6 Wet Chemistry: The Science of Substances in Solution

Learning Objectives

As you work through this chapter you will learn how to:

- describe the dissolving process in terms of the interactions between molecules and ions.
- identify substances that are electrical conductors.
- determine the concentration of a solution.
- use molarity in dilution calculations.
- use molarity in stoichiometric calculations.
- describe acid-base titration chemistry.

6.1 General Characteristics of Solutions

You may remember from Chapter 3 that a solution is a homogeneous mixture. This means that it has a uniform composition throughout. The major component of a solution is called the **solvent** and a minor component is called a **solute**. When table salt dissolves in water to form an aqueous solution, water is the solvent and the salt is the solute. Usually a solution has the same physical state as the solvent. Homogeneous mixtures can be formed from a variety of solvents and solutes. For example, carbonated beverages contain dissolved solids, liquids and a gas (CO_2) as solutes with water as the solvent. In brass, copper metal is the solvent with zinc as the primary solute and various amounts of other metals including aluminum, nickel and iron as additional solutes. Clear vodka is an aqueous solution with ethyl alcohol as the main solute.

By definition a solution (a homogeneous mixture) does not have a specific composition. There may be very little solute dissolved in the solvent (a **dilute solution**) or a large amount of solute dissolved in the solvent (a **concentrated solution**). However, in both types of solutions the composition is the same throughout. Even though a solution is not a pure substance, if the composition of a solution is known, then chemists are more inclined to use this solution in experiments because they know what each sample of the solution consists of. Section 6.3 discusses various ways to describe solutions quantitatively.

Finally, many chemical reactions only occur efficiently in solution. Reactant molecules or ions must collide in order to react, and dissolving solid reactants in a liquid solvent creates mobile molecules and ions that can more easily interact.

6.2 The Dissolving Process

Most of you have probably watched a sample of table salt (mostly NaCl) disappear when it is placed in a container of water and stirred. Have you ever wondered what causes it to dissolve and why the salt disappears? In order to answer these questions we need to look at the dissolving process at the atomic level. Recall that an ionic compound like NaCl consists of oppositely charged ions held in place by strong electrostatic attractions between the cations and anions. The ions are held together in a 3-dimensional packing arrangement (Fig. 3.7). Since these ions are not free to move around, an ionic solid will not conduct an electric current. **Electrical conductivity** requires the presence of mobile electric charges. In solid conductors such as copper and silver, these mobile charges are electrons that are loosely bound to the nuclei of the metal atoms. For other conductors these mobile charges may be ions. If you heat a sample of NaCl until it melts (this requires a temperature greater than 800 °C) you will find that the molten salt is an electrical conductor because the ions are now able to move somewhat freely.

The ability of various substances to conduct an electric current can be monitored easily using a simple electrical circuit such as that diagrammed in Figure 6.1. The circuit

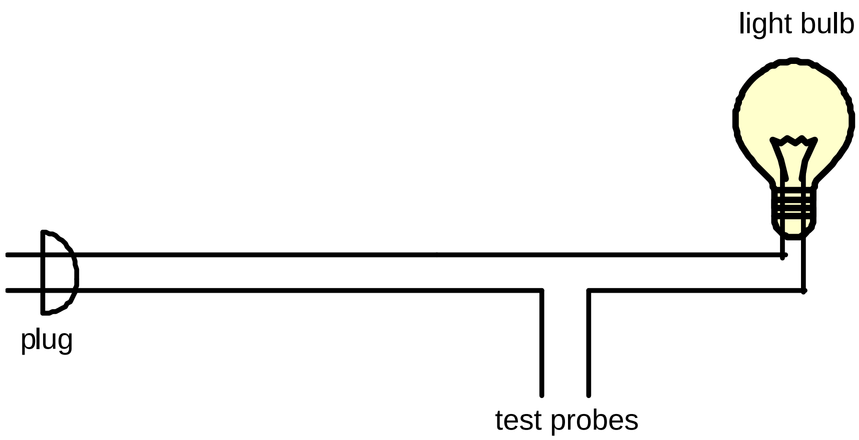
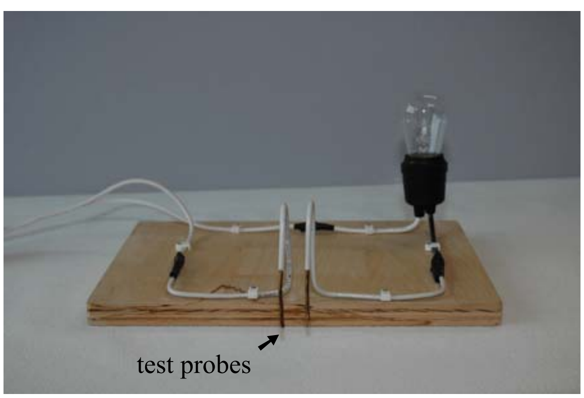
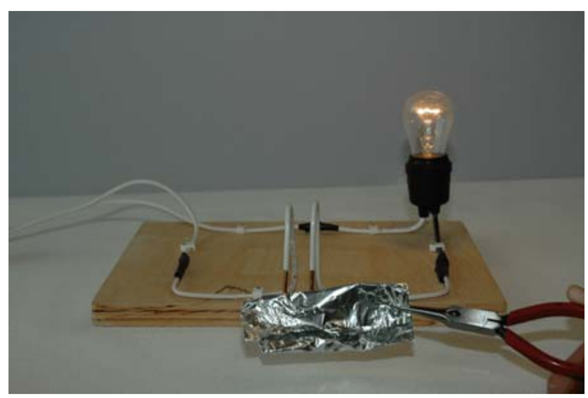


Figure 6.1 Simple circuit to measure electrical conductivity

consists of a plug, copper wire, a light bulb and two copper test probes. When this circuit is plugged into an electrical outlet no current flows in the circuit because there is a nonconducting gap between the two probes (Fig. 6.2a). However, if an electrical conductor, such as a piece of aluminum foil, is then placed in contact with the two probes, current flows in the completed circuit and the light bulb lights up (Fig. 6.2b).



(a)



(b)

Figure 6.2 Simple conductivity test circuit with (a) no conductor between the test probes and (b) aluminum foil placed between the probes

By placing various substances in contact with both probes the electrical conductivity of each substance can be assessed. No light indicates a nonconductor (few, if any, mobile charges are present), a bright light means a good conductor (numerous mobile charges are present), and a faint light means a weak conductor (some mobile charges are present).

If the probes are placed in pure water the bulb does not light up. Water is a molecular substance and the molecules are electrically neutral. Thus, there are no mobile charges present and water is a nonconductor.[1] This is the general result for pure molecular substances such as table sugar ($C_{12}H_{22}O_{11}$) and carbon tetrachloride (CCl_4).

