Chapter 10 – Solutions

Introduction

Solutions are homogeneous mixtures, i.e., mixtures whose properties are uniform throughout. Solutions are all around us. We live in a solution of gases called the atmosphere. A carbonated beverage is a solution of a gas in a liquid. Brass and solder are solutions of a solid in a solid. Solutions that are predominately water are called aqueous solutions. Drinks, blood, and the ocean are all aqueous solutions. All of the reactions we discuss at the end of this chapter and in the following two chapters take place in aqueous solutions, and an understanding of solutions is necessary to understanding these reactions. In this chapter, we examine the properties of solutions, predict whether one substance will dissolve in another, and discuss the nature of aqueous solutions of ionic substances.

10.1 Concentration Introduction

Introduction

The properties of a solution made from substances A and B depend upon the dominant type of interaction in the solution. The dominant interaction, A-A, B-B, or A-B, depends upon the relative number of each type of molecule, which is given by their concentrations. If the concentration of A is much greater than that of B, then A-A interactions dominate, and the solution properties are similar to those of A. Thus, the concentration of each substance in a solution is an important property of the solution. Although there are many ways to express concentration, we focus on the most common form used in the chemistry laboratory in this section.

Prerequisites

• 7.1 Partial Pressures

Objectives

- Define the terms *solution*, *solvent*, and *solute*.
- Distinguish between *homogeneous* and *heterogeneous* mixtures.
- Determine the molarity of a solution given the amount of solute a given volume of solution contains.
- Determine the volume required to deliver a given number of moles of solute or the number of moles of solute in a given volume of a solution of known molarity.

10.1-1. Definitions

Solutions involving liquids are comprised of a solvent and at least one solute.

homogeneous mixture	Homogeneous mixtures are mixtures that have constant composition throughout. A mixture made by mixing water and alcohol or by dissolving sugar in water is homogeneous because the alcohol, sugar, and water molecules are dispersed evenly throughout the mixture. Thus, the ratio of sugar or alcohol molecules to water molecules is the same no matter the location or size of the sample. Consequently, the properties of the mixture are also the same throughout.
heterogeneous mixture	Heterogeneous mixtures do not have uniform composition. Mixing table salt and sugar or water and oil produces a heterogeneous mixture because the properties of a sample of the mixture can vary from those of one substance to those of the other.
solution	A solution is a homogeneous mixture. A mixture of water and alcohol is a solution as is a mixture made by dissolving sugar in water.
solvent	The component of a solution that dictates the phase of a solution. If a liquid is present, it is the solvent. Water is the most common solvent. If more than one liquid is present, the liquid in greater amount is usually considered to be the solvent, but water is sometimes considered the solvent even if it is not present in the greatest amount.
solute	A solute is a component of a solution that is not the solvent. A solution is made by dissolving one or more solutes in a solvent.
concentration	The concentration of a solute is the ratio that relates the amount of the solute to the amount of either the solvent or the entire solution.

Table 10.1: Some Definitions

10.1-2. Molarity

The molarity of a solute is the number of moles of that solute per liter of solution.

The concentration of a solute gives the amount of solute present in a given amount of solution or solvent. There are many ways to give concentration, but the most common method in the chemistry laboratory is molarity. The **molarity** of a solute is defined as the number of moles of solute per liter of solution, which can be stated mathematically as follows.

 $M_{\rm A} = [{\rm A}] = \frac{\text{moles of solute}}{\text{liters of solution}}$

The expression "[A] = 0.1 M" is read as "the concentration of A is 0.1 molar." It means that each liter of solution contains 0.1 mol A.

Molarity is useful in determining how much solute is needed to prepare a solution.

EXAMPLE:

For example, to determine the mass of NaCl required to make 2.0 L of a 0.20 M solution of NaCl:

 $2.0 \text{ L solution} \times \frac{0.20 \text{ mol NaCl}}{1 \text{ L sol'n}} \times \frac{58.5 \text{ g NaCl}}{1 \text{ mol NaCl}} = 23.4 \text{ g NaCl}$

It is also useful in determining the amount of solute in a given amount of solution.

