sulfate ion?
The mass fraction of sulfate ion equals its mass divided by the mass of the solution. However, both masses must have the same units, so we convert both to grams.

\[
\text{mass fraction} = \frac{0.0686 \text{ g SO}_4^{2-}}{1.24 \times 10^3 \text{ g solution}} = 5.53 \times 10^{-5}
\]

The fraction is the number of parts of sulfate per one part of solution. In order to arrive at a more convenient number, we multiply the answer by 10^6 to obtain ppm.

\[
(5.53 \times 10^{-5})(10^6 \text{ ppm}) = 55.3 \text{ ppm}
\]

Example 2.7
A 0.40-L glass of very sweet iced tea contains 3 heaping teaspoons of sugar. Assume that the density of the iced tea is ~1.0 g/mL and that a heaping teaspoon of sugar has a mass of 8.0 g to calculate the mass percent of sugar in the tea.

First calculate the mass of three teaspoons of sugar.

\[
(3 \text{ tsp})(8.0 \text{ g tsp}^{-1}) = 24 \text{ g sugar}
\]

Next, use the density of the iced tea to calculate the mass of the solution.

\[
(4.0 \times 10^2 \text{ mL})(1.0 \text{ g mL}^{-1}) = 4.0 \times 10^2 \text{ g solution}
\]

The composition of the solution expressed as a mass percent is

\[
\frac{24 \text{ g sugar}}{4.0 \times 10^2 \text{ g sol'n}} \times 100% = 6.0% \text{ sugar}
\]

Example 2.8
What mass of NaF must be dissolved in 250. mL of deionized water to produce a solution that is 7.0 ppm F^−, a level comparable to that in drinking water?
The density of water is 1.0 g mL\(^{-1}\), so the mass of water is 250. g. At such dilute levels, the mass of NaF is negligible compared to the mass of the solvent, so the mass of the solution is also 250. g. Use the concentration of 7.0 ppm to convert the total mass to the mass of fluoride ion present.

\[
250. \text{ g sol'n} \times \frac{7.0 \text{ g } F^-}{10^6 \text{ g sol'n}} \times \frac{1000 \text{ mg}}{g} = 1.75 \text{ mg } F^- \text{ ion}
\]

PRACTICE EXAMPLE 2.3
Determine the mass fractions of the solutes in the following solutions. Express each fraction as a mass percent, ppm, or ppb such that your answer is between 1 and 1,000.

a) 1.0 kg of solution contains 200. g of solute.

mass fraction =
answer = _______________

b) 3.0 mg of solute is dissolved in 1.0 kg of water

mass fraction =
answer = _______________

c) 65 μg of solute is dissolved 2.6 kg of water

mass fraction =
answer = _______________

PRACTICE EXAMPLE 2.4
The solubility of AgCN in water at 25 °C is 1.1x10\(^{-8}\) M. What is the Ag\(^{1+}\) ion concentration expressed in ppb in a saturated AgCN solution?

Determine masses present in 1.0 L of solution

\[
\text{Ag}\text{^1+} = \text{______________} \text{ g}
\]

\[
\text{Solution} = \text{______________} \text{ g}
\]

Then determine their ratio

\[
\text{mass fraction} = \text{______________}
\]

\[
\text{mass fraction in ppb} = \text{______________}
\]
The mass of NaF ($M_m = 42.0 \text{ g mol}^{-1}$) is then determined to be

$$1.75 \text{ mg F}^{1-} \text{ ion} \times \frac{1 \text{ mmol F}^{1-}}{19.0 \text{ mg F}^{1-}} \times \frac{1 \text{ mmol NaF}}{1 \text{ mmol F}^{1-}} \times \frac{42.0 \text{ mg NaF}}{1 \text{ mmol NaF}} = 3.9 \text{ mg NaF}$$

**MOLALITY (m)**

Molality ($m$) is the number of moles of solute in a kilogram of solvent,

$$m = \frac{\text{moles of solute}}{\text{kg of solvent}} \quad \text{Eq. 2.4}$$

A solution that has a concentration of 1 m is said to be "one molal". Neither mass nor moles depends upon the temperature, so molality is temperature independent. However, the volume of a solution does depend upon the temperature, so the molarity of a solution does depend upon the temperature. Consequently, molality is commonly used in applications involving changes in temperature.

**Example 2.9**

A solution is prepared by mixing 3.75 g of the sugar glucose, $C_6H_{12}O_6$, and 25.0 g of water. What is the molality of the resulting glucose solution?

First, determine the number of moles of glucose and the number of kilograms of water, then use Equation 2.2 to determine the molality of the solution.

$$3.75 \text{ g } C_6H_{12}O_6 \times \frac{1 \text{ mol } C_6H_{12}O_6}{180. \text{ g } C_6H_{12}O_6} = 0.0208 \text{ mol } C_6H_{12}O_6$$

$$25.0 \text{ g } H_2O \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0250 \text{ kg } H_2O$$

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}} = \frac{0.0208 \text{ mol } C_6H_{12}O_6}{0.0250 \text{ kg } H_2O} = 0.832 \text{ m}$$

**Example 2.10**

How many grams of ethanol ($C_2H_5OH$) must be added to 29.3 g of water to prepare a 1.22 m solution?

Rearrange Equation 2.4 to solve for moles of solute (ethanol):

$$\text{moles ethanol} = (\text{molality})(\text{kg water}) = (1.22 \text{ m})(0.0293 \text{ kg}) = 0.0357 \text{ mol ethanol}$$

Multiply moles by molar mass to obtain the mass of ethanol.

$$(0.0357 \text{ mol})(46.07 \text{ g mol}^{-1}) = 1.65 \text{ g ethanol}$$

**PRACTICE EXAMPLE 2.5**

How many grams of water should be added to 23.7 g of ethylene glycol ($C_2H_6O_2$, $M_m = 62.1 \text{ g mol}^{-1}$) to make a solution that is 4.85 m in ethylene glycol?

$$\text{moles ethylene glycol used} = \text{______________ mol}$$

$$\text{mass of water required} = \text{______________ g}$$
2.2 CHANGING CONCENTRATION UNITS

Changing concentration units is a task that must be performed routinely in the chemistry laboratory because concentrations of stock solutions are frequently not the most useful for the experiment in which the solution is to be used. The easiest way to accomplish a conversion is to convert the numerator and denominator independently. The numerator is always moles or mass of solute, so conversion of the given numerator to the desired numerator can be accomplished with the molar mass of the solute. Converting the given denominator into the desired denominator is often more challenging because the denominator can represent either solution or solvent and mass or volume. Examples 2.11 - 2.13 and Practice Example 2.6 demonstrate three of the more common concentration unit conversions.

Example 2.11

Concentrated sulfuric acid is 18.0 M and has a density of 1.839 g·cm⁻³. What percent of the mass of this aqueous solution is due to H₂SO₄?

We are asked to convert molarity to mass percent.

\[
\frac{18.0 \text{ mol H}_2\text{SO}_4}{1 \text{ L soln}} \Rightarrow \frac{\text{g H}_2\text{SO}_4}{\text{g soln}} \times 100\%
\]

Once the problem is set up as above, it is much easier to see how to proceed.

1. Convert 18.0 mol H₂SO₄ to grams H₂SO₄ (Mₘ = 98.1 g·mol⁻¹).

\[
18.0 \text{ mol H}_2\text{SO}_4 \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \text{ mol H}_2\text{SO}_4} = 1.766 \times 10^3 \text{ g H}_2\text{SO}_4
\]

Note that extra figures have been kept to avoid rounding errors in the answer.

2. Convert 1 liter of solution to grams of solution using the solution density.

\[
\frac{1000 \text{ mL soln}}{\text{mL soln}} \times \frac{1.839 \text{ g soln}}{\text{mL soln}} = 1.839 \times 10^3 \text{ g soln}
\]

3. Take the ratio to obtain the percent by mass, which must be reported to three significant figures because the mass is good to only 3 significant figures.

\[
\frac{1.766 \times 10^3 \text{ g H}_2\text{SO}_4}{1.839 \times 10^3 \text{ g soln}} \times 100\% = 96.0\%
\]

Only 4.0% of the mass is due to water, which is inconsistent with our definition of the solvent as the material present in the greater amount. However, H₂SO₄ is made by dissolving SO₃ in water (SO₃ + H₂O → H₂SO₄). The reaction is extensive and consumes much of the water.

PRACTICE EXAMPLE 2.6

A 30.0% (w/w) solution of sulfuric acid has a density of 1.218 g·mL⁻¹. Recall that w/w is used to indicate that it is a mass (weight) percent.

What is the mole fraction of H₂SO₄?

Masses in a liter of solution:

\[
\text{=} \quad \text{g soln}
\]

\[
\text{=} \quad \text{g H}_2\text{SO}_4
\]

\[
\text{=} \quad \text{g H}_2\text{O}
\]

Moles in a liter of solution:

\[
\text{=} \quad \text{mol H}_2\text{SO}_4
\]

\[
\text{=} \quad \text{mol H}_2\text{O}
\]

\[
\text{n}_{\text{total}} = \text{mol}
\]

Mole fractions:

\[
X_{\text{H}_2\text{SO}_4} = \quad \text{=} \quad \text{=}
\]

\[
X_{\text{H}_2\text{O}} = \quad \text{=} \quad \text{=}
\]

What is the molarity of the H₂SO₄?

\[
\text{=} \quad \text{M}
\]

What is the molality of the H₂SO₄?

\[
\text{=} \quad \text{m}
\]
Example 2.12

What is the molality of the sulfuric acid solution discussed in Example 2.11?

We are asked to convert a molarity (18.0 M) to a molality:

\[
\frac{18.0 \text{ mol } \text{H}_2\text{SO}_4}{1 \text{ L sol'n}} \Rightarrow \frac{\text{mol } \text{H}_2\text{SO}_4}{\text{kg solvent}}
\]

The numerators are the same, so we must only convert 1 L of solution into kg of solvent. We know from Example 2.11 that one liter of solution has a mass of 1.839 kg and contains 1.77 kg H₂SO₄ (18.0 mol). We get the solvent mass by difference.

\[
\text{solvent mass} = \text{solution mass} - \text{solute mass} = 1.839 - 1.766 = 0.073 \text{ kg}
\]

Note that we have again retained an extra significant figure in the mass of H₂SO₄ to minimize rounding errors. The mass of solvent should be reported as 0.07 kg. Thus, the molality, which is good to only one significant figure because the mass of water is good to only one significant figure, is determined to be

\[
\frac{18.0 \text{ mol } \text{H}_2\text{SO}_4}{0.073 \text{ kg } \text{H}_2\text{O}} = 2 \times 10^4 \text{ m}
\]

In this example, the molality and molarity are very different. That is not usually the case. The difference in this example arises because the solution is very concentrated. The density of a dilute aqueous solution is ~1 g.mL⁻¹, so the mass of a liter of solution is essentially 1 kg, and the molarity and molality are nearly the same.