Look what happens when NaCl (a nonconductor) is dissolved in water (a nonconductor). When you put the probes in a salt water mixture the light bulb shines very brightly, indicating the presence of many mobile ions and a good electrical conductor. Where are the mobile charges coming from? When the salt dissolves the 3-dimensional array of ions breaks apart and the ions become mobile. But how can these opposite charges suddenly break away from each other and move around in solution? The reason for this has to do with the attractions that develop between the sodium cations and chloride anions in the salt lattice and the water molecules.

Recall that water is a 3-atom, bent molecule (Fig. 3.8) in which the oxygen atom is bonded to each hydrogen atom by a covalent bond. Each oxygen and hydrogen atom are held closely together because their nuclei have strong attractions for the same electron cloud (they share electrons). This covalent bonding between oxygen and hydrogen can be represented using the notation O—H in which the dash (—) between the symbols of the elements indicates the shared electrons.

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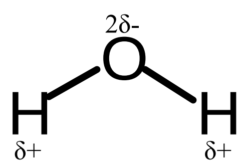
[1]Water molecules actually break apart to form H^+ ions and OH^- ions to a very limited extent. However, only about two in every billion water molecules ionize in this way in pure water. A simple circuit such as that described above is not sensitive enough to detect these.

Often when two atoms form a covalent bond the attraction for the “shared electrons” is essentially the same. When the two atoms are identical, such as in a nitrogen molecule (N_2), the electron sharing is exactly equal and the electron cloud is evenly (symmetrically) dispersed between the atoms. A molecule having an average electric charge distribution that is neutral throughout is referred as a **nonpolar molecule**. All of the elements that exist as diatomic molecules are nonpolar. However, when oxygen is covalently bonded to hydrogen, the oxygen atom has a stronger attraction for the electron cloud than the hydrogen atom. As a result, the shared electrons are drawn closer to the oxygen atom and away from the hydrogen atom. This asymmetric or uneven electron cloud distribution causes a partial negative charge (δ-) to develop at the oxygen atom and a partial positive charge (δ+) to develop at the hydrogen atom. Because there is a permanent separation of electric charge due to the unequal sharing of electrons, the water molecule is known as a **polar molecule**. The partial charges in water can be represented as:



Since the oxygen atom is drawing shared electrons from both hydrogen atoms toward it, it has a partial charge of 2δ-. Even though there is an uneven charge distribution, the water molecule is not an ion; it does not have a net electric charge.

When an ionic solid such as NaCl is placed in water the partially charged portions of the water molecule can interact with the cations and anions of the ionic compound. The oxygen end of water will have an electrostatic attraction for the positively-charged sodium ions, and the hydrogen end will have an electrostatic attraction for the negatively-charged chloride ions. If the attractions between the cations and anions in the ionic compound are not too strong (as when you have +1 and -1 ions such as for NaCl), the cumulative effect of many water molecules exerting a small attraction toward an ion in the solid causes the ions to separate and stay apart as many water molecules cluster around each type of ion; the salt dissolves. These interactions between polar water molecules and the constituent ions of an ionic compound are represented in Figure 6.3.

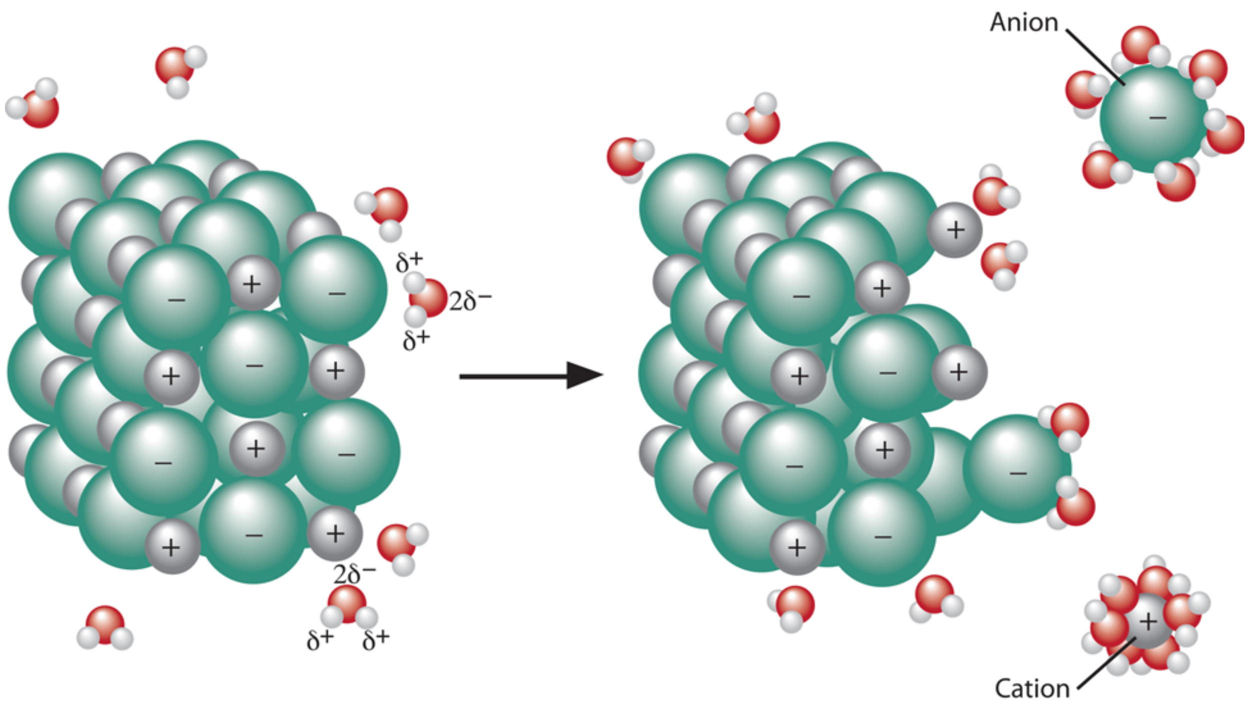


Figure 6.3 Polar water molecules interacting with the ions of an ionic compound causing it to dissolve

The separated ions, surrounded by a coating of water molecules and designated with the (aq) notation, are now mobile in solution so this mixture is an electrical conductor. Since NaCl is very soluble in water, there are many mobile ions present and an aqueous solution of NaCl is a good electrical conductor. This is a general result; whenever an ionic compound readily dissolves in water the solution is a good electrical conductor. A substance that ionizes or dissociates into ions in water is called an **electrolyte**. Some electrolytes, such as KNO_3, contain polyatomic ions. When such a salt dissolves in water, the polyatomic ion (NO_3^-) remains intact as it gets surrounded by water molecules.