EXAMPLE:

For example, to determine the number of moles of NaCl present in 250 mL of 0.20 M NaCl:

250 mL sol'n × $\frac{1 \text{ L sol'n}}{1000 \text{ mL sol'n}}$ × $\frac{0.20 \text{ mol NaCl}}{1 \text{ L sol'n}} = 0.050 \text{ mol NaCl}$

10.1-3. Molarity Exercise

EXERCISE 10.1:

100 mL of solution contains 4.8 g sugar. What is the molar concentration of sugar (sucrose) in the solution $[C_{12}H_{22}O_{11}]$? How many mL of this solution would contain 0.0030 mol $C_{12}H_{22}O_{11}$?

1. First compute the molar mass of sugar.

_____ g/mol

2. Next, determine the number of moles of sugar.

____ mol sugar

3. Determine the molarity of the sugar as the number of moles of sugar divided by the number of liters of solution in which it is dissolved.

_____ M

4. Use the molarity and the desired number of moles to determine the volume of solution required.

_ mL sol'n

10.1-4. Solute to Solvent Ratio

Most of the solutions that we encounter are aqueous solutions, and their properties depend upon the ratio of solute to water particles. In this section, we examine the ratio of solute and solvent particles in a typical aqueous solution. We can determine the number of moles of solute present in a given volume of solution of known molarity, but, in order to determine the number of moles of solvent in a liter of solution, we must know the density of the solution, i.e., we must know the mass of a unit volume of the solution.

 $density = \frac{mass \text{ of solution}}{volume \text{ of solution}}$

The density of water is 1.0 g/mL, or 1.0 g/cm^3 . The density of a solution that is predominately water will be close to that of pure water.

EXERCISE 10.2:

How many water molecules are present for each sugar molecule ($C_{12}H_{22}O_{11}$, $M_m = 342$ g/mol) in a 0.1 M aqueous solution of sugar? Assume that the density of the solution is the same as pure water (1.0 g/mL).

Solution: We need to determine the ratio of moles of sugar to moles of water. We know there is 0.10 mol of sugar in a liter of solution, so we need to determine how many moles of water are in a liter of solution, which we can get from the mass of water in the solution since the mass of the solution = mass of water + mass of sugar.

1. First, we determine the mass of 1.0 L of solution.

_____ g soln

2. Next, compute the mass of sugar in 1.0 L of solution.

_____ g sugar

3. Next, determine the mass of water in 1.0 L of solution.

_____ g H₂O

4. Now, determine the number of moles of water in 1.0 L of solution.

 $_$ mol H₂O

5. Finally, determine the ratio of water molecules to sugar molecules in the 0.10 M solution.

____ mol water/mol sugar

The properties of the solution are much more like those of water than those of sugar because there are so many more water molecules present. Indeed, this is why the density of the solution is nearly the same as that of pure water.

10.2 Solution Process Introduction

In this section, we break the solution process into steps and examine the energy requirements of each step.

Prerequisites

- 9.2 Enthalpy (definition of enthalpy)
- 9.7 Free Energy (relationship between the standard free energy and the extent of a process)
- 9.11 Equilibrium and the Equilibrium Constant
- 9.5 Entropy (meaning of entropy)

Objectives

- Define the term solubility.
- Explain the three events involved in dissolving one substance in another and predict the sign of the enthalpy change for each.

10.2-1. Solubility

A substance is usually soluble when ΔH° of solution is negative or only slightly positive.

The maximum concentration that a solute can have in a given solvent at a given temperature is called its *solubility* in that solvent at that temperature. We will use the following terms to describe relative solubilities.

- soluble: A solute is soluble if its solubility is at least 0.1 M.
- slightly soluble: Substances with solubilities between 0.01 M and 0.1 M are slightly soluble.
- **insoluble**: Substances with solubilities less than 0.01 M are insoluble.
- **miscible**: Two liquids that are completely soluble in one another are said to be miscible. For example, alcohol and water are miscible, but water and gasoline are not.