Example 2.13

What is the molarity of a 7.0 ppm F⁻ ion solution described in Example 2.8?

1) Restate the question in units (ppm to molarity)

\[
\frac{7.0 \text{ g } \text{F}^-}{10^6 \text{ g sol'n}} \Rightarrow \frac{\text{mol } \text{F}^-}{\text{L sol'n}}
\]

2) convert the numerator

\[
7.0 \text{ g } \text{F}^- \times \frac{1 \text{ mol } \text{F}^-}{19.0 \text{ g } \text{F}^-} = 0.37 \text{ mol } \text{F}^-.
\]

3) Convert the denominator

\[
10^6 \text{ g sol'n} \times \frac{1.0 \text{ mL sol'n}}{1.0 \text{ g sol'n}} \times \frac{1 \text{ L}}{10^3 \text{ mL}} = 10^3 \text{ L}
\]

4) Take the appropriate ratio

\[
\frac{0.37 \text{ mol } \text{F}^-}{1000 \text{ L sol'n}} = 3.7 \times 10^{-4} \text{ M or 0.37 mM}
\]
2.3  DILUTIONS

When additional solvent is added to a solution, the volume of the solution and the mass of the solvent are increased, but the amount of solute is unchanged. In the process, the concentration of the solute is reduced; that is, the solution is diluted by the addition of solvent. The key point is that the amount of solute is the same in the initial and final solutions, which is expressed quantitatively in Equation 2.5*:

\[ C_i V_i = C_f V_f \]  

Eq. 2.5

\( C_i V_i \), the product of concentration and volume of the initial solution, is the amount of solute in the initial solution, while \( C_f V_f \) is the amount of solute in the final solution.* Equation 2.5 can be rearranged to solve for the final concentration as follows:

\[ C_f = \frac{C_i V_i}{V_f} \]  

Eq. 2.6

Equation 2.6* shows that the final concentration equals the initial concentration times the ratio of the initial to final volume, which is unitless and called the dilution factor. Dilution factors depend only on the ratio of volumes not on the volumes themselves. Consequently, they are often given in terms of the ratio. For example, diluting 20 mL to 60 mL would be referred to as a 1:3 dilution, and diluting 20 mL to 50 mL would be a 2:5 dilution.

Example 2.14

a) 30.0 mL of concentrated H\textsubscript{2}SO\textsubscript{4} (18.0 M) is added slowly† to 400 mL of H\textsubscript{2}O. After the solution has cooled, its volume is adjusted to 500.0 mL with more water. What is the molarity of the resulting sulfuric acid solution?

Use Equation 2.6 to determine the final concentration.

\[ C_f = C_i \times \frac{V_i}{V_f} = 18.0 \text{ M} \times \frac{30.0 \text{ mL}}{500.0 \text{ mL}} = 1.08 \text{ M H}_2\text{SO}_4 \]

b) How would 300. mL of 1.5 M H\textsubscript{2}SO\textsubscript{4} be prepared from the concentrated acid?

We are given the final volume and concentration as well as the initial concentration (18.0 M), so we solve Equation 2.5 for the initial volume.

\[ V_i = \frac{V_f \times C_f}{C_i} = 300. \text{ mL} \times \frac{1.5 \text{ M}}{18 \text{ M}} = 25 \text{ mL H}_2\text{SO}_4 \]

The solution would be prepared by adding 25 mL of the acid to some volume (~200 mL) of water. After the solution has cooled, the volume would be adjusted to 300. mL with H\textsubscript{2}O.

† Sulfuric acid must be added to water slowly because the dilution is very exothermic, and the acid is much denser than water. If water is added to the more dense acid, the water stays on top and boils, which causes splattering. However, when the acid is added to the water, the acid sinks to the bottom of the solution, which cools the reaction.

* Equations 2.5 and 2.6 are valid only if the concentration units involve the volume of solution. Thus, they hold for concentrations such as g/mL and molarity, but they cannot be used with molality or percent. However, they can usually be applied to solutions whose concentrations are given in ppm or ppb because the concentrations are generally so low in such solutions that their densities are 1.0 g mL\textsuperscript{-1}, which makes the mass of the solution in grams numerically equal to its volume in mL.
Example 2.15

2.00 mL of a 500. ppm Zn\(^{2+}\) solution is diluted to a total volume of 1.00 L. What is the final concentration in ppm?

This is a very dilute solution, so the concentration in Equation 2.5 can be expressed with the mass fraction.

\[
C_f = \frac{C_i V_i}{V_f} = \frac{(500. \text{ ppm})(2.00 \text{ mL})}{1000 \text{ mL}} = 1.00 \text{ ppm}
\]

Frequently, unknown solutions must be diluted to a certain level in order to run an experiment. Since the solution concentration is unknown, the required dilution factor is also unknown. In cases like this, several successive dilutions may be required to obtain a solution concentration that is appropriate for the experiment. As shown in Equation 2.7, the concentration of the final solution after a series of successive dilutions is equal to the initial concentration times the product of the dilution factors used in the successive dilutions.

\[
C_f = C_i \times \frac{V_1}{V_2} \times \frac{V_3}{V_4} \times \frac{V_5}{V_6} \times \cdots
\]

Eq. 2.7

In Equation 2.7, \(V_1\) mL of a solution with concentration \(C_i\) is diluted to a volume of \(V_2\) mL. \(V_3\) mL of the resulting solution is then diluted to \(V_4\) mL to make a third solution. The process is continued until the desired concentration is made. Example 2.16 and Practice Example 2.7 demonstrate the procedure.

Example 2.16

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 then diluted to 750.00 mL to prepare solution \(C\). 15.00 mL of solution \(C\) is diluted to 1.000 L. The concentration of solution \(C\) is found to be 1.47 \(\mu\)M. What is the concentration of solution \(A\)?

We are asked to determine the initial concentration from the final concentration (\(C_c = 1.47 \times 10^{-6}\) M) and the dilution factors. We substitute into Equation 2.7 as follows:

\[
1.47 \times 10^{-6} \text{ M} = C_A \times \frac{50.00}{500.00} \times \frac{25.00}{750.00} \times \frac{15.00}{1000} = (C_A)(5.000 \times 10^{-5})
\]

Solving for the initial concentration, we obtain the following:

\[
C_A = \frac{1.47 \times 10^{-6} \text{ M}}{5.000 \times 10^{-5}} = 0.0294 \text{ M}
\]

PRACTICE EXAMPLE 2.7

Solution \(C\) is prepared by diluting a 0.100 M HCl stock solution as follows:

1. Solution \(A\) is prepared by diluting 20.0 mL of the stock solution to 50.0 mL.
2. Solution \(B\) is prepared by diluting 10.0 mL of Solution \(A\) to 75.0 mL.
3. Dilution of 20.0 mL of Solution \(B\) to 250.0 mL produces Solution \(C\).

Solution \(A\):

\[\text{[HCl]} = \quad \text{[HCl]} = \quad \text{M}\]

Solution \(B\):

\[\text{[HCl]} = \quad \text{[HCl]} = \quad \text{M}\]

Solution \(C\):

\[\text{[HCl]} = \quad \text{[HCl]} = \quad \text{M}\]

Alternatively, use Equation 2.7 and determine the concentration of HCl in Solution \(C\) from the initial concentration and the dilution factors.

\[\text{[HCl]} = \quad \text{[HCl]} = \quad \text{M}\]
2.4 DETERMINING CONCENTRATIONS

We treat two of the more common methods used for determining the concentration of a solution: spectrophotometry and solution stoichiometry.

SPECTROPHOTOMETRY

Colored solutions absorb light that is the complementary color of the color they appear. As shown in the color wheel in Figure 2.2, orange is the complement of blue, so a blue solution is one that absorbs orange light. The amount of light that it absorbs depends upon the concentration of the absorbing solute, so measuring the amount of light absorbed by a solution is an easy way to determine the concentration of the absorbing solute.

The amount of light absorbed by a sample at a particular wavelength is known as the sample’s absorbance at that wavelength (Figure 2.3). Beer’s law (Equation 2.8) relates the absorbance ($A$) of a solution to the molar concentration ($c$) of the solute that absorbs the light, the cell’s path length ($l$) in centimeters, and the molar absorptivity of the absorbing substance ($\varepsilon$), which is a measure of how strongly absorbing the solute is.

$$A = \varepsilon lc \quad \text{Eq. 2.8}$$

Absorbance is unitless, so the units of molar absorptivity ($\varepsilon$) are M$^{-1}$·cm$^{-1}$. Both $l$ and $c$ are defined by the experiment, but $\varepsilon$ depends only on the absorbing species. Absorption is a nearly ideal way to measure concentration because it is easily done and the measured parameter, the absorbance, is directly proportional to the concentration.

Experimentally, the absorbance of a solution of known concentration is determined first to establish the value of $\varepsilon$. Although only one such measurement is required to determine the value of $\varepsilon$, several are usually done in order to construct a calibration curve (a plot of absorbance versus concentration). The absorbance of the unknown is then measured and its concentration determined using the value of $\varepsilon$ or the calibration curve obtained for the known solution. However, if the concentration of one component of a mixture is to be measured by absorption spectroscopy, there must be a wavelength of light where only that one component absorbs. Solvent absorbance can also be a problem because the concentration of the solvent is so much greater than that of the solute that a significant absorbance can occur even at wavelengths where $\varepsilon$ of the solvent is quite small. To correct for this problem, spectroscopists measure the absorbance of a sample that contains all of the components in the mixture except the solute of interest. This sample is called the blank. The absorbance of the blank is subtracted from the solution absorbance to obtain the absorbance of the solute of interest.
Example 2.17

The concentration of a solution containing a cyanine dye in a 1.00 cm cell is determined as follows:

1) The absorbance of a solution in which a dye concentration is 86.9 μM is too high to be measured, but the absorbance after a 1:100 dilution is 0.185.