When a molecular substance such as sugar dissolves in water, the individual molecules in the solid separate from each other and become mobile as they are surrounded by water molecules. However, since both the sugar and water molecules have no net electric charge there are no mobile charges and the solution is nonconducting. If the test probes are placed in an aqueous sugar solution the light bulb will not go on. Molecular substances tend to be **nonelectrolytes**, however, there is an important exception to this trend. If the molecular substance is an acid, such as nitric acid (HNO_3), when it dissolves in water the molecule breaks apart into a H^+ ion and the corresponding anion (NO_3^-). Now you have mobile ions and the solution is an electrical conductor. If the test probes are placed in a nitric acid solution the light bulb will shine brightly. So it is important to remember that both soluble salts and acids are electrolytes.

Take note that not all molecular or ionic substances readily dissolve in water. As was noted in Chapter 4, ionic compounds that consist of highly charged ions tend to be insoluble. The attractions of these ions to the polar water molecules are not sufficient to overcome the electrostatic attractions between such ions. A molecular substance like sugar readily dissolves in water because it, like water, is a polar molecule and can develop significant electrostatic attractions with polar water. However, molecular substances like gasoline and vegetable oil do not significantly dissolve in or mix with water. These substances are composed of nonpolar molecules. The electron sharing in the hydrocarbon molecules found in gasoline is nearly equal so the molecules do not have partially charged regions like in water. This minimizes the electrostatic attractions that can develop between the hydrocarbon molecules of gasoline and water, and prevents water from separating them from each other and thus dissolving them. Carbon tetrachloride (CCl_4) is another nonpolar molecular substance that does not mix with water. The electron sharing between the C and Cl atoms is not equal, but the molecule is nonpolar because the electron cloud is symmetrically distributed among the atoms in this molecule because of its particular shape.

These results suggest a very fundamental connection between the atomic structure of a substance and its properties, and have led to the adage:

"like dissolves like."

This means that ionic solutes and polar solutes tend to dissolve in polar solvents, and nonpolar solutes tend to dissolve in nonpolar solvents. This explains why gasoline, composed of mostly nonpolar hydrocarbon molecules like C_8H_{18}, does not mix with polar water but will mix with vegetable oil. Take note that nonpolar solutes like O_2 can dissolve in polar solvents like water, but only to a very limited extent. In subsequent chemistry classes you will learn how to predict the geometry of molecules and determine if a molecule is polar or nonpolar. This will enable you to anticipate its properties, such as its solubility in water or its boiling point relative to another substance.

This model of the dissolving process also accounts for why the sample of table salt disappears as it dissolves.[2] When a teaspoon of table salt dissolves in a cup of water the separated ions are not visible because the individual Na^+ and Cl^- ions are too small to be seen and they are vastly outnumbered by the water molecules. In this case there are about 75 water molecules for every ion in solution. We only see the solid table salt sample because it consists of a very large number ($>10^{15}$) of these ions arranged in a 3-dimensional structure. This situation is somewhat analogous to a group of kindergarten students each wearing the same brightly colored t-shirt going to the mall. As a group they are quite conspicuous, but if the group is completely dispersed among a large crowd of shoppers the individual students will not stand out.

Check for Understanding 6.1 **Solutions**

1. Indicate whether each of the following is a good electrical conductor.

   a) mixture of $CaCl_2(s)$ and $H_2O(l)$

   b) $Na(s)$

   c) mixture of $CH_3OH(l)$ and $H_2O(l)$

   d) $Br_2(l)$

   e) mixture of $CaCO_3(s)$ and $H_2O(l)$

   f) $HCl(aq)$

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[2]Even though the salt disappears it remains in the water. Can you think of a simple experiment to show this?

6.3 Solution Composition

The relative amount of solvent and solute in a solution is indicated by the **concentration**. Two quantities that we have already discussed, density and mass percent, vary with the concentration of a solution. The solution density (d_{soln}) is given by:

$$d_{soln} = \frac{\text{mass of solution}}{\text{volume of solution}}$$

For aqueous solutions, higher solute concentration usually results in a greater solution density.

The solute mass percent is given by

$$\text{mass \% of solute} = \frac{\text{solute mass}}{\text{solution mass}} \text{ x } 100$$

Since solution mass = solvent mass + solute mass,

$$\text{mass \% of solute} = \frac{\text{solute mass}}{\text{solvent mass + solute mass}} \text{ x } 100$$

The higher the solute concentration the greater the mass percent of solute. Mass percent values do not depend on temperature. However, as was noted in Chapter 2, density is temperature dependent since the volume of a substance, especially a liquid, changes with temperature. Example 6.1 illustrates the use of both of these quantities.

Example 6.1

Problem

What is the mass percent of solute in a solution formed by dissolving 6.8 g KCl in 75 mL of water? Assume a water density of 1.0 g/mL.

Solution

What we know: g KCl; mL H_2O; g H_2O/mL

Desired answer: mass % KCl

The mass percent KCl in this solution is given by:

$$\text{mass}\,\%\,\text{KCl} = \frac{\text{g KCl}}{\text{g H}_2\text{O} + \text{g KCl}} \text{ x } 100$$

Since the mass of KCl is given, the only quantity needed is the mass of the water solvent. This can be obtained from the water volume and density values.

The solution map involves two stages. First,

mL H_2O → g H_2O

then,

g H_2O and g KCl → mass % KCl

The conversion factor needed in the first step is the water density in the form $\frac{1.0\,\text{g H}_2\text{O}}{\text{mL H}_2\text{O}}$.

Using this, we see that the 75 mL of water corresponds to a mass of 75 g.

$$75\,\cancel{\text{mL H}_2\text{O}} \text{ x } \frac{1.0\,\text{g H}_2\text{O}}{\cancel{\text{mL H}_2\text{O}}} = 75\,\text{g H}_2\text{O}$$

Combining this with the mass of solute yields the mass percent of KCl.

$$\text{mass}\,\%\,\text{KCl} = \frac{6.8\,\text{g KCl}}{75\,\text{g H}_2\text{O} + 6.8\,\text{g KCl}} \text{ x } 100 = 8.3\%$$

Check for Understanding 6.2 **Solution**

1. Cow's milk typically contains 4.6 % lactose sugar ($C_{12}H_{22}O_{11}$) by mass. What is the mass of lactose present in 8 oz of milk having a mass of 245 g?

Since it is usually much more convenient to dispense a specific volume of an aqueous solution, the most common concentration unit used in chemistry is **molarity** (M). Molarity is defined as

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liter of solution}}$$

Molarity is the conversion factor between a specific volume of a solution and the amount of solute in that volume. Note that it is not necessary to have a liter of solution in order to obtain molarity. All that is required is the mass of solute which can then be converted to moles of solutes and the total volume of solution in which the solute is dissolved. The ratio of these quantities is the solution molarity. An exact solution volume is prepared using a long-necked piece of glassware called a **volumetric flask** (Fig. 6.4). There is a

Figure 6.4 Volumetric flasks of various sizes

calibration mark on the long neck and when the flask is filled to this mark it contains the stated volume of liquid. An aqueous solution having a particular solvent molarity is prepared by dissolving a certain mass of solute in water and diluting the mixture to a specific volume. This is done by the following steps:

- transfer a specific mass of solute to the desired size of volumetric flask containing a small amount of water;
- swirl the mixture to dissolve the solute;
- fill the volumetric flask to the calibration mark with water;
- stopper the flask and thoroughly mix the solution by repeatedly inverting the stoppered flask.