	Solubility in			Solubility in	
Substance	Water at 25 $^{\circ}\mathrm{C}$	Description	Substance	Water at 25 $^{\circ}\mathrm{C}$	Description
NaCl	6 M	soluble	$CaSO_4$	0.02 M	slightly soluble
MgO	0.0003 M	insoluble	CuS	$10^{-18} {\rm M}$	insoluble

Table 10.2: Some Solubilities

A solution in which the solute concentration is equal to its solubility is said to be **saturated**. When excess solid is added to a saturated solution, an equilibrium is established between the solid and the dissolved solute. For example, the following equilibrium is established when an excess of NaCl solid is added to water.

$$\operatorname{NaCl}(s) \rightleftharpoons \operatorname{NaCl}(aq)$$

The solubility of NaCl is given by the extent of the above reaction, which is given by the value of ΔG° for the reaction. $\Delta G^{\circ} = 0$ when [NaCl] = 1 M, which is above the minimum concentration established for a soluble substance (0.1 M). Thus, a substance is considered soluble when ΔG° is negative or only slightly positive.

 ΔS° is frequently positive for the solution process, so a substance is usually soluble if ΔH° of solution is negative or only slightly positive. We consider the factors that determine ΔH° of solution in the next section.

10.2-2. Solution Process for Dissolving a Polar Solute in H_2O

To form a solution, the solute particles must be separated, cavities must be created in the solvent, and the solute particles must enter the cavities.

The following enthalpy changes must take place in order to create a solution. Note that all changes are at standard conditions, but the superscript zero has been omitted.

- ΔH_{solute} is the energy required to separate the solute particles.
- $\Delta H_{\text{solvent}}$ is the energy required to create the cavities in the solvent that will accommodate the solute particles.
- ΔH_{mixing} is the energy change produced when the solute particles enter the cavities in the solvent.

The processes and the energies involved when a polar solute dissolves in water are shown below.

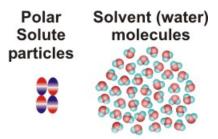


Figure 10.1a: Solution Process: Initial Conditions

Dipolar and dispersion forces between solute particles keep the solute in the solid state, while dispersion, dipolar, and hydrogen bonding forces keep the solvent in the liquid state. For ionic solutes, it is the ionic bonds that are holding the ions in the solid.

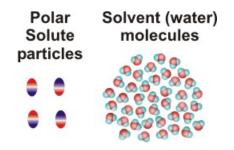


Figure 10.1b: Solution Process: ΔH_{solute}

 ΔH_{solute} is the energy required to overcome the forces that hold the solute particles together. Dipolar and dispersion forces must be overcome for polar solutes, and ionic bonds must be broken for ionic solutes. ΔH_{solute} is always positive because separating the solute particles always requires energy.

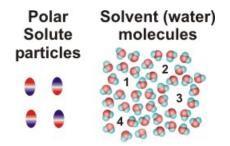


Figure 10.1c: Solution Process: $\Delta H_{\text{solvent}}$

 $\Delta H_{\text{solvent}}$ is the energy required to separate solvent molecules to create cavities for the solute particles. $\Delta H_{\text{solvent}}$ is always positive because intermolecular forces must be overcome when the solvent particles are separated. When water is the solvent, the primary contribution to $\Delta H_{\text{solvent}}$ is the energy required to break hydrogen bonds.

Hydrated Solute

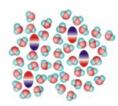


Figure 10.1d: Solution Process: ΔH_{mixing}

 ΔH_{mixing} is the energy change that results when the solute enters the solvent cavities. ΔH_{mixing} is negative because interactions between the solvent and the solute always lower the energy of the system. The negative ends of the water dipoles interact with the positive ends of the solute dipoles (blue), while the positive ends of the water dipoles interact with the negative ends of the solute dipoles (red) to lower the energy. The solute is said to be solvated (hydrated when the solvent is water) as a result of these interactions.

10.2-3. Solvation

Solvation involves the creation of cavities in the solvent and solute particles entering those cavities.

The last two steps of the solution process (creating the cavities and placing the solute in the cavities) are combined into one term called *solvation*.

$$\Delta H_{\rm solvation} = \Delta H_{\rm solvent} + \Delta H_{\rm mixing}$$

The result is that the solute becomes *solvated*. When the solvent is water, the process is called *hydration* and the solute becomes **hydrated**.

The energy change of the solution process can then be expressed as: $\Delta H_{\text{solution}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvation}}$.