2) The absorbance of the unknown after a 1:20 dilution is 0.352.

What is the concentration of the unknown, undiluted cyanine dye solution?

Account for the 1:100 dilution of the original sample to obtain the concentration of the solution whose absorbance was measured.

\[ c_i = c_x \frac{V_f}{V_f} = 86.9 \ \mu M \times \frac{1}{100} = 0.869 \ \mu M = 8.69 \times 10^{-7} \ \text{M} \]

Determine the molar absorptivity of the dye from the absorbance of the known sample.

\[ \varepsilon = \frac{A}{lc} = \frac{0.185}{(1.00 \text{ cm})(8.69 \times 10^{-7} \ \text{M})} = 2.13 \times 10^5 \ \text{M}^{-1} \cdot \text{cm}^{-1} \]

Use the above molar absorptivity to determine the concentration of the unknown solution whose absorbance was measured.

\[ c = \frac{A}{l \varepsilon} = \frac{0.352}{(1.00 \text{ cm})(2.13 \times 10^5 \ \text{M}^{-1} \cdot \text{cm}^{-1})} = 1.65 \times 10^{-6} \ \text{M} = 1.65 \ \mu M \]

Account for the 1:20 dilution to determine the concentration of the initial sample.

\[ c_i = c_x \frac{V_f}{V_f} = 1.65 \ \mu M \times \frac{20}{1} = 33.0 \ \mu M \]

Example 2.18

The concentration of Fe\textsuperscript{3+} in an aqueous solution is determined by the addition of an excess o-phenanthroline (phen), which forms a blue complex with the Fe\textsuperscript{3+} that absorbs at 610 nm.\textsuperscript{*} The following solutions are prepared:

1) Blank: 2.0 mL of iron-free water mixed with 0.001 mL of phen solution.
2) Standard: 2.0 mL of water that is 5.0 ppm Fe\textsuperscript{3+} mixed with 0.001 mL of phen.
3) Sample: 2.0 mL of unknown mixed with 0.001 mL of phen.

The spectrometer was adjusted to read 0.000 absorbance with the blank at the 610 nm wavelength, thereby eliminating problems due to the solvent. The absorbance of the standard solution was then measured to be 0.730 and that of the sample to be 0.562. What is the concentration of Fe\textsuperscript{3+} in this sample?

* Farmers with sandy soils often need to apply iron (Fe\textsuperscript{3+}) to their fields, and they check for the level of iron by testing the runoff water in drainage ditches with this procedure.

PRACTICE EXAMPLE 2.8

A 1.86 μM solution of β-carotene, the precursor to vitamin A and the source of the orange color in carrots, has an absorbance of 0.259 in a 1-cm cell at 450 nm. What is the molar absorptivity of β-carotene at 450 nm?

What is the concentration of β-carotene in a solution that has an absorbance of 0.187 at 450 nm?
Because the absorbance of the same complex is being measured, the value of $\varepsilon$ is the same in both the standard and the sample solutions. All measurements are made under identical circumstances, so $l$ is also the same in both experiments. Thus, we can express the two absorbances as

$$A_{\text{std}} = \varepsilon c_{\text{std}} \quad \text{and} \quad A_{\text{sample}} = \varepsilon c_{\text{sample}}$$

where $A_{\text{std}}$ is the absorbance of the standard and $A_{\text{sample}}$ is the absorbance of the sample. $\varepsilon$ and $l$ have no subscripts because their values do not change in the two experiments. Dividing the two expressions eliminates $\varepsilon$ and $l$.

$$\frac{A_{\text{std}}}{A_{\text{sample}}} = \frac{c_{\text{std}}}{c_{\text{sample}}}$$

Solving for the concentration of the sample, we obtain

$$c_{\text{sample}} = c_{\text{std}} \times \frac{A_{\text{sample}}}{A_{\text{std}}} = 5.0 \, \text{ppm} \times \frac{0.562}{0.730} = 3.8 \, \text{ppm} \, \text{Fe}^{3+}$$

REACTION STOICHIOMETRY

Another way to determine an unknown concentration is to measure the amount of a known reactant that is required to completely react with the solute. The determination can be gravimetric (mass is measured) or volumetric (volume is measured). We now combine the concepts of stoichiometry presented in Chapter 1 with those dealing with solutions presented in this chapter to discuss solution stoichiometry. The calculations are generally identical to those presented in Chapter 1 except that solution reactions are often written as net ionic equations and the given amounts are expressed as concentrations and volumes rather than masses. However, these two differences do not change the fundamentals of the calculations. We consider two types of solution stoichiometry problems: precipitation (gravimetric) and titrations (volumetric).

Precipitation Reactions (gravimetric)

Precipitation reactions occur when ions in solution combine to produce an insoluble salt. The rules used to predict whether or not a salt is insoluble are given in Table 2.2. However, the solubility rules in Table 2.2 are only rough guidelines, and there are many exceptions.

### Table 2.2 Solubility rules for ionic compounds in water

<table>
<thead>
<tr>
<th>Rule</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rule 1</td>
<td>Compounds of NH$_4$$^{+}$ and group 1A metal ions are soluble.</td>
</tr>
<tr>
<td>Rule 2</td>
<td>Compounds of NO$_3^-$, ClO$_4^-$, ClO$_3^-$, and C$_2$H$_3$O$_2^-$ are soluble.</td>
</tr>
<tr>
<td>Rule 3</td>
<td>Compounds of Cl$^-$, Br$^-$, and I$^-$ are soluble except those of Ag$^{+}$, Cu$^{+}$, Tl$^+$, Hg$_2^{2+}$ and Pb$^{2+}$.</td>
</tr>
<tr>
<td>Rule 4</td>
<td>Compounds of SO$_4^{2-}$ are soluble except those of Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, and Pb$^{2+}$.</td>
</tr>
<tr>
<td>Rule 5</td>
<td>Most other ionic compounds are insoluble.</td>
</tr>
</tbody>
</table>

**PRACTICE EXAMPLE 2.9**

What is the silver ion concentration in a solution of AgNO$_3$ if the addition of an excess of K$_3$PO$_4$ to 50.00 mL of the AgNO$_3$ solution produces 0.3634 g of precipitate?

Identity of precipitate: ______________

Molar mass of precipitate: ____________ g mol$^{-1}$

millimoles of silver ion present in 50.00 mL of solution

__________ mmol Ag$^{+}$

concentration of Ag$^{+}$ ion

$[\text{Ag}^{+}] =$ ______________ M
Example 2.19

What is the \( I^- \) ion concentration in a solution if the addition of an excess of 0.100 M \( \text{Pb(NO}_3\text{)}_2 \) to 25.0 mL of the \( I^- \) solution produces 987 mg of \( \text{PbI}_2 \)?

This is a gravimetric determination of iodide. Use the factor-label method and the molar mass of \( \text{PbI}_2 \) (461.0 g/mol) to convert the given mass of \( \text{PbI}_2 \) into the number of moles of \( I^- \) ion that it contains.

\[
\frac{987 \text{ mg PbI}_2 \times 1 \text{ mmol PbI}_2}{461.0 \text{ mg PbI}_2} \times \frac{2 \text{ mmol I}^-}{1 \text{ mmol PbI}_2} = 4.28 \text{ mmol I}^-.
\]

25.0 mL of solution contained 4.28 mmol \( I^- \), so the concentration of \( I^- \) in the unknown solution is determined to be

\[
[I^-] = \frac{4.28 \text{ mmol I}^-}{25.0 \text{ mL solution}} = 0.171 \text{ M}
\]

Example 2.20

Determine the amount of precipitate that forms and the concentration of the excess reactant present in a solution after 75.0 mL of 0.0856 M \( \text{AgNO}_3 \) solution and 100.0 mL of a 0.0315 M \( \text{K}_3\text{PO}_4 \) solution have been mixed.

Step 1. Write a balanced chemical equation. \( \text{AgNO}_3 \) and \( \text{K}_3\text{PO}_4 \) are strong electrolytes, so we use the net equation. Referring to the solubility rules, we conclude that \( K^+ \) and \( \text{NO}_3^- \) ions are spectator ions, but \( \text{Ag}_3\text{PO}_4 \) is insoluble (Rule 5). The net equation for the reaction is \( 3\text{Ag}^+ + \text{PO}_4^{3-} \rightarrow \text{Ag}_3\text{PO}_4 \).

Step 2. Determine the limiting reactant. The limiting reactant is that reactant with the smallest mole/coefficient ratio. The amount of each reactant is given in terms of its molarity and its volume in mL, so Equation 2.1 is used to determine the number of mmoles of each.

\[
(75.0 \text{ mL})(0.0856 \text{ mmol mL}^{-1}) = 6.42 \text{ mmol Ag}^+ \\
(100.0 \text{ mL})(0.0315 \text{ mmol mL}^{-1}) = 3.15 \text{ mmol PO}_4^{3-}
\]

Divide the mmoles of each by the coefficient in the balanced chemical equation to obtain

\[
\frac{6.42 \text{ mmol Ag}^+}{3 \text{ mmol Ag}^+} = 2.14; \quad \frac{3.15 \text{ mmol PO}_4^{3-}}{1 \text{ mmol PO}_4^{3-}} = 3.15
\]

2.14 < 3.15, so \( \text{Ag}^+ \) is the limiting reactant.

Step 3. Construct the reaction table. All quantities on the \( \Delta \) line are based on the amount of limiting reactant, 6.42 mmol \( \text{Ag}^+ \).

\[
\begin{array}{ccc}
\text{Initial} & 6.42 & 3.15 \\
\Delta & -6.42 & -2.14 & +2.14 \\
\text{Final} & 0 & 1.01 & 2.14
\end{array}
\]

Net reaction: \( 3\text{Ag}^+ + \text{PO}_4^{3-} \rightarrow \text{Ag}_3\text{PO}_4 \)

Limiting reactant:

\[
\text{Ag}^+ \]

Reaction Table:

\[
\begin{array}{ccc}
\text{Initial} & 6.42 & 3.15 \\
\Delta & -6.42 & -2.14 & +2.14 \\
\text{Final} & 0 & 1.01 & 2.14
\end{array}
\]

Mass of precipitate

Concentration of excess reactant

PRACTICE EXAMPLE 2.10

32.0 mL of 0.112 M \( \text{Pb(NO}_3\text{)}_2 \) is mixed with 58.0 mL of 0.0886 M \( \text{KCl} \). Determine the mass of precipitate that forms and assume additive volumes to determine the concentration of the excess reactant.