For example, suppose you wish to prepare 500. mL of a 0.100 M (pronounced *molar*) aqueous solution of KCl. The concentration of this solution indicates there is 0.100 mole of KCl per liter of solution. Since you wish to make 500. mL (0.500 L) of solution, you need only 0.0500 mole of KCl. The molar mass of KCl is 74.55 g/mol, therefore 0.0500 mol of KCl weighs:

$$0.0500\,\cancel{\text{mol KCl}} \text{ x } \frac{74.55\text{ g KCl}}{1\,\cancel{\text{mol KCl}}} = 3.73\text{ g KCl}$$

Weigh out this amount of KCl and follow the steps above to prepare the solution. Note that:

$$\frac{0.0500\text{ mol KCl}}{0.500\text{ L solution}} = 0.100\text{ M KCl}$$

Since molarity is based on the solution volume it is temperature dependent like density. Volumetric flasks are calibrated to contain a specified volume at a particular temperature. Notice that molarity and molar mass have the same symbol (M). This could be confusing, but it doesn't need to cause a problem because you will always find the concentration term preceded by a number, such as 0.2003 M, while molar mass is written as an equality with the numerical quantity having units of g/mol. For example, for ammonia (NH_3) the molar mass (M) = 17.03 g/mol.

The volume of a solution used in a typical laboratory experiment is usually much less than a liter so it is convenient to express this volume in milliliters. Your calculations involving molarity can often be simplified by recalling that there are exactly 1000 mL in a liter, thus allowing you to express molarity as:

$$\text{molarity} = \frac{\text{moles of solute}}{1000\,\text{mL of solution}}$$

A unit such as molarity can be looked at in the same way as a mathematical equation involving three quantities. For molarity the three quantities are moles of solute, volume of solution and molarity. If any two of the three quantities are known, the remaining one can be calculated. Rearrangement of the definition of molarity results in the useful expression:

$$\text{mol solute} = M \times V$$

where M is the solute molarity and V is the volume of solution in liters. Thus, if you know the solute concentration you can readily determine how much solute is present in any volume of solution that you use. This relationship is what makes molarity the workhorse concentration unit in chemistry. Examples 6.2 and 6.3 illustrate basic calculations involving molarity.

Example 6.2

Problem

What is the molarity of a solution made by dissolving 0.2491 g Na_2CO_3 in a total volume of 50.0 mL?

Solution

Known information: g Na_2CO_3; mL of solution

Desired answer: mol Na_2CO_3/L solution

Molarity requires two pieces of information: moles Na_2CO_3 and liters of solution. The solution map for this problem is:

$$\frac{\text{g } Na_2CO_3}{\text{mL solution}} \rightarrow \frac{\text{mol } Na_2CO_3}{\text{mL solution}} \rightarrow \frac{\text{mol } Na_2CO_3}{\text{L solution}}$$

The conversion factor needed in the first step is the molar mass of Na_2CO_3 in the form $\frac{1 \text{ mol } Na_2CO_3}{106.0 \text{ g } Na_2CO_3}$.

The conversion factor needed in the second step is $\frac{1 \text{ mL solution}}{10^{-3} \text{ L solution}}$.

Putting these together yields:

$$\frac{0.2491 \cancel{\text{g } Na_2CO_3}}{50.0 \cancel{\text{mL soln}}} \text{ x } \frac{1 \text{ mol } Na_2CO_3}{106.0 \cancel{\text{g } Na_2CO_3}} \text{ x } \frac{1 \cancel{\text{mL soln}}}{10^{-3} \text{ L soln}} = \frac{0.0470 \text{ mol } Na_2CO_3}{\text{L soln}}$$

Thus, the solution concentration is 0.0470 M Na_2CO_3.

Example 6.3

Problem

What mass of $AgNO_3$ is needed to prepare 2.000 L of a 0.2013 M $AgNO_3$ solution?

Solution

What we know: L solution; mol $AgNO_3$/L solution

Desired answer: g $AgNO_3$ needed

The solution map for this problem is:

$$\text{L solution} \rightarrow \text{mol } AgNO_3 \rightarrow \text{g } AgNO_3$$

The conversion factor needed in the first step is the solution concentration in the form $\dfrac{0.2013\,\text{mol } AgNO_3}{\text{L solution}}$.

The conversion factor needed in the second step is the molar mass of $AgNO_3$ in the form $\dfrac{169.9\,\text{g } AgNO_3}{1\,\text{mol } AgNO_3}$.

Putting these together yields:

$$2.000\,\cancel{\text{L solution}} \times \frac{0.2013\,\cancel{\text{mol } AgNO_3}}{\cancel{\text{L solution}}} \times \frac{169.9\,\text{g } AgNO_3}{1\,\cancel{\text{mol } AgNO_3}} = 68.40\ AgNO_3$$

Check for Understanding 6.3 **Solutions**

1. How many moles of HCl are in 23.18 mL of 0.1006 M HCl(aq)?

2. How many grams of $KMnO_4$ are needed to prepare 250. mL of a 0.0988 M $KMnO_4$ solution?

3. What volume (in mL) of 0.2006 M NaOH contains 0.0150 mol NaOH?

When you know the solute mass % and the solution density, you can calculate the solute molarity. In fact, knowing two of these three quantities enables you to calculate the third no matter which two quantities are known. This is illustrated in Example 6.4.

Example 6.4

Problem

What is the molarity of a hydrochloric acid solution that is 37.2% HCl by mass and has a density of 1.19 g/mL?

Solution

What we know: g HCl/100 g solution; g solution/mL solution

Desired answer: mol HCl/L solution

The solution map for this problem is:

$$\frac{\text{g HCl}}{\text{100 g solution}} \rightarrow \frac{\text{g HCl}}{\text{mL solution}} \rightarrow \frac{\text{mol HCl}}{\text{mL solution}} \rightarrow \frac{\text{mol HCl}}{\text{L solution}}$$

The conversion factor needed in the first step is the solution density in the form $\frac{\text{1.19 g solution}}{\text{mL solution}}$.

The conversion factor needed in the second step is the molar mass of HCl in the form $\frac{\text{1 mol HCl}}{\text{36.46 g HCl}}$.

The conversion factor needed in the third step is $\frac{\text{1 mL solution}}{10^{-3}\text{ L solution}}$.