Recall that a substance is soluble in a solvent when $\Delta H_{\text{solution}}$ is negative or only slightly positive. Thus, a solute is most soluble in solvents in which the energy of solvation ($\Delta H_{\text{solvation}}$) is sufficiently exothermic to overcome the energy required to separate the solute particles (ΔH_{solute}). Consequently, *a solute is most soluble in a solvent* when the solute-solvent interactions are strong, but interactions between different particles are strong when the same type of interactions are common to both types of particles. This is summarized by the general statement that like dissolves like, which implies the following.

- Ionic and polar solutes are soluble in polar solvents.
- Nonpolar molecules are soluble in nonpolar solvents.

Thus, water is a good solvent for ionic compounds, such as NaCl and NH_4NO_3 , and polar molecules, such as HCl and NH_3 , but it is a poor solvent for nonpolar molecules, such as I_2 and CCl_4 .

10.2-4. Like Dissolves Like Exercise

EXERCISE 10.3:

Use the rule that **like dissolves like** to answer the following.

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Which of the following is more soluble in water?

HBr

Br<sub>2</sub>

Which of the following is a better solvent for I_2?

CS_2

H_2O

In which of the following solvents would KCl be more soluble?

CCl_4

H_2O
```

10.3 Organic Compounds

Introduction

We concluded the last section with "like dissolves like." That is, polar solutes tend to be soluble in polar solvents such as water, while nonpolar molecules tend to be soluble in nonpolar solvents and insoluble in polar solvents such as water. However, large molecules can have both polar and nonpolar regions. In this section, we examine the solubility of such molecules in water.

Prerequisites

• 7.3 Intermolecular Interactions

Objectives

- Distinguish between hydrophobic and hydrophilic and explain the hydrophobic effect.
- Relate the solubility of a substance in water to the relative sizes of its hydrophilic and hydrophobic regions.

10.3-1. Organic Compounds

Regions of a molecule that interact well with water are hydrophilic, while regions that do not are hydrophobic.

Water is such an important solvent that we classify molecules by how well they interact with it. The term hydrophilic comes from the Greek for "water-loving" and is applied to molecules and regions of molecules that interact strongly with water. HCl and NH₃ are both polar molecules, so they are hydrophilic and water soluble molecules. The term hydrophobic comes from the Greek for "water-hating" and is applied to molecules that do

not interact well with water and are not water soluble. I_2 and CCl_4 are nonpolar molecules that do not interact well with water, so they are both hydrophobic and water insoluble.

Organic compounds are based on carbon and usually contain a number of C–C and C–H bonds, both of which are nonpolar and hydrophobic, but organic molecules can also contain C–O and C–N bonds, both of which are polar and hydrophilic. Thus, organic compounds can contain both hydrophilic and hydrophobic regions.

Water molecules interact so much better with one another than with hydrophobic regions that water excludes or avoids hydrophobic regions whenever possible. In fact, water sets up an ice-like structure around hydrophobic regions. Indeed, it is the entropy decrease resulting from the formation of the ice-like structure that is most responsible for the low solubilities of hydrophobic substances. This effect is so strong and important that it is called the *hydrophobic effect*. This effect is critical in the folding of proteins and formation of biological membranes.

10.3-2. Hydrophobic and Hydrophilic Examples