Net reaction: ____________________________

Limiting reactant:

\[
\text{Pb}^2+ \]

Mass of precipitate

Concentration of excess reactant
Use the moles and molar mass of Ag₃PO₄ to determine the mass of precipitate:

\[(2.14 \text{ mmol Ag₃PO₄})(418.6 \text{ mg mmol}^{-1}) = 896 \text{ mg or 0.896 g}\]

We assume additive volumes; i.e., the final volume is the sum of the two initial volumes:

\[75.0 + 100.0 = 175.0 \text{ mL}\]

The molar concentration of phosphate ion remaining in the solution is then determined to be:

\[\text{[PO}_4^{3-}\] = \frac{1.01 \text{ mmol}}{175.0 \text{ mL}} = 0.00577 \text{ M or 5.77 mM}\]

In Chapter 8, we will show that the final concentration of the limiting reactant is small, but it is not zero because equilibrium is established.

**Titrations (volumetric)**

A titration is an analytical procedure in which the stoichiometric volume of one reactant, the **titrant** that is required to react with a known amount of another reactant, the **analyte**, is determined. The experimental setup is shown in Figure 2.4. The **buret**, which contains the titrant, is calibrated so that the volume of solution it delivers can be determined precisely (usually to 0.01 mL). The rate of delivery of the titrant is adjusted with the stopcock. In a common titration, the concentration of the titrant is known and the amount of the analyte is determined. A known amount of volume or dissolved mass of analyte is placed in the reaction flask, and the titrant is added slowly until the stoichiometric volume has been delivered. This point, known as the **equivalence point**, is usually approximated by a color change produced by one of the reactants or by an indicator that is added to the analyte solution. The point at which the color change occurs is called the **end point** of the titration. Typically, the equivalence point is approximated by an end point.

**Example 2.21**

3.86 g of impure NaOH pellets are dissolved in sufficient water to make 1.00 L of solution. What is the purity of the pellets if the titration of 30.0 mL of 0.107 M HCl required 38.6 mL of the resulting solution?

1) Determine the number of millimoles of H₃O⁺:

\[
\text{30.0 mL H}_3\text{O}^+ \times \frac{0.107 \text{ mmol } \text{H}_3\text{O}^+}{\text{mL } \text{H}_3\text{O}^+} = 3.21 \text{ mmol } \text{H}_3\text{O}^+
\]

2) Convert mmol H₃O⁺ to mmol OH⁻ using \text{H}_3\text{O}^+ + \text{OH}⁻ \rightarrow 2\text{H}_2\text{O}

\[
\text{3.21 mmol } \text{H}_3\text{O}^+ \times \frac{1 \text{ mmol } \text{OH}^-}{1 \text{ mmol } \text{H}_3\text{O}^+} = 3.21 \text{ mmol } \text{OH}^-.
\]
3) Convert the mmol of OH\(^-\) in 38.6 mL of solution to mass of NaOH.

\[
3.21 \text{ mmol OH}^- \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol OH}^-} \times \frac{40.0 \text{ mg NaOH}}{1 \text{ mmol NaOH}} = 128 \text{ mg NaOH}
\]

4) Use the amount of NaOH in 38.6 mL to determine the amount in original 1.00 L

\[
\frac{128 \text{ mg NaOH}}{38.6 \text{ mL solution}} \times 1000 \text{ mL solution} = 3.32 \times 10^3 \text{ mg NaOH} = 3.32 \text{ g NaOH}
\]

5) Use the mass of NaOH and the mass of pellets to determine the purity.

\[
\frac{3.32 \text{ g NaOH}}{3.86 \text{ g pellets}} \times 100\% = 85.9\% \text{ pure}
\]

Only 85.9\% of the mass of the pellets is actually NaOH.

Example 2.22

What is the percent H\(_2\)O\(_2\) in a sample if 20.00 g of the H\(_2\)O\(_2\) solution* required titration with 40.85 mL of 0.1728 M K\(\text{MnO}_4^-\)?

\[
2\text{MnO}_4^-+5\text{H}_2\text{O}_2+6\text{H}^+\rightarrow 5\text{O}_2+2\text{Mn}^{2+}+8\text{H}_2\text{O}
\]

The number of mmols of H\(_2\)O\(_2\) in the sample is determined from the number of mmoles of \(\text{MnO}_4^-\) required for the titration and the stoichiometric ratio between H\(_2\)O\(_2\) and \(\text{MnO}_4^-\).

\[
\frac{40.85 \text{ mL MnO}_4^-}{\text{mL MnO}_4^-} \times \frac{0.1728 \text{ mmol MnO}_4^-}{2 \text{ mmol MnO}_4^-} \times \frac{5 \text{ mmol H}_2\text{O}_2}{2 \text{ mmol MnO}_4^-} = 17.65 \text{ mmol H}_2\text{O}_2
\]

The mass of the H\(_2\)O\(_2\) in the sample is

\[
17.65 \text{ mmol H}_2\text{O}_2 \times \frac{34.014 \text{ mg H}_2\text{O}_2}{1 \text{ mmol H}_2\text{O}_2} = 600.2 \text{ mg H}_2\text{O}_2
\]

Note that the result of the calculation for the number of millimoles of H\(_2\)O\(_2\) is used in the above, not the rounded value, which does change the last significant figure. The percentage of the total mass of the sample that is H\(_2\)O\(_2\) is then

\[
\text{% H}_2\text{O}_2 = \frac{0.6002 \text{ g H}_2\text{O}_2}{20.00 \text{ g sol'n}} \times 100\% = 3.001\% \text{ H}_2\text{O}_2
\]

Hydrogen peroxide that is purchased in a drug store is also 3%.

2.5 COLLIGATIVE PROPERTIES

Colligative properties depend on the concentration of the solute particles, not their identity, so a sodium ion has the same effect on these properties as does a sugar molecule. In this section, we discuss the quantitative relationships between solute particle
Concentrations and the effects that they cause.

Colligative properties depend upon the concentration of particles, so particle concentrations are often referred to as colligative concentrations. For example, the molarity of all particles in a solution is often referred to as the **colligative molarity**, \( M_c \). This is not an important distinction for nonelectrolytes, but it is very important for electrolytes. Consider that a 0.020 M solution of the strong electrolyte \( \text{CaCl}_2 \) is 0.020 M in \( \text{Ca}^{2+} \) and \( 2(0.020) = 0.040 \text{ M in } \text{Cl}^{-} \). Consequently, the colligative molarity of a 0.020 M solution of \( \text{CaCl}_2 \) is \( M_c = [\text{Ca}^{2+}] + [\text{Cl}^{-}] = 0.020 + 0.040 = 0.060 \text{ M} \). The **colligative molality**, \( m_c \), is defined analogously. The difference between the concentration of a solution and its colligative concentration is shown in Equation 2.9.

\[
M_c = i \, M \quad \text{&} \quad m_c = i \, m \quad \text{Eq. 2.9}
\]

\( i \) is the van’t Hoff factor. In this text, we assume that the van’t Hoff factor is simply the number of moles of particles produced when one mole of a solute dissolves. However, because of interactions between the ions, \( i \) is usually somewhat less than this ideal number. Practice Example 2.13 gives more examples of van’t Hoff factors.

### Example 2.23

**Determine the colligative molarity of each of the following solutions:**

a) 0.080 M \( \text{K}_3\text{PO}_4 \)

\( \text{K}_3\text{PO}_4(s) \rightarrow 3 \text{K}^{+}(aq) + \text{PO}_4^{3-}(aq) \)

\( i = 3 \text{K}^{+} \text{ions} + 1 \text{PO}_4^{3-} \text{ion} = 4 \text{ ions} \Rightarrow M_c = iM = 4M = 4(0.080) = 0.32 \text{ M} \)

b) 0.042 M \( \text{C}_6\text{H}_12\text{O}_6 \)

\( \text{C}_6\text{H}_12\text{O}_6(s) \rightarrow \text{C}_6\text{H}_12\text{O}_6(aq) \)

This organic compound is a nonelectrolyte so \( i = 1 \Rightarrow M_c = M = 0.042 \text{ M} \)

As shown in Figure 2.5, adding a solute to a solvent depresses the freezing point by \( \Delta T_f \), elevates the boiling point by \( \Delta T_b \), and lowers the vapor pressure at temperature \( T \) by \( \Delta P \). The effect 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.

### Practice Example 2.13

**Determine the van’t Hoff factor for each of the following.**

- \( \text{CaSO}_4: \) _____
- \( \text{Ba(OH)}_2: \) _____
- \( \text{CH}_3\text{OH}: \) _____
- \( \text{HCl}: \) _____
- \( \text{NH}_4\text{ClO}_3: \) _____
- \( \text{SF}_4: \) _____

---

**Figure 2.5 Phase diagram of a pure solvent and a solution**

The green region is the liquid region of the pure solvent. The blue region is liquid in the solution but solid or gas in the solvent. The arrows indicate the changes in the freezing point (freezing point depression, \( \Delta T_f \)), the normal boiling point (boiling point elevation, \( \Delta T_b \)), and the vapor pressure at temperature \( T \) (vapor pressure lowering, \( \Delta P \)) caused by the addition of a solute to a pure solvent.
VAPOR PRESSURE LOWERING

The liquid ⇌ 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 2.6 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

\[ ΔP = X_{solute}P^o \]  \hspace{1cm} \text{Eq. 2.10}

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^o is the vapor pressure of the pure solvent at the temperature under consideration. The vapor pressure of water is given at several temperatures in Table 2.3. The vapor pressure of the solution is lower than that of the solvent by ΔP, so \[ P = P^o - ΔP = P^o - X_{solute}P^o = (1-X_{solute})P^o. \]

However, \( 1 - X_{solute} = X_{solvent} \), so we can rewrite Equation 2.10 as

\[ P = X_{solvent}P^o \]  \hspace{1cm} \text{Eq. 2.11}

Equation 2.11 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. Thus far, we have determined mole fractions of solutes rather than solvents, so be careful not to use the wrong mole fraction in Equation 2.11.