Putting these together yields:

$$\frac{37.2\ \cancel{\text{g HCl}}}{100\ \cancel{\text{g solution}}} \text{ x } \frac{1.19\ \cancel{\text{g solution}}}{\cancel{\text{mL solution}}} \text{ x } \frac{\text{1 mol HCl}}{36.46\ \cancel{\text{g HCl}}} \text{ x } \frac{1\ \cancel{\text{mL solution}}}{10^{-3}\text{ L solution}} = \frac{\text{12.1 mol HCl}}{\text{L solution}}$$

The solution has a HCl concentration of 12.1 M.

Check for Understanding 6.4

Solution

1. A 14.8 M NH_3 aqueous solution has a density of 0.90 g/mL. What is the mass % NH_3 in this solution?

6.4 Dilutions

Acids are usually purchased as concentrated solutions. Often an experiment will require a lower concentration in order to control the rate of the reaction. This is obtained by diluting the concentrated solution. **Dilution** refers to the process of adding solvent to a solution to lower the solute concentration. Since there is no change in the moles of solute as the solvent is added and the total volume increases, the solute molarity will decrease. Mathematically the dilution process can be represented in the following way.

The moles of solute in the initial solution is equal to the molarity of the initial, more concentrated, solution (M_1) times the volume of the initial solution (V_1).

$$(\text{mol solute})_{\text{initial}} = M_1 \times V_1$$

The moles of solute in the final solution is equal to the molarity of the final, diluted solution (M_2) times the volume of the final solution (V_2).

$$(\text{mol solute})_{\text{final}} = M_2 \times V_2$$

Since the moles of solute are constant,

$$(\text{mol solute})_{\text{initial}} = (\text{mol solute})_{\text{final}}$$

Therefore,

$$M_1 \times V_1 = M_2 \times V_2.$$

This relationship can be applied to all dilutions.

dilution equation: $\boldsymbol{M_1V_1 = M_2V_2}$

If any three of the four quantities in the dilution equation are known, the equation can be solved for the remaining quantity. In practice, dilutions are done by taking a specific volume (V_1) of the more concentrated solution with a device known a **pipet**. A transfer pipet is a piece of glassware such as that shown in Figure 6.5. Liquid is drawn into the pipet up to the calibration mark using a bulb and then allowed to flow out under the force of gravity into the appropriate container. Alternatively, a mechanical pipet (Fig. 6.6) can be used. A disposable tip is attached and when the plunger is depressed the tip is submerged in the solution. Slow release of the plunger draws a specific volume of liquid into the tip. The liquid is then dispensed by depressing the plunger again. When a specific (quantitative) dilution is being made a volumetric flask is used to establish V_2 precisely. Examples 6.5 illustrates the application of the dilution equation.

Example 6.5

Problem

What volume of 12.1 M hydrochloric acid is needed to prepare 2.5 L of 2.0 M HCl solution?

Solution

What we know: initial concentration of HCl (M_1); final volume of HCl solution (V_2); final concentration of HCl (M_2)

Desired answer: initial volume of the more concentrated HCl solution (V_1)

Note that this is a dilution problem. Solve the dilution equation for V_1.

$$V_1 = \frac{M_2V_2}{M_1} = \frac{\left(\frac{2.0\ \cancel{\text{mol HCl}}}{\cancel{\text{L dil soln}}}\right)(2.5\ \cancel{\text{L dil soln}})}{\frac{12.1\ \cancel{\text{mol HCl}}}{\text{L conc soln}}} = 0.41\,\text{L}$$

Take note that when using the dilution equation, V_1 and V_2 can be expressed in either mL or L units as long as they are both the same.

Figure 6.5 Liquid being drawn into a transfer pipet. It is calibrated to deliver a fixed volume.

Figure 6.6 Liquid being drawn into the tip of a mechanical pipet

Check for Understanding 6.5 Solution

1. What is the solution concentration if 3.00 mL of 1.83 x 10^{-3} M $FeSO_4$ is diluted to 250. mL?

6.5 Solution Stoichiometry

Since many reactions occur in solution, molarity is a useful conversion factor for stoichiometric calculations. It allows us to connect the volume of a solution to moles of a reactant or product. Examples 6.6 and 6.7 illustrate such calculations.

Example 6.6

Problem

What is the minimum volume (in mL) of 6.0 M HCl(aq) needed to dissolve 3.1 g of aluminum? The balanced equation for this reaction is shown below.

$$2Al(s) \; + \; 6HCl(aq) \; \rightarrow \; 2AlCl_3(aq) \; + \; 3H_2(g)$$

Solution

What we know: mol HCl/L solution; g Al; balanced equation relating HCl and Al

Desired answer: mL HCl solution

The solution map for this problem is:

g Al ➔ mol Al ➔ mol HCl ➔ mL HCl solution

The conversion factor needed in the first step is the molar mass of Al in the form $\dfrac{1\,\text{mol Al}}{26.98\,\text{g Al}}$.

The conversion factor needed in the second step is the mole ratio from the balanced equation in the form $\dfrac{6\,\text{mol HCl}}{2\,\text{mol Al}}$.

The conversion factor needed in the last step is the HCl concentration in the form $\dfrac{1000\,\text{mL solution}}{6.0\,\text{mol HCl}}$.

Putting these together yields:

$$3.1\,\cancel{\text{g Al}} \times \frac{1\,\cancel{\text{mol Al}}}{26.98\,\cancel{\text{g Al}}} \times \frac{6\,\cancel{\text{mol HCl}}}{2\,\cancel{\text{mol Al}}} \times \frac{1000\,\text{mL solution}}{6.0\,\cancel{\text{mol HCl}}} = 57\,\text{mL solution}$$

Example 6.7

Problem

If 125 mL of 0.227 M $FeCl_3$ is mixed with 294 mL of 0.109 M NaOH, what is the theoretical yield in moles of $Fe(OH)_3$? The balanced equation for this reaction is shown below.

$$FeCl_3(aq) + 3NaOH(aq) \rightarrow Fe(OH)_3(s) + 3NaCl(aq)$$

Solution

Known information: mol $FeCl_3$/1000 mL solution; mL $FeCl_3$ solution; mol NaOH/1000 mL solution; mL NaOH solution; balanced equation relating $FeCl_3$, NaOH and $Fe(OH)_3$

Desired answer: maximum mol $Fe(OH)_3$ produced

First determine the limiting reactant by calculating how many moles of $Fe(OH)_3$ can possibly be produced from each starting amount of reactant. The solution maps for these calculations are:

mL $FeCl_3$ soln ➔ mol $FeCl_3$ ➔ mol $Fe(OH)_3$

mL NaOH soln ➔ mol NaOH ➔ mol $Fe(OH)_3$

For the first calculation the conversion factors needed are the molarity of the $FeCl_3$ solution and the $Fe(OH)_3/FeCl_3$ mole ratio.