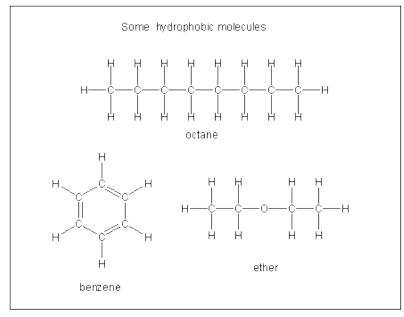


Figure 10.2a: Hydrophobic Molecules Hydrophobic molecules are not soluble in water because they contain many C–H bonds and are not very polar.

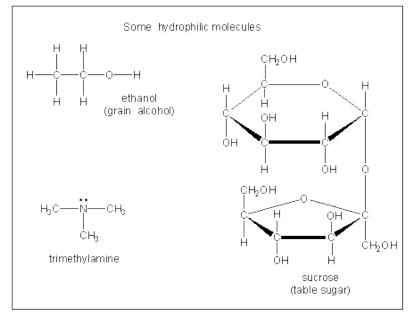


Figure 10.2b: Hydrophilic Molecules Hydrophilic compounds are water soluble because they contain O–H groups or a nitrogen lone pair that can interact strongly with water.

10.3-3. Acetone

Acetone, $(CH_3)_2C=0$, is a common laboratory solvent because many organic substances are soluble in it, and it is miscible with water. Acetone contains CH_3 groups that interact with other organic compounds through dispersion forces, so many organic substances dissolve in acetone. However, it also contains a polar C=O group, which makes the molecule hydrophilic. As with alcohols, the water solubility of compounds like this depends upon the lengths of the carbon chains; as the hydrophobic portion of the molecule increases, its solubility in water decreases. For example, $(CH_3CH_2CH_2CH_2)_2C=O$ is only slightly soluble in water.



Figure 10.3: Ball-and-Stick Model of Acetone

10.3-4. Alcohols

The solubility of alcohols decreases as the hydrophobic region gets larger.

The water solubility of compounds that contain both hydrophobic and hydrophilic regions depends upon the relative sizes of the two regions. Consider the solubilities of alcohols in water and hexane (C_6H_{14}) shown in

Table 10.3. The hydroxyl (O–H) group is hydrophilic, while the CH₂ groups are hydrophobic. Consequently, the solubility of an alcohol in water depends upon the relative number of O–H and CH₂ groups in the alcohol. As the relative number of CH₂ groups increases, the hydrophobic nature of the alcohol increases and its solubility in water decreases, while its solubility in nonpolar solvents, such as C_6H_{14} , increases. Increasing the relative number of hydroxyl groups makes the alcohol more hydrophilic and more soluble in water. Thus, hexanol (CH₃(CH₂)₅OH) is only slightly soluble in water (0.059 M), but hexanediol (HO(CH₂)₆OH), which has one hydroxyl group at each end, is miscible with water.

		Solvent
Alcohol	H_2O	C_6H_{14}
CH ₃ OH	∞	0.12 M
CH ₃ CH ₂ OH	∞	∞
$CH_3(CH_2)_2OH$	∞	∞
$CH_3(CH_2)_3OH$	0.91 M	∞
$CH_3(CH_2)_4OH$	0.31 M	∞
$CH_3(CH_2)_5OH$	$0.059 \ { m M}$	∞
$CH_3(CH_2)_6OH$	0.015 M	∞

Table 10.3: Solubilities of Some Alcohols

10.3-5. Ether or Water Exercise

Ether is a common solvent that contains hydrophobic regions and is not very polar, but water is a very polar solvent with no hydrophobic regions.

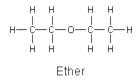
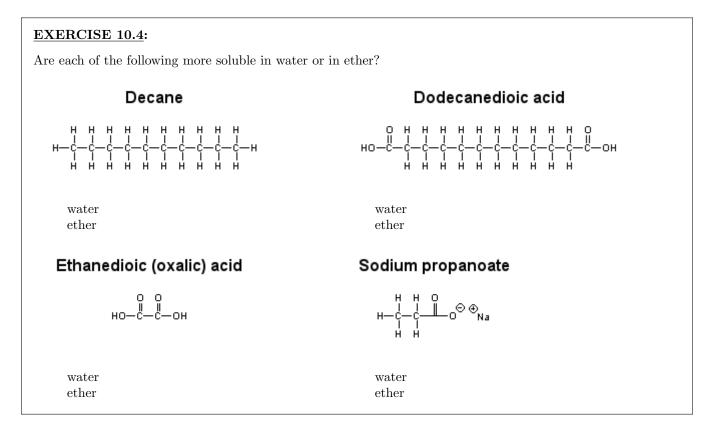


Figure 10.4

Consequently, polar substances are more soluble in water, and nonpolar substances are more soluble in ether (like dissolves like).



10.4. Detergents and Micelles Introduction

Grease and stains are hydrophobic, but we remove them by washing our dishes and clothing in water. We can do this because of the special properties of detergents, the topic of this section.

Prerequisites

• 7.3 Intermolecular Interactions

Objectives

- Describe a detergent and identify its head and tail.
- Describe *monolayers* and explain why they form.
- Describe micelles and explain how they function to dissolve hydrophobic materials in water.

10.4-1. Detergents and Soaps

Detergents and soaps each have a hydrophilic (polar) head and a long hydrophobic tail.

A *detergent* is a substance that has both a hydrophobic region, which interacts well with grease and stains, and a hydrophilic region, which interacts well with water. As an example, consider sodium dodecyl sulfate (SDS), which is a small detergent molecule. There are four different representations used for detergents.

- 1 space-filling
- 2 ball-and-stick