Example 2.24

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

The van’t Hoff factor for NaCl is \( i=2 \) (Na\(^{+}\) + Cl\(^{-}\)), so there are two moles of ions (particles) for each mole of NaCl. The total number of moles of solute in solution is

\[ 10.0 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}} \times \frac{2 \text{ mol ions}}{1 \text{ mol NaCl}} = 0.342 \text{ mol ions} \]
The number of moles of solvent (water) in the solution is
\[ 100. \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 5.56 \text{ mol H}_2\text{O} \]
The total number of moles of particles is 0.34 mol ions + 5.56 mol H\text{2O} = 5.90 mol. The mole fraction of the solvent is then calculated to be
\[ X_{\text{solvent}} = \frac{5.56 \text{ mol H}_2\text{O}}{5.90 \text{ mol total}} = 0.942 \]
The vapor pressure of water is found to be \( P^o = 23.8 \text{ torr} \) (Table 2.3), so the vapor pressure of the solution can be determined with Equation 2.11 to be
\[ P = X_{\text{solvent}}P^o = (0.942)(23.8 \text{ torr}) = 22.4 \text{ torr} \]
Dissolving NaCl in water lowers the vapor pressure of the water by 23.8 - 22.4 = 1.4 torr or 5.9%, which is the mole percent of NaCl. This is the same result that would have been obtained had we used Equation 2.10.

**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, \( \Delta T_b \). The magnitude of the increase is proportional to the colligative molality of the solute:
\[ \Delta T_b = k_{b,m} = i k_{b,m} \quad \text{Eq. 2.12} \]

\( k_b \) is the boiling point elevation constant of the solvent; it has units °C·m\(^{-1}\) (degrees per molal). The boiling point elevation constants and boiling points of some common solvents are included in Table 2.4. \( \Delta T_b \) is the amount by which the boiling point of the solvent (\( T_b^o \)) is raised, so the boiling point of the solution is given as
\[ T = T_b^o + \Delta T_b \]

### Table 2.3 Vapor pressure of water at various temperatures

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>( P^o ) (torr)( ^a )</th>
<th>T (°C)</th>
<th>( P^o ) (torr)( ^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.6</td>
<td>50</td>
<td>92.5</td>
</tr>
<tr>
<td>5</td>
<td>6.5</td>
<td>55</td>
<td>118.0</td>
</tr>
<tr>
<td>10</td>
<td>9.2</td>
<td>60</td>
<td>149.4</td>
</tr>
<tr>
<td>15</td>
<td>12.8</td>
<td>65</td>
<td>187.5</td>
</tr>
<tr>
<td>20</td>
<td>17.5</td>
<td>70</td>
<td>233.7</td>
</tr>
<tr>
<td>25</td>
<td>23.8</td>
<td>75</td>
<td>289.1</td>
</tr>
<tr>
<td>30</td>
<td>31.8</td>
<td>80</td>
<td>355.1</td>
</tr>
<tr>
<td>35</td>
<td>41.2</td>
<td>85</td>
<td>433.6</td>
</tr>
<tr>
<td>40</td>
<td>55.3</td>
<td>90</td>
<td>525.8</td>
</tr>
<tr>
<td>45</td>
<td>71.9</td>
<td>95</td>
<td>633.9</td>
</tr>
</tbody>
</table>

\( ^a \) 1 torr = 1 mm Hg.

### Table 2.4 Freezing point depression and boiling point elevation data for some solvents

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

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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, $\Delta T_f$, and is shown in Equation 2.13:

$$\Delta T_f = k_f m_c = i k_f m$$

Eq. 2.13

In Equation 2.13, $k_f$ 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. The freezing point depression constants and freezing points of some common solvents are listed in Table 2.4. $\Delta T_f$ is the amount by which the freezing point of the solvent ($T_f^0$) is lowered, so the freezing point of the solution is given as

$$T = T_f^0 - \Delta T_f$$

Example 2.25

Antifreeze is ethylene glycol, $C_2H_6O_2$ [$M_m = 62.1$ g·mol⁻¹; $d = 1.11$ g·mL⁻¹]. What are the boiling and freezing points of a 50.0% (v/v) aqueous solution?

Ethylene glycol has a very low vapor pressure, so we can assume that it is a nonvolatile solute for our calculation. The first step is to determine the molality. 50.0% (v/v) denotes a volume/volume percent, which means that 50.0% of the volume of the antifreeze is ethylene glycol and 50.0% of the volume is water. We need a quantity of solution for which the number of moles of solute and kg of solvent can be determined, but we are free to choose any amount. For simplicity, we base our calculations on 1 L = 1000 mL of antifreeze. The mixture is a 50/50 mixture, so we can write

1000. mL of mixture = 500. mL $H_2O$ + 500. mL $C_2H_6O_2$

Use the densities of the two liquids and the molar mass of ethylene glycol to determine the mass of water and the number of moles of ethylene glycol.

$$\frac{500. \text{ mL } H_2O \times \frac{1.00 \text{ g } H_2O}{\text{mL } H_2O}}{\text{mL } H_2O} = 500. \text{ g } H_2O = 0.500 \text{ kg } H_2O$$

$$\frac{500. \text{ mL } C_2H_6O_2 \times \frac{1.11 \text{ g } C_2H_6O_2}{\text{mL } C_2H_6O_2}}{\text{mL } C_2H_6O_2} \times \frac{1 \text{ mol } C_2H_6O_2}{62.1 \text{ g } C_2H_6O_2} = 8.94 \text{ mol } C_2H_6O_2$$

The molality of ethylene glycol in the 50.0% mixture is

$$\text{molality} = \frac{8.94 \text{ mol } C_2H_6O_2}{0.500 \text{ kg } H_2O} = 17.9 \text{ m}$$

The freezing point depression caused by the undissociated ($i = 1$) ethylene glycol is

PRACTICE EXAMPLE 2.14

The salt that is commonly used to melt ice on roads and sidewalks is CaCl₂ ($M_m = 111$ g·mol⁻¹). What are the melting point, boiling point, and vapor pressure at 20 °C of a solution of CaCl₂ made by dissolving 62.3 g of CaCl₂ in 100. mL of H₂O?

$$\text{molality of CaCl}_2: \quad = \text{_______ m}$$

$$\text{van't Hoff factor for CaCl}_2 \quad i = \text{_______}$$

$$\Delta T_f = \text{_______}^\circ \text{C} \cdot \text{m}^{-1} \times \text{_______ m} = \text{_______}^\circ \text{C}$$

$$\Delta T_b = \text{_______}^\circ \text{C} \cdot \text{m}^{-1} \times \text{_______ m} = \text{_______}^\circ \text{C}$$

Freezing point: $T_f = \text{_______}^\circ \text{C}$

Boiling point: $T_b = \text{_______}^\circ \text{C}$

Moles and mole fraction of water in solution

$$X(H_2O) = \text{_______}$$

$$\text{molality} = \text{_______} \times \text{_______} = \text{_______ m}$$

$$\text{Vapor pressure of water at 20 °C from Table 2.2} = \text{_______ torr}$$

The vapor pressure of the solution at 20 °C is

$$\text{_______} \times \text{_______} = \text{_______ torr}$$
\[ \Delta T_f = (1.86 \, ^\circ C \cdot m^{-1})(17.9 \, m) = 33.3 \, ^\circ C. \]

where 1.86 \, ^\circ C \cdot m^{-1} is the freezing point depression constant of water from Table 2.4. The freezing point of pure water is 0 \, ^\circ C, so the freezing point of the antifreeze is -33 \, ^\circ C (-27 \, ^\circ F), a substantial protection. The protection against boil-over is not as good.

\[ \Delta T_b = (0.512 \, ^\circ C \cdot m^{-1})(17.9 \, m) = 9.16 \, ^\circ C \]

where 0.512 \, ^\circ C \cdot m^{-1} is the boiling point elevation constant for water. The boiling point \textit{elevation} is 9 \, ^\circ C. Because water boils at 100 \, ^\circ C, the boiling point of the antifreeze is 109 \, ^\circ C (228 \, ^\circ F). The pressure in your car’s cooling system is elevated above 1 atm, however, which also increases the boiling point.

Colligative properties depend only on the concentration of the solute particles, so they can be used to determine the number of moles of solute particles present in a solution. If the mass of the solute is known, then its molar mass can also be determined. Example 2.26 demonstrates the use of freezing point depressions in determining a molar mass, once a common procedure.

**Example 2.26**

1.00 g of an unknown, non-dissociating (\(i = 1\)) solute is added to 10.00 g of \textit{para}-xylene. The freezing point of the solution is 1.95 \, ^\circ C lower than that of the pure solvent. What is the molar mass of the unknown?

From Table 2.4, we find that \(k_f = 4.30 \, ^\circ C \cdot m^{-1}\) for \textit{para}-xylene. This is a good solvent for this experiment because of its relatively large \(k_f\). The freezing point depression of \textit{para}-xylene is over twice that for the same sample in water.

1. Equation 2.11 is used to determine the molality of the solution.

\[ m = \frac{\Delta T_f}{k_f} = \frac{1.95 \, ^\circ C}{4.30 \, ^\circ C \cdot m^{-1}} = 0.453 \, m \]

2. The number of moles of solute present is determined from the mass of the solvent and the molality.

\[ (0.453 \, \text{mol-kg}^{-1})(0.0100 \, \text{kg}) = 4.53 \times 10^{-3} \, \text{mol} \]

3. The molar mass is determined from the number of moles and the mass of the sample.

\[ M_m = \frac{\text{grams of sample}}{\text{moles of sample}} = \frac{1.00 \, \text{g}}{4.53 \times 10^{-3} \, \text{mol}} = 221 \, \text{g/mol} \]
OSMOTIC PRESSURE

A semipermeable membrane is a membrane that allows solvent molecules (usually water) to pass through while denying passage to solute particles. The movement of the solvent molecules though the membrane is called osmosis. The rate of osmosis depends upon the rate at which the solvent molecules collide with the membrane. The presence of a solute reduces the rate at which solvent molecules pass through the membrane by reducing the concentration of the solvent and blocking solvent access to portions of the membrane.