Putting these together yields:

$$125\,\cancel{\text{mL FeCl}_3\text{ soln}} \times \frac{0.277\,\cancel{\text{mol FeCl}_3}}{1000\,\cancel{\text{mL FeCl}_3\text{ soln}}} \times \frac{1\,\text{mol Fe(OH)}_3}{1\,\cancel{\text{mol FeCl}_3}} = 0.0346\,\text{mol Fe(OH)}_3$$

For the second calculation the conversion factors needed are the molarity of the NaOH solution and the $Fe(OH)_3$/NaOH mole ratio.

Putting these together yields:

$$294\,\cancel{\text{mL NaOH soln}} \times \frac{0.109\,\cancel{\text{mol NaOH}}}{1000\,\cancel{\text{mL NaOH soln}}} \times \frac{1\,\text{mol Fe(OH)}_3}{3\,\cancel{\text{mol NaOH}}} = 0.0107\,\text{mol Fe(OH)}_3$$

Since the starting amount of NaOH solution produces the smaller amount of $Fe(OH)_3$, NaOH is the limiting reactant and the theoretical yield is 0.0107 mol $Fe(OH)_3$.

6.6 Acid-Base Titrations

One of the most common types of chemical reactions that occurs in aqueous solution is a **neutralization reaction** between an acid and a base. Recall that an acid is a substance that produces H^+ ions when dissolved in water. A **base** is a substance, such as NaOH, that produces OH^- ions when dissolved in water.[3] When an acid and a base are present in solution, H^+ ions from the acid combine with OH^- ions from the base to form water molecules. A neutralization reaction is another example of a double displacement reaction. The equation for the neutralization reaction between hydrobromic acid and sodium hydroxide is shown below. Note that the other product in a neutralization reaction is a salt (an ionic compound).

$$\underset{\text{(acid)}}{HBr(aq)} \quad + \quad \underset{\text{(base)}}{NaOH(aq)} \quad \rightarrow \quad \underset{\text{(salt)}}{NaBr(aq)} \quad + \quad \underset{\text{(water)}}{H_2O(l)}$$

Neutralization reactions occur when you treat acid indigestion (heartburn) with a product like TUMS or Rolaids that contains a base, and also occur when you amend soils to promote plant growth by adding a base such as lime or an acid such as ammonium nitrate.

In the laboratory it is often necessary to determine quantitatively the amount of an acid (or base) present in a sample. This can be done by a procedure called an **acid-base titration**. In this process, an acid in one solution is completely reacted with a base in another solution. Knowing the concentration and volume of the base solution used allows you to calculate the moles of base that have reacted. This can then be linked to the moles of acid reacting by a balanced equation for the titration reaction.

[3]In subsequent chemistry classes you will discover that not all bases are ionic compounds containing hydroxide ions. In this class a base will have the formula MOH where *M* represents an alkali metal ion such as Na^+ of K^+.

Consider the titration of a sample such as vinegar, which contains acetic acid, with a base solution containing NaOH. The balanced equation for the titration reaction is

$$\underset{\text{(acid)}}{HC_2H_3O_2(aq)} + \underset{\text{(base)}}{NaOH(aq)} \rightarrow \underset{\text{(salt)}}{NaC_2H_3O_2(aq)} + \underset{\text{(water)}}{H_2O(l)}$$

This indicates that 1 mole of NaOH reacts with each mole of acid present. Suppose it takes 23.61 mL of a 0.1586 M NaOH solution to titrate a 5.00-mL vinegar sample. From this information we can calculate the molarity of the acetic acid in the vinegar. The desired answer will have units of mol $HC_2H_3O_2$/L solution. Since the volume of solution is given (5.00 mL), it is only necessary to determine the moles of $HC_2H_3O_2$ present.

When all of the acetic acid has reacted, the number of moles of acetic acid present in the sample will equal the number of moles of NaOH added. The moles of base added is determined from the base solution concentration and the volume needed to react all of the acid. Let us look at how this calculation is done.

The solution map for solving this problem is

$$\text{mL NaOH soln} \rightarrow \text{mol NaOH soln} \rightarrow \text{mol } HC_2H_3O_2 \rightarrow \text{mol } HC_2H_3O_2/\text{L soln}$$

The conversion factor needed in the first step is the NaOH concentration in the form $\dfrac{0.1586\,\text{mol NaOH}}{1000\,\text{mL NaOH soln}}$.

The conversion factor needed in the second step is the mole ratio from the balanced equation in the form $\dfrac{1\,\text{mol } HC_2H_3O_2}{1\,\text{mol NaOH}}$.

Putting these together yields the moles of $HC_2H_3O_2$.

$$23.61\,\cancel{\text{mL NaOH soln}} \times \frac{0.1586\,\cancel{\text{mol NaOH}}}{1000\,\cancel{\text{mL NaOH soln}}} \times \frac{1\,\text{mol } HC_2H_3O_2}{1\,\cancel{\text{mol NaOH}}} = 0.003745\,\text{mol } HC_2H_3O_2$$

Next, convert the vinegar solution volume from mL to L.

$$5.00\ \cancel{\text{mL vinegar soln}}\ \text{x}\ \frac{10^{-3}\ \text{L vinegar soln}}{1\ \cancel{\text{mL vinegar soln}}} = 0.00500\ \text{L soln}$$

Finally, calculate the molarity of the acetic acid.

$$\text{molarity} = \frac{0.003745\ \text{mol}\ HC_2H_3O_2}{0.00500\ \text{L soln}} = 0.749\ \text{M}\ HC_2H_3O_2$$

Acid-base titrations are commonly used in the chemistry lab, in the pharmaceutical industry, in food testing, in manufacturing and in biochemistry.

Example 6.8

Problem

If 25.0 mL of a perchloric acid ($HClO_4$) solution requires 45.3 mL of 0.101 M NaOH for complete neutralization, what is the molarity of the $HClO_4$ solution?

$$HClO_4(aq) + NaOH(aq) \rightarrow H_2O(l) + NaClO_4(aq)$$

Solution

What we know: mL $HClO_4$ solution; mol NaOH/1000 mL solution; mL NaOH solution; balanced equation relating $HClO_4$ and NaOH

Desired answer: mol $HClO_4$/L solution

First determine the number of moles of $HClO_4$. The solution map for this calculation is:

$$\text{mL NaOH soln} \rightarrow \text{mol NaOH soln} \rightarrow \text{mol } HClO_4$$

The conversion factors needed are the molarity of the NaOH solution and the $HClO_4$/NaOH mole ratio.