- 3 condensed structure that does not show C–H bonds explicitly

4 common abbreviation that is a skeletal drawing that indicates carbon atoms in the tail as the junction of two or more lines; the polar head is represented by a circle

Each drawing type is shown in Figures 10.5a, 10.5b, 10.5c, and 10.5d. The hydrophobic region of SDS consists of eleven CH_2 groups and one CH_3 group. The hydrophilic region consists of an anionic sulfate group. These regions are referred to as the hydrophobic **tail** and the hydrophilic or polar **head** of the detergent. The tails of most detergents contain 15 to 19 carbon atoms, so the 12-carbon chain of SDS is short for a detergent.

Soaps are derived from fatty acids and are similar to detergents except the polar head is a COO^{1-} (carboxylate) group. Their Ca²⁺ salts are water insoluble, and, since Ca²⁺ is a major source of water hardness, they do not function very well in hard water.



Figure 10.5a: Space-Filling Representation of SDS, a Detergent

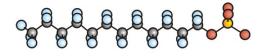


Figure 10.5b: Ball-and-Stick Representation of SDS, a Detergent

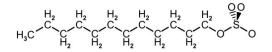


Figure 10.5c: Condensed Structure Representation of SDS, a Detergent

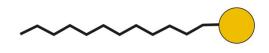


Figure 10.5d: Common Abbreviation Representation of SDS, a Detergent

10.4-2. Monolayers

At low concentrations, detergents form monolayers in which the tails extend out of solution.

The hydrophobic tails of a detergent interact well with one another, but the hydrophobic effect is so strong that they avoid water. Thus, when a small amount of a detergent is added to water, the polar heads enter the water but the hydrophobic tails do not. Consequently, a layer of detergent molecules that is only one molecule thick forms on the surface.

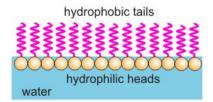


Figure 10.6: SDS Monolayer At small concentrations, SDS forms a monolayer (a layer that is one molecule thick) on the surface of the water. The hydrophobic tails stick up out of the water, while the hydrophilic heads enter the water.

10.4-3. Micelles

Micelles, which are composed of many detergent molecules, contain a hydrophobic center and a hydrophilic shell.

An increase in detergent concentration coupled with agitation forces the tails into the water, but the hydrophobic interaction is so strong that the tails attract one another (dispersion forces). The result is the formation of spheres, called *micelles*, that are composed of 80–100 molecules. The surface of the micelle is composed of the polar heads, while the interior is an organic solvent (the strongly interacting tails). Thus, grease and stains are removed in water by the addition of a detergent, which forms micelles with agitation. The hydrophobic grease and stain molecules "dissolve" in the center of the micelle. The micelle, which dissolves in water because the surface is formed of the ionic heads, can then be washed away.

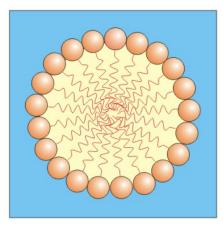


Figure 10.7: A Cross-Sectional View of a Micelle The polar heads are in direct contact with the aqueous environment and form a spherical shell around the hydrophobic interior.

10.5 Electrolytes Introduction

Ionic compounds are not soluble in most solvents, but water is so polar that some ionic compounds do dissolve in it. Blood contains many ions, and the concentrations of those ions are critical to our well-being. Ions in water are responsible for water "hardness." In this section, we examine the nature of aqueous solutions of ionic compounds.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 7.3 Intermolecular Interactions

Objectives

• Indicate whether a substance is an electrolyte or a nonelectrolyte.

10.5-1. Definitions