Figure 2.7a shows two containers (I and II) filled with water and separated by a semipermeable membrane. The concentration of water on both sides is identical, so the rate of osmosis is the same in both directions, I = II. However, a solute (larger blue spheres) has been added to container II in Figure 2.7b. The presence of the solute reduces the solvent concentration, which reduces the rate at which solvent molecules collide with and penetrate the membrane. Consequently, the rate of passage of solvent molecules in direction I ← II drops below that in the I → II direction, so there is a net passage of solvent from I into II, which dilutes the solution in side II. We conclude that

When solutions with different concentrations are separated by a semipermeable membrane, solvent molecules pass from the more dilute solution into the more concentrated solution. The result is a dilution of the more concentrated solution.

In Figure 2.8, a semipermeable membrane separates pure water and a concentrated aqueous solution. Initially, the two levels are the same, but there is a net movement of water molecules from the pure water into the solution. As a result, the solution level rises and the pure water level drops. The rising column on the solution side exerts an increasing pressure on the membrane that increases the rate at which water molecules pass from the solution pass back into the pure water. Equilibrium is established when the pressure is sufficient to drive the water molecules out of the solution at the same rate that they leave the pure water. The pressure exerted by the column at equilibrium is the osmotic pressure. The osmotic pressure developed by a solution is given by Equation 2.14.

\[ \pi = M_c RT = i MRT \]  

In Equation 2.14, \( \pi \) is the osmotic pressure in atmospheres, \( M_c \) is the colligative molarity, \( T \) is the absolute temperature, and \( R = 0.0821 \text{ L·atm·K}^{-1}\text{·mol}^{-1} \) is the ideal gas law constant. Note that \( L·mol^{-1} = M^{-1} \), so the constant \( R \) can also be expressed as 0.0821 atm·K\(^{-1}\)·M\(^{-1}\).

If a pressure exceeding the osmotic pressure is applied to the concentrated side of Figure 2.8, water can be forced from the solution side into the pure water in a process called osmosis.
called reverse osmosis. Reverse osmosis has been used to purify seawater on ships and in the Middle East.

**Example 2.27**

Assume sea water is 0.53 M NaCl and determine what minimum pressure is required to purify sea water by reverse osmosis at 25 °C.

Using \(i = 2\) for NaCl and 298 K for 25 °C in Equation 2.14, we determine the osmotic pressure of sea water to be:

\[
\pi = iMRT = 2(0.53 \text{ M})(0.0821 \text{ atm·K}^{-1}·\text{M}^{-1})(298 \text{ K}) = 26 \text{ atm}
\]

The applied pressure in reverse osmosis must exceed the osmotic pressure, so a pressure over 26 times that of atmospheric pressure must be applied. The biggest challenge preventing the general use of reverse osmosis to obtain drinking water from sea water is finding membranes that can withstand such high pressures.

Osmotic pressure has many applications in biology because cell membranes are semipermeable. When the solution around a cell has the same colligative concentration as within the cell, water enters and leaves the cell at the same rate and the cell maintains its size and shape. However, when a cell is placed in pure water, it expands and eventually ruptures as water flows into the cell faster than it flows out. Placing a cell in a solution with a greater colligative concentration causes the cell to shrink as water flows out faster than it flows in. This is the reason that drinking salt water does not quench your thirst and actually makes you thirstier. Osmotic pressure is responsible for the transport of water from the roots to the tops of plants. Water enters a tree through the membranes in its roots, but evaporates from the leaves resulting in a substantial concentration difference between the roots and the leaves. The large concentration difference can develop osmotic pressures of up to ~20 atm in very tall trees. As demonstrated in Example 2.28, osmotic pressure can also be used to determine molar mass.
Example 2.28

0.75 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?

The procedure followed in this problem is very similar to that used in Example 2.26. We begin by realizing that peptides do not dissociate in water, so \( i = 1 \).

1. Convert the given pressure to atmospheres by dividing the given pressure in torr by 760 torr atm\(^{-1}\), then solve Equation 2.13 for the molarity of the solution.

\[
M = \frac{\pi}{RT} = \frac{(3.74/760) \text{ atm}}{(0.0821 \text{ atm \cdot K}^{-1} \cdot \text{M}^{-1})(300 \text{ K})} = 2.0 \times 10^{-4} \text{ M}
\]

2. Determine the number of moles of peptide in 0.75 L of solution.

\[
n = (0.75 \text{ L})(2.0 \times 10^{-4} \text{ mol.L}^{-1}) = 1.5 \times 10^{-4} \text{ mol}
\]

3. Calculate the molar mass from the number of moles and mass of peptide.

\[
M_m = \frac{\text{grams peptide}}{\text{moles peptide}} = \frac{0.40 \text{ g}}{1.5 \times 10^{-4} \text{ mol}} = 2.7 \times 10^3 \text{ g mol}^{-1}
\]

2.6 COLLOIDS

Sometimes materials will suspend as small aggregates rather than dissolve. For example, 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.

Suspensions in which the particle size is very small (1 nm to 1 \( \mu \)m) 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 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.

PRACTICE EXAMPLE 2.15

What osmotic pressure would develop between the solution described in Practice Example 2.14 and pure water at 298K? Assume that the solution has a density of 1.2 g mL\(^{-1}\).

Volume of solution

\[ V = \underline{\text{L}} \]

Colligative Molarity

\[ M_c = \underline{\text{M}} \]

Osmotic Pressure

\[ \pi = \underline{\text{atm}} \]
2.7 CHAPTER SUMMARY AND OBJECTIVES

Several concentration units were defined:

Molarity of A \( M_A = \frac{\text{mol A}}{\text{L solution}} = \frac{\text{mmol A}}{\text{mL solution}} \)

Mole Fraction of A \( X_A = \frac{\text{mol A}}{\text{total mol of all substances in mixture}} \)

Mass Fraction of A \( \text{mass fraction} = \frac{\text{mass A}}{\text{total mass of mixture}} \)

Molality of A \( m_A = \frac{\text{mol A}}{\text{kg solvent}} \)

Mass percent, parts per million, and parts per billion were also defined. Concentrations and volumes give us yet another way to determine the number of moles of a sample and can be applied to the stoichiometry of reactions occurring in solution. An easy way to convert from one concentration unit to another is to put the given and desired units side-by-side and convert the numerators and the denominators independently.

Addition of a solvent to a solution dilutes the solution. Calculations of resulting concentrations or required volumes can be done by using the dilution formula: \( C_iV_i = C_fV_f \) (Equation 2.5) where \( C_iV_i \) is the amount (moles or mass) of solute in the initial solution, and \( C_fV_f \) is the amount of solute in the final solution. It is important to remember that dilution changes the volume of the solution and the concentration of the solute, but it does *not* change the amount of solute.

Concentrations can be determined by measuring the absorbances of a blank, a standard, and the sample. Beer’s law relates the absorbance (A) of a sample to its molar absorptivity (ε), its concentration (c), and to the path length (l) that the light travels through the sample: \( A = \varepsilon lc \) (Equation 2.8).

Colligative properties are those properties of a solution that depend on the concentration but not on the identity of the solute particles. The colligative concentration of a solution is the total concentration of all particles in the solution. For example, in a solution consisting of only one solute, the colligative molarity is \( M_c = iM \) (Equation 2.9) where \( i \), the van’t Hoff factor, is the number of moles of particles that results when one mole of solute dissolves. \( i \) is one for nonelectrolytes but is greater than one for electrolytes.

There are four colligative properties:

**ANSWERS TO PRACTICE EXAMPLES**

2.1 \([\text{Ba}^{2+}] = 0.0490 \text{ M}; \ [\text{OH}^{-}] = 0.0980 \text{ M}; 17.1 \text{ mmol OH}^{-}; 61.2 \text{ mL}\)

2.2 Mole fractions: \( \text{N}_2 = 0.17; \ \text{O}_2 = 0.41; \ \text{He} = 0.41 \)

2.3 a) 20.\% b) 3.0 ppm  c) 25 ppb

2.4 1.2 ppb \( \text{Ag}^{+} \)

2.5 78.8 g \( \text{H}_2\text{O} \)

2.6 Mole fractions: \( \text{H}_2\text{SO}_4 = 0.0730; \ \text{H}_2\text{O} = 0.927 \)
molarity = 3.73 M; molality = 4.37 m

2.7 \( A = 40.0 \text{ mM}; \ B = 5.33 \text{ mM}; \ C = 0.427 \text{ mM} \)

2.8 \( \varepsilon = 1.39 \times 10^5 \text{ M}^{-1}\cdot\text{cm}^{-1}; \ c = 1.34 \mu\text{m} \)

2.9 \( \text{Ag}_3\text{PO}_4; \ 418.58 \text{ mg/mmol}; \ 2.605 \text{ mmol}; \ 0.0521 \text{ M} \)

2.10 \( \text{Pb}^{2+} + 2\text{Cl}^{-} \rightarrow \text{PbCl}_2; \ 714 \text{ mg PbCl}_2; \ [\text{Pb}^{2+}] = 11.2 \text{ mM} \)

2.11 3.743 mmol \( \text{OH}^{-}; \ [\text{OH}^{-}] = 0.1125 \text{ M} \)

2.12 4.452 mmol \( \text{Fe}^{2+}; \ 28.73\% \)

2.13 \( \text{CaSO}_4 = 2; \ \text{Ba(OH)}_2 = 3; \ \text{CH}_3\text{OH} = 1; \)
\( \text{HCl} = 2; \ \text{NH}_4\text{ClO} = 2; \ \text{SF}_4 = 1 \)

2.14 \( T_1 = -31.3 ^\circ\text{C}; \ T_b = 108.6 ^\circ\text{C}; \ P = 13.4 \text{ torr} \)

2.15 \( V = 0.14 \text{ L}; \ M_c = 12 \text{ M}; \ \pi = 3.1 \times 10^2 \text{ atm} \)
1. vapor pressure lowering  \[ \Delta P = X_{\text{solute}}P^0 \]
2. boiling point elevation  \[ \Delta T_b = k_b m_c = i k_b m \]
3. freezing point depression  \[ \Delta T_f = k_f m_c = i k_f m \]
4. osmotic pressure  \[ \pi = M_c RT = i M R T \]

Colloids are suspensions of very small (1 nm to 1 \( \mu m \)) particles that can stay suspended for years.