Putting these together yields:

$$45.3\,\cancel{\text{mL NaOH soln}} \times \frac{0.101\,\cancel{\text{mol NaOH}}}{1000\,\cancel{\text{mL NaOH soln}}} \times \frac{1\,\text{mol HClO}_4}{1\,\cancel{\text{mol NaOH}}} = 0.00458\,\text{mol HClO}_4$$

Next, convert the $HClO_4$ solution volume to liters.

$$25.0\,\cancel{\text{mL HClO}_4\text{ soln}} \times \frac{10^{-3}\,\text{L HClO}_4\text{ soln}}{1\,\cancel{\text{mL HClO}_4\text{ soln}}} = 0.0250\,\text{L HClO}_4\text{ soln}$$

Finally, calculate the molarity of the $HClO_4$ solution.

$$\text{molarity} = \frac{0.0458\,\text{mol HClO}_4}{0.0250\,\text{L HClO}_4\text{ soln}} = 0.183\,\text{M HClO}_4$$

Check for Understanding 6.6 **Solution**

1. How many mL of 0.244 M HCl(aq) are needed to completely neutralize 20.0 mL of 0.0984 M KOH?

Chapter 6 Keywords

Glossary

solvent	polar molecule	dilution
solute	electrolyte	dilution equation
dilute solution	nonelectrolyte	pipet
concentrated solution	concentration	neutralization reaction
electrical conductivity	molarity	base
nonpolar molecule	volumetric flask	acid-base titration

Supplementary Chapter 6 *Check for Understanding* questions

Chapter 6 Exercises

Answers

(You may use a periodic table as needed.)

1. Would you expect crystals of I_2 to dissolve readily in water? Explain your thinking.

2. If the test probes of the circuit shown in Figure 6.1 are placed in tap water and the switch is closed the light bulb shines faintly. Suggest an explanation for this.

3. Explain in your own words why the oil and vinegar in a vinaigrette salad dressing separate upon sitting.

4. If a solid is a good conductor of electricity, the material is likely to be:

   A. an element.
   B. an ionic compound.
   C. a molecular compound.
   D. either A or B.
   E. none of the above.

5. In your own words, describe what is meant by a polar molecule.

6. In a mixture of some sand in a bucket of water, water is:

A. the solvent.
B. the solute.
C. the solution.
D. both A and C.
E. none of the above.

7. How many moles of H_3PO_4 does a 125-g sample of a phosphoric acid solution that is 85.5% H_3PO_4 by mass contain?

8. In 75.0 g of an aqueous solution that is 6.8% $AgNO_3$ by mass, how many grams of solvent are present?

9. What is the mass percent of solute in a solution formed by dissolving 0.365 mol NaI in 275 mL of water? Assume a water density of 1.0 g/mL.

10. How many grams of $CaCl_2$ are needed to prepare 0.250 L of a 1.56 M solution?

11. What is the molarity of a solution prepared by dissolving 7.31 g of Na_2SO_4 in enough water to make 225 mL of solution?

12. What volume of a 0.150 M solution of potassium chloride can be made with 2.50 g of potassium chloride?

13. What volume of water must be added to 50.0 mL of a 1.5 M NaCl solution to make a 0.60 M solution of NaCl?

14. What volume of 0.1017 M $HC_2H_3O_2$ contains the same number of moles of acetic acid as are in 325 mL of 17.4 M $HC_2H_3O_2$?

15. If you add 300.0 mL of water to 250.0 mL of a 4.00 M sugar solution, what is the concentration of the sugar solution after the water has been added?

16. What is the molarity of a sulfuric acid solution that is 96.0% H_2SO_4 by mass and has a density of 1.84 g/mL?

17. What minimum volume of 6.0 M HCl is needed to dissolve a 2.53 g sample of zinc?

18. a) If 50.0 mL of 0.221 M KOH is mixed with 145 mL of 0.174 M HCl, which is the limiting reactant?

    b) How many moles of the reactant in excess remain?

19. What is the theoretical yield in grams of NO_2 when 25.0 mL of 6.0 M HNO_3 solution is added to 2.25 g copper?

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

20. How many milliliters of 0.102 M NaOH are needed to completely neutralize 50.0 mL of 0.178 M H_3PO_4?

$$3NaOH\ (aq) + H_3PO_4\ (aq) \rightarrow Na_3PO_4\ (aq) + 3H_2O\ (g)$$

Chapter 6

Check for Understanding 6.1

1. Indicate whether each of the following is a good electrical conductor.

a) mixture of $CaCl_2(s)$ and $H_2O(l)$

b) Na(s)

c) mixture of $CH_3OH(l)$ and $H_2O(l)$

d) $Br_2(l)$

e) mixture of $CaCO_3(s)$ and $H_2O(l)$

f) HCl(aq)

Answers:

a) good electrical conductor

b) good electrical conductor

c) nonconductor

d) nonconductor

e) nonconductor

f) good electrical conductor

Solutions

a) This mixture contains a soluble ionic compound that will produce many mobile ions when it dissolves in water.

b) This is a metallic solid which has mobile electrons.

c) This is a mixture of two molecular compounds, neither of which is an acid, so there are very few mobile charges present.

d) This is a pure molecular substance so there are no mobile charges present.

e) This mixture contains an insoluble ionic compound and a molecular compound so there are very few mobile charges present.

f) There are many mobile charges present because when this acid dissolves in water many mobile H^+ and Cl^- ions are produced.

Check for Understanding 6.2

1. Cow's milk typically contains 4.6 % lactose sugar ($C_{12}H_{22}O_{11}$) by mass. What is the mass of lactose present in 8 oz of milk having a mass of 245 g?

Answer: 11 g

Solution

What we know: g milk; g lactose/100 g milk

Desired answer: g lactose

The solution map for this problem is:

g milk ➔ g lactose

Remember that the mass percent of lactose in milk refers to the g of lactose per 100 g of milk. This is exactly the conversion factor needed for this calculation. Applying this yields:

$$245\,\cancel{\text{g milk}} \times \frac{4.6\,\text{g lactose}}{100\,\cancel{\text{g milk}}} = 11\,\text{g lactose}$$

Check for Understanding 6.3

1. How many moles of HCl are in 23.18 mL of 0.1006 M HCl(aq)?

Answer: 2.332×10^{-3} mol

Solution

What we know: mL solution; mol HCl/1000 mL solution

Desired answer: mol HCl

The solution map for this problem is:

mL solution ➔ mol HCl

The conversion factor needed is the solution concentration in the form $\frac{0.1006\,\text{mol HCl}}{1000\,\text{mL soln}}$.