After studying the material in this chapter, you should be able to:

1. determine the molarity, molality, mole fraction, and mass fraction of a solution from the amounts of solute and solvent or solution (Section 2.1);
2. determine the number of moles in a volume of solution of known molarity (Section 2.1);
3. prepare a solution given the volume and concentration of the solution (Section 2.1);
4. use prefixes m (milli), \( \mu \) (micro) and n (nano) (Section 2.1);
5. convert between different concentration units (Section 2.2);
6. calculate the concentration of a solution after a dilution (Section 2.3);
7. dilute solution of known concentration to one of a desired concentration (Section 2.3);
8. use Beer's Law to determine the concentration of a solution (Section 2.4);
9. determine the limiting reactant from a balanced chemical equation and the concentrations and volumes of the reactants (Section 2.4);
10. determine the volume of one reactant of known concentration that reacts with a known volume of another of known concentration (Section 2.4);
11. determine the concentrations of the excess reactants (Section 2.4);
12. describe the causes of the colligative properties at the molecular level (Section 2.5);
13. determine the van't Hoff factor (i) for a compound (Section 2.5);
14. convert normal concentrations into colligative concentrations (Section 2.5);
15. calculate the vapor pressure of a solution given the mole fraction of the solute and the vapor pressure of the solvent (Section 2.5);
16. determine the boiling and freezing points of a solution from the solute concentration and the boiling and freezing point depression constants of the solvent (Section 2.5);
17. determine the osmotic pressure of a solution of known concentration (Section 2.5);
18. explain how osmosis is important in biological systems (Section 2.5);
19. explain the utility of reverse osmosis (Section 2.5);
20. distinguish between a colloid and a solute (Section 2.6); and
21. name the five classes of colloids and give an example of each (Section 2.6).
2.7 EXERCISES

CONCENTRATION UNITS
1. How many grams of CuSO₄ are required to make 650. mL of a 0.115 M solution?
2. How many grams of NaCl are required to prepare 250. mL of a 0.241 M solution?
3. How many grams of Na₂SO₄ are required to make 90.0 mL of a solution that is 0.200 M in Na¹⁺?
4. How many mmoles of each ion are present in 325 mL of a 0.0817 M solution of K₂Cr₂O₇?
5. How many mmoles of chloride ion are in 55.0 mL of 0.0688 M BaCl₂ solution?
6. How many mL of a 0.338 M Na₃PO₄ are required to deliver 23.6 mmol of sodium ion?
7. How many mL of 0.124 M Ba(OH)₂ are required to deliver 38.6 mmol of hydroxide ion?
8. How many mL of a 0.125 M aqueous solution of NaNO₃ could be made from 3.50 g of NaNO₃?
9. How many grams of sodium should be added to 15.0 g Hg to make a mixture in which the mole fraction of sodium is 0.800?
10. Drinking water in the USA cannot exceed 0.5 ppm mercury. What mass of mercury is present in 1.0 L of water at this concentration? What is the molar concentration of mercury?
11. The density of a 1.140 M solution of NH₄Cl at 20 °C is 1.0186 g·mL⁻¹. What mass of water does 100. mL of this solution contain?
12. What is the mass percent sucrose in a 0.180 M aqueous solution of sucrose (C₁₂H₂₂O₁₁, Mₘ = 342 g·mol⁻¹)?
13. What mass of Fe(ClO₄)₃ is required to make 275 mL of a solution that is 0.100 M in ClO₄¹⁻?
14. How many grams of Na₂SO₄ should be added to 285 g of water to make a solution with a colligative molality of 0.500 m?
15. How many grams of CaCl₂ should be added to 50.0 g of water to make a solution in which the mole fraction of Cl⁻ is 0.150?

CHANGING CONCENTRATION UNITS
16. The label on a bottle of vinegar indicates that it is 4.2% acetic acid (CH₃COOH). If the density of the solution is 1.01 g·mL⁻¹, what is the molarity of the solution?
17. Concentrated H₃PO₄ is 75% and has a density of 1.57 g·mL⁻¹. a) What is the molarity of concentrated phosphoric acid?
   b) How many mL of the concentrated acid would be required to prepare 1.5 L of a 0.20 M solution of H₃PO₄?
18. The concentration of grain alcohol (C₂H₅OH) in whisky is given in ‘proof’, which is twice the percent alcohol by volume (v/v). What are the mole fraction and molality of C₂H₅OH in 90 proof vodka? Assume that vodka is a solution of only C₂H₅OH and water and that the volumes are additive. The density of C₂H₅OH is 0.79 g·mL⁻¹.
19. A 60/40 solder is a solution that is 60% Pb and 40% Sn. What are the two mole fractions in the solder?
20. The solubility of Mg₃(PO₄)₂ is 6 μM. How many ppm of magnesium ion are in a saturated solution?
21. What is the molality of a sucrose solution if its mole fraction is 0.025?
22. Cisplatin, (NH₃)₂Cl₂Pt, is a chemotherapy agent for the treatment of some cancers. Determine the mass of cisplatin in 100. mL of each of the following solutions: a) 1.0 μM (NH₃)₂Cl₂Pt b) 1.0 ppm (NH₃)₂Cl₂Pt c) 1.0 ppm (NH₃)₂Cl₂Pt
23. Pure, crystalline Si is a poor conductor, but it can be converted into a p-type semiconductor by dissolving 1.0 ppm Ga in the Si crystal. This is a process called “doping” in the semiconductor industry. Given that the molar mass of Si is 28.086 and of Ga is 69.72, what is the mole fraction of Ga in the crystal? The density of the p-type Si semiconductor is 2.33 g·cm⁻³.
24. What is the concentration of CaCl₂ expressed as percent in an aqueous solution that is 0.820 M in CaCl₂ and has a density of 1.070 g·mL⁻¹.
25. What is the molality of a 2.06 M solution of H₂SO₄ (d = 1.124 g·mL⁻¹)?
26. 265 mL of a 0.125 M NaCl solution is left uncovered. What is the molarity of the solution if evaporation reduces the volume to 186 mL?

27. What is the molarity of a solution prepared by adding 30.0 mL of water to 57.0 mL of a 0.114 M CuSO₄ solution? Assume additive volumes.

28. To what volume should 10 mL of 12 M HF be diluted to make 0.50 M HF?

29. What volume of an 18.0 M stock solution of H₂SO₄ is needed in order to make 100. mL of 3.0 M H₂SO₄ solution?

30. How many mL of 9.85 M H₂SO₄ are needed to prepare 500. mL of 0.0850 M H₂SO₄?

31. What is the [H⁺] in a solution prepared by diluting 20.0 mL of 12.0 M HCl to 350. mL?

32. What is the [H⁺] in a solution prepared by mixing 1.0 L of 2.0 M HCl, 1.6 L of 0.80 M HCl, 0.50 L of 3.0 M HCl, and 1.4 L of water?

33. What is the molarity of the chloride ion in a solution prepared by mixing 75 mL of 0.20 M NaCl and 55 mL of 0.15 M MgCl₂? Assume that volumes are additive.

34. 20.0 mL of 2.50 M stock solution is diluted to 50.0 mL. A 15.0-mL sample of the resulting solution is then diluted to 45.0 mL. A 20.0-mL sample of this solution is then diluted to 75.0 mL. What is the concentration of sucrose in the final solution?

35. 100.0 mL of a stock solution of hydrochloric acid was diluted to 250.0 mL. A 10.0-mL sample of the resulting solution was then diluted to 250.0 mL. The final solution was prepared by diluting 30.0 mL of this solution to 100.0 mL. A 40.0-mL sample of the final solution was titrated with 0.0887 M NaOH. If the titration required 32.6 mL of the base, what is the concentration of the original stock solution?

36. A solution, which is prepared by four consecutive 1:4 dilutions of a stock solution, has a concentration of 0.244 mM. What is the concentration of the stock solution?

37. A stock solution that is 0.4762 M undergoes the following successive dilutions: 1:3, 2:5, 1:10, and 2:15. What is the concentration of the final solution?

BEER’S LAW

38. The manganese concentration in steel can be determined spectrophotometrically by dissolving the steel in acid and oxidizing Mn to MnO₄⁻. The resulting solution is purple and the absorbance at 525 nm can be monitored. A standard solution that is 0.228 mM in MnO₄⁻ has an absorbance of 0.343 in a 1.00-cm cell. The absorbance of an unknown manganese solution in the same cell is 0.468. What is the molar concentration of Mn in the unknown solution?

39. Formaldehyde, CH₂O (Mₘ = 30.03 g mol⁻¹), is an atmospheric pollutant that can be measured in aqueous solutions by reaction with 1,3,5-trihydroxy-benzene to produce a red-orange dye. A standard solution was prepared by dissolving 1.50 mL of formaldehyde gas (at 1.00 atm pressure and 25 °C) in 1.00 L of water. This solution was treated with an excess of 1,3,5-trihydroxy-benzene. A couple of milliliters of the resulting solution was placed in a spectrophotometric cell with a thickness of 1.00 cm and the absorbance was found to be 0.967 at 470 nm. A 1.00-L sample of rainwater was similarly treated and the absorbance, measured in the same cell, was determined to be 0.426. What is the concentration of formaldehyde in the rainwater? Express your answer in both molar and ppm units.

40. A 2.78x10⁻⁴ M solution has an absorbance of 0.449 at 520 nm in a 1.00-cm cell. The solvent’s absorbance under the same conditions is 0.012.
   a) What is the molar absorptivity of the solute?
   b) What is the solute concentration in a solution with an absorbance of 0.368 in a 1.00-cm cell at 520 nm?

41. Ru(bpy)₂⁺ (bpy = 2,2’-bipyridine) was investigated for its possible use in solar energy conversion. A solution was prepared by dissolving 58.2 mg Ru(bpy)₂(ClO₄)₂ (Mₘ = 612 g mol⁻¹) in enough water to make 100.0 mL of solution. However, the resulting solution absorbed too strongly at 450 nm to be measured, so 5.0 mL of the solution was diluted to 100.0 mL. The absorbance of the final solution at 450 nm in a 1.00-cm cell was determined to be 0.571.
   a) What is the molar absorptivity of Ru(bpy)₂⁺ at 450 nm?
   b) What is the concentration of Ru(bpy)₂⁺ in a solution with an absorbance of 0.885 at 450 nm?
42. Ammonia can be determined spectrophotometrically by reaction with phenol (C₆H₅OH) in the presence of OCl⁻ ion. The product of the reaction absorbs at 625 nm. The nitrogen in a protein was determined in the following manner.

a) Reference: A solution was made by dissolving 10.0 mg NH₄Cl in water. Phenol and KOCl were then added. After reaction, the solution was diluted to 1.00 L. 20.0 mL of the solution was then diluted to 100.0 mL, and the absorbance was found to be 0.168 at 625 nm. What is the molar absorptivity of the product of the reaction between ammonia and phenol in the presence of hypochlorite?

b) Sample: All of the nitrogen in 5.02 mg of a protein was converted into ammonia. Then phenol and KOCl were added. After the reaction, the solution was diluted to 500. mL and the absorbance was measured to be 0.564 at 625 nm. How many mmoles of nitrogen were in the original sample? What is the mass percent of nitrogen in the protein?

COLLIGATIVE PROPERTIES

43. What is the colligative molality of a solution prepared by dissolving 15.2 g of AlCl₃ (Mₘ = 133.3 g·mol⁻¹) in 155 mL of water?

44. List the freezing points of 0.10 m aqueous solution of the following in decreasing order. Explain your reasoning.

C₁₂H₂₂O₁₁ CaCl₂ CaSO₄

45. What is the freezing point of a 0.11 m aqueous CaCl₂ solution?

46. What is the osmotic pressure of a 0.056 M aqueous NaCl at 298 K?

47. What is the osmotic pressure of a 0.20 M CaCl₂ solution at 298 K?

48. As a very rough general rule, increasing the temperature of a reaction by 10 °C doubles the rate of reaction. Approximately how many grams of salt should be added to 1.5 qts (~ 1.5 L) of water to increase the boiling water by 10 °C? Would this be a satisfactory way in which to reduce the time required to make “boiled potatoes”?

49. A solution is prepared by dissolving 1.0 g of CaCl₂ in 100. mL of water to produce a solution with a density 1.1 g·mL⁻¹.

a) What is the vapor pressure of the solution at 20 °C? The vapor pressure of water at 20 °C is 17.5 mm Hg.

b) What is the boiling point of the solution?

c) What is the freezing point of the solution?

d) What osmotic pressure would develop at 25 °C when the solution is placed in contact with pure water at a semipermeable membrane?

50. The colligative molality of seawater is about 1.10 m, and its density is about 1.05 g·mL⁻¹.

a) What is the vapor pressure of the solution at 20 °C? The vapor pressure of water at 20 °C is 17.5 mm Hg.

b) What is the normal boiling point of seawater?

c) What is the freezing point of seawater?

51. The colligative molarity of living cells is typically 0.3 M. What osmotic pressure would develop when the cells are placed in pure water at 37 °C? What effect would this have on the cell?

52. Pepsin is the principal digestive enzyme of gastric juice. A 1.50-g sample of pepsin is dissolved in enough water to make 5.00 mL of solution. The osmotic pressure of the solution is found to be 0.213 atm at 25 °C. What is the molar mass of pepsin?

53. 15.8 mg of a protein is dissolved in enough water to make a 5.00-mL solution. What is the molar mass of the protein if the osmotic pressure of the solution at 15 °C is 4.65 torr?

54. A solution is prepared by dissolving 1.63 g of an unknown organic compound in 15.00 g of cyclohexane. What is the molar mass of the compound if the solution has a melting point of -5.1 °C? See Table 2.4 for information about cyclohexane.

55. Vitamin K is involved in normal blood clotting. When 1.00 g of vitamin K is dissolved in 20.0 g of camphor, (k_f = 40.0 °C·m⁻¹) the freezing point of the solution is lowered by 4.43 °C. What is the molar mass of vitamin K?
SOLUTION STOICHIOMETRY

56. Alcohol levels can be determined by reaction with dichromate (breathalyzer).
\[
\text{C}_2\text{H}_5\text{OH}(l) + 2\text{Cr}_2\text{O}_7^{2-}(aq) + 16\text{H}^+(aq) \rightarrow 4\text{Cr}^{3+}(aq) + 11\text{H}_2\text{O}(l) + 2\text{CO}_2(g)
\]
What is the alcohol level expressed in parts per thousand of a blood plasma if a 30.0-g sample of plasma requires 27.43 mL of a 0.02226-M solution of K_2Cr_2O_7 for complete reaction?

57. What is the concentration of the excess reactant in a solution prepared by mixing 25.0 mL of 0.242 M HCl with 36.3 mL of 0.167 M Ba(OH)_2? Is this solution acidic, basic or neutral?

58. Given the unbalanced chemical equation:
\[
\text{___Al(OH)}_3(s) + \text{___HCl(aq)} \rightarrow \text{___AlCl}_3(aq) + \text{___H}_2\text{O(l)}
\]
How many mL of 2.00 M HCl are required to react completely with 50.0 g of Al(OH)_3?

59. Determine the amount of precipitate that will form if 50.0 mL of 0.100 M Na_2SO_4(aq) and 100. mL of 0.300 M BaCl_2 are mixed.

60. Construct the reaction table for the net reaction resulting when 45.0 mL of 0.0886 M AgNO_3 and 35.0 mL of 0.106 M K_2CrO_4 are mixed.
   a) What mass of precipitate would form?
   b) Assume additive volumes and determine the concentration of the excess reactant after the reaction is complete?

61. Construct the reaction table for the net reaction of 36.6 mL of 0.0668 M FeCl_3 and 24.2 mL of 0.100 K_2S.
   a) What mass of FeS_3 precipitates?
   b) What is the concentration of the excess reactant after complete reaction? Assume additive volumes.

MISCELLANEOUS PROBLEMS

62. Trichloroethylene, C_2HCl_3 is used as a dry cleaning solvent and an industrial extraction agent. The EPA (Environmental Protection Agency) has set a limit of 5.0 ppb C_2HCl_3 in drinking water. Assuming that the average person consumes 2.0 L of drinking water in a day, what is the maximum mass of trichloroethylene to which a person could be exposed through drinking water? Drinking water has a density of 1.0 g·mL⁻¹.

63. Given the unbalanced chemical equation:
\[
\text{___Zn(s) + ___HCl(aq)} \rightarrow \text{___H}_2(g) + \text{___ZnCl}_2(aq)
\]
If 130. mL of HCl(aq) reacts with an excess of Zn, the reaction produces 7.00 L of H_2(g) at 273 K and 1.00 atm. What is the molarity of the HCl?

64. A 0.250 m aqueous solution of Co(NH_3)_6Cl_3 freezes at -0.93 °C. Determine the van’t Hoff factor for the complex ion.

65. A solution is prepared by dissolving 5.863 g of impure NaOH in sufficient water to make 1.00 L of solution. The solution is added to a buret and used to titrate 25.00 mL of a 0.1173 M solution of HCl.
   a) What is the molarity of the NaOH solution if the titration requires 28.04 mL of base.
   b) What is the percent purity of the original NaOH sample?

66. A 0.5843-g sample of impure Ca(OH)_2 is dissolved in 50.00 mL of water. 20.00 mL of the resulting solution is then titrated with 0.1164 M HCl. What is the percent purity of the Ca(OH)_2 if the titration requires 22.18 mL of acid?

67. A 10.00-mL sample of blood was diluted to 100.00 mL. 10.00 mL of the resulting solution was analyzed for calcium by precipitating all of the calcium as calcium oxalate, CaC_2O_4. The solid CaC_2O_4 was then re-dissolved in H_2SO_4 and titrated with KMnO_4. What is the Ca^{2+} ion concentration in the blood sample expressed as (milligrams Ca^{2+})/(mL blood) if the endpoint was reached with the addition of 1.14 mL of 0.00886 M KMnO_4?

5 C_2O_4^{2-} + 2MnO_4^{-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O

68. Vitamin C or ascorbic acid (C_6H_8O_6) can be analyzed by first oxidizing it with an excess of I_2 by the following reaction:
   \[
   \text{C}_6\text{H}_8\text{O}_6 + \text{I}_2 \rightarrow \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 2\text{I}^- + 2\text{H}_2\text{O}
   \]
   and then determining the amount of excess I_2 by titration with S_2O_3^{2-}.
   \[
   \text{I}_2 + \text{2S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}
   \]
A tablet that is supposed to contain 500-mg of vitamin C was dissolved in water and 100.00 mL of 0.06246 M I_2 was added. After complete oxidation of the ascorbic acid, the solution was titrated with S_2O_3^{2-}. How many milligrams of vitamin C were in the tablet if the titration required 63.69 mL of 0.1127 M K_2S_2O_3?
69. All of the iron in 1.314 g of an ore was converted to Fe\(^{2+}\), which was then analyzed by titration with dichromate. What is the mass percent of iron in the ore if 38.64 mL of 0.02063 M K\(_2\)Cr\(_2\)O\(_7\) was required to reach the equivalence point? The chemical equation for the titration is
\[
14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

70. The chloride ion concentration in a sample of seawater was analyzed by titration with 0.1126 M AgNO\(_3\) to precipitate AgCl. What is the chloride ion concentration in a 10.00-mL sample, if the titration required 46.78 mL of 0.1126 M AgNO\(_3\) to reach the endpoint? If the density of seawater is 1.012 g·mL\(^{-1}\), what is the mass percent of chloride ion in the sample?

71. The concentration of a stock solution of Rhodamine B, a commercial dye (\(\varepsilon = 1.060 \times 10^5 \text{ M}^{-1} \text{cm}^{-1}\) at 543 nm) is determined spectrophotometrically, but the absorbance of the stock solution was too great to read on a spectrometer, so 15.00 mL of the solution was diluted to 250.00 mL. The resulting solution was still too concentrated, so 10.00 mL of that solution was diluted to 500.00 mL, but the solution was still too concentrated. However, a dilution of 25.00 mL of the resulting solution to a final volume of 500.00 mL provided an acceptable solution with an absorbance of 0.1814 in a 1.000-cm cell. What is the concentration of the stock solution? What volume of stock solution would be required to make 2.000 L of a solution with an absorbance of 1.000 in a 1.000-cm cell?

72. What is the iron(III) concentration in an acidified solution if adding an excess of hydroxide to 20.00 mL of the solution produced 181 mg of Fe(OH)\(_3\)?

73. How many grams of NaCl must be added to 120 mL of water at 25 °C to prepare a solution with a vapor pressure of 20.0 torr? At 25 °C, the density of water is 1.0 g·mL\(^{-1}\), and its vapor pressure is 23.8 torr.