Applying this yields:

$$23.18 \cancel{\text{mL soln}} \times \frac{0.1006 \text{ mol HCl}}{1000 \cancel{\text{mL soln}}} = 2.332 \times 10^{-3} \text{ mol HCl}$$

2. How many grams of $KMnO_4$ are needed to prepare 250. mL of a 0.0988 M $KMnO_4$ solution?

Answer: 3.90 g

Solution

What we know: mL solution; mol $KMnO_4$/1000 mL solution

Desired answer: g $KMnO_4$ needed

The solution map for this problem is:

mL solution ➔ mol $KMnO_4$ ➔ g $KMnO_4$

The conversion factor needed in the first step is the solution concentration in the form $\frac{0.0988 \text{ mol } KMnO_4}{1000 \text{ mL soln}}$.

The conversion factor needed in the second step is the molar mass of $KMnO_4$ in the form $\frac{158.04 \text{ g } KMnO_4}{1 \text{ mol } KMnO_4}$.

Putting these together yields:

$$250. \cancel{\text{mL soln}} \times \frac{0.0988 \cancel{\text{mol } KMnO_4}}{1000 \cancel{\text{mL soln}}} \times \frac{158.04 \text{ g } KMnO_4}{1 \cancel{\text{mol } KMnO_4}} = 3.90 \text{ g } KMnO_4$$

3. What volume (in mL) of 0.2006 M NaOH contains 0.0150 mol NaOH?

Answer: 74.8 mL

Solution

What we know: mol NaOH; mol NaOH/1000 mL solution

Desired answer: mL NaOH solution

The solution map for this problem is:

mol NaOH → mL solution

The conversion factor needed is the solution concentration in the form $\frac{1000\,\text{mL soln}}{0.2006\,\text{mol NaOH}}$.

Applying this yields:

$$0.0150\,\cancel{\text{mol NaOH}} \times \frac{1000\,\text{mL soln}}{0.2006\,\cancel{\text{mol NaOH}}} = 74.8\,\text{mL soln}$$

Check for Understanding 6.4

1. A 14.8 M NH_3 aqueous solution has a density of 0.90 g/mL. What is the mass % NH_3 in this solution?

Answer: 28%

Solution

What we know: mol NH_3/1000 mL solution; g solution/mL solution

Desired answer: g NH_3/100 g solution

The solution map for this problem is:

$$\frac{\text{mol NH}_3}{\text{mL solution}} \rightarrow \frac{\text{g NH}_3}{\text{mL solution}} \rightarrow \frac{\text{g NH}_3}{\text{g solution}} \rightarrow \frac{\text{g NH}_3}{100\,\text{g solution}}$$

The conversion factor needed in the first step is the molar mass of NH_3 in the form $\frac{17.03\,\text{g NH}_3}{1\,\text{mol NH}_3}$.

The conversion factor needed in the second step is the solution density in the form $\frac{1\,\text{mL soln}}{0.90\,\text{g soln}}$.

Putting these together yields:

$$\frac{14.8\,\cancel{\text{mol NH}_3}}{1000\,\cancel{\text{mL soln}}} \times \frac{17.03\,\text{g NH}_3}{1\,\cancel{\text{mol NH}_3}} \times \frac{1\,\cancel{\text{mL soln}}}{0.90\,\text{g soln}} = \frac{0.28\,\text{g NH}_3}{\text{g soln}}$$

The final step is:

$$\text{mass \% NH}_3 = \frac{0.28\text{ g NH}_3}{\text{g soln}} \times 100 = 28\%$$

Check for Understanding 6.5

1. What is the solution concentration if 3.00 mL of 1.83 x 10^{-3} M $FeSO_4$ is diluted to 250. mL?

Answer: 2.20 x 10^{-5} M

Solution

What we know: initial concentration of $FeSO_4$ (M_1); initial volume of $FeSO_4$ solution (V_1); final volume of $FeSO_4$ solution (V_2)

Desired answer: concentration of diluted $FeSO_4$ solution (M_2)

Note that this is a dilution problem. Solve the dilution equation for M_2. It is useful to first convert the final volume to liters.

$$250.\,\cancel{\text{mL}} \times \frac{10^{-3}\text{ L}}{1\,\cancel{\text{mL}}} = 0.250\text{ L}$$

$$M_2 = \frac{M_1V_1}{V_2} = \frac{\left(\frac{1.83\times10^{-3}\text{ mol FeSO}_4}{1000\,\cancel{\text{mL conc soln}}}\right)(3.00\,\cancel{\text{mL conc soln}})}{0.250\text{ L dil soln}} = \frac{2.20\times10^{-5}\text{ mol FeSO}_4}{\text{L dil soln}} = 2.20\times10^{-5}\text{ M}$$

Check for Understanding 6.6

1. How many mL of 0.244 M HCl(aq) are needed to completely neutralize 20.0 mL of 0.0984 M KOH?

Answer: 8.07 mL

Solution

What we know: mL KOH solution; mol KOH/1000 mL solution; mol HCl/1000 mL solution

Desired answer: mL HCl solution

A balanced equation for the neutralization reaction is needed.

$$HCl(aq) + KOH(aq) \rightarrow H_2O(l) + KCl(aq)$$

The solution map for this calculation is:

$$\text{mL KOH soln} \rightarrow \text{mol KOH} \rightarrow \text{mol HCl} \rightarrow \text{mL HCl soln}$$

The conversion factor needed in the first step is the KOH solution concentration in the form $\frac{0.0984\,\text{mol KOH}}{1000\,\text{mL soln}}$.

The conversion factor needed in the second step is the HCl/KOH mole ratio from the balanced equation.

The conversion factor needed in the last step is the HCl solution concentration in the form $\frac{1000\,\text{mL soln}}{0.244\,\text{mol HCl}}$.

Putting these together yields:

$$20.0\,\cancel{\text{mL KOH soln}} \times \frac{0.0984\,\cancel{\text{mol KOH}}}{1000\,\cancel{\text{mL KOH soln}}} \times \frac{1\,\cancel{\text{mol HCl}}}{1\,\cancel{\text{mol KOH}}} \times \frac{1000\,\text{mL HCl soln}}{0.244\,\cancel{\text{mol HCl}}} = 8.07\,\text{mL HCl soln}$$

Chapter 6

1. No. I_2 is a nonpolar molecule and does not have a strong affinity for polar water molecules.

2. The faint light suggests the presence of some mobile ions. Tap water is not pure water. It contains small amounts of dissolved solutes, including some salts which will produce mobile ions such as Ca^{2+}, Mg^{2+} and Cl^- in solution.

3. Vegetable oil is composed of large molecules that are mainly nonpolar. Vinegar is primarily an aqueous solution of acetic acid and hence a mixture of polar molecules and ions. The two substances do not have a strong affinity for each other and hence do not mix readily.

4. A

6. E

7. 1.30 mol

8. 69.9 g

9. 17%

10. 43.3 g

11. 0.229 M

12. 224 mL

13. 75 mL

14. 55.6 L

15. 1.82 M

16. 18.0 M

17. 13 mL

18. a) KOH

    b) 0.0142 mol

19. 3.26 g

20. 262 mL