Aqueous solutions of electrolytes conduct electricity due to the presence of ions in solution. Ionic compounds, acids, and bases are electrolytes.

Consider the apparatus shown in Figures 10.8a and 10.8b. Two pieces of metal (electrodes) are immersed in a solution and connected to a power supply. The light bulb glows only if the solution conducts electricity, which completes the circuit. In order for solutions to conduct electricity, they must contain charged particles, i.e., ions. Thus, the light bulb glows only if the electrodes are dipped into a solution that contains ions.

Materials that dissolve in water as ions are called *strong electrolytes*, and those that dissolve as molecules are called nonelectrolytes. However, some compounds dissolve as molecules that react with water to produce ions. If their reaction with water is extensive, they too are classified as strong electrolytes, but if the reaction produces some ions but is not extensive, the compound is classified as a *weak electrolyte*. Solutions of strong electrolytes cause the light to burn brightly, those of nonelectrolytes do not cause the light to burn at all, and those of weak electrolytes cause the light to burn, but not as brightly because the concentrations of the ions are low.

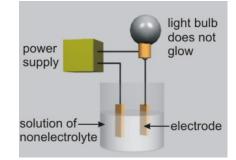


Figure 10.8a: Solutions of Nonelectrolytes Do Not Conduct Electricity

When no electrolytes (ions) are present, electricity is not conducted through the solution and the light bulb does not glow. Compounds whose aqueous solutions do not conduct electricity are called nonelectrolytes.

 Molecular compounds that are not acids or bases are nonelectrolytes. H₂O and most organic compounds are nonelectrolytes.

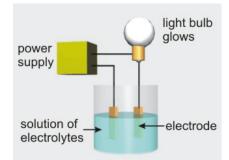


Figure 10.8b: Solutions of Electrolytes Do Conduct Electricity

Electrolytes (ions) conduct charge through the solution and complete the circuit, so the light bulb glows. Two types of compounds are electrolytes.

- **Ionic compounds** dissolve to produce metal cations and nonmetal anions. The ions can also be derived from polyatomic ions, such as ammonium or sulfate ions.
- Acids are compounds that produce H^{1+} when they dissolve in water. Production of the H^{1+} also produces a cation. For example, an aqueous solution of HCl is hydrochloric acid: $HCl \rightarrow H^{1+} + Cl^{1-}$. Since ions are produced when acids dissolve in water, acids are electrolytes. However, not all hydrogen-containing compounds are acids. Acids are those compounds whose formulas begin with an H. For example, HNO_3 , $HClO_4$, and H_2SO_4 are some other common acids, while CH_4 is not an acid.

Solution	Glow	Solution Type	Solution Particles
water	none	nonelectrolyte	H ₂ O molecules
table salt	bright	strong electrolyte	$Na^{1+} + Cl^{1-}$ ions
HCl	bright	strong electrolyte	$\mathrm{HCl} \to \mathrm{H}^{1+} + \mathrm{Cl}^{1-}$ is extensive.
HF	dim	weak electrolyte	$\text{HF} \rightarrow \text{H}^{1+} + \text{F}^{1-}$ is NOT extensive.
table sugar	none	nonelectrolyte	$C_{12}H_{22}O_{11}$ molecules
NaNO ₃	bright	strong electrolyte	$Na^{1+} + NO_3^{1-}$ ions
NaOH	bright	strong electrolyte	$Na^{1+} + OH^{1-}$ ions
rubbing alcohol	none	nonelectrolyte	C ₃ H ₅ OH molecules
ammonia	dim	weak electrolyte	$\rm NH_3 + H_2O \rightarrow \rm NH_4^{1+} + OH^{1-}$ is NOT extensive.

Table 10.4: Conduction Properties of Some Aqueous Solutions

10.5-2. Ionic Compounds as Electrolytes

Ionic compounds are strong electrolytes, so when a solid ionic compound is dissolved in water, it goes into solution completely as ions. We will no longer use (aq) to indicate that an ion is in solution because isolated ions in chemcial equations are always in solution. Consider the following dissociations.

$$NaCl(s) \rightarrow Na^{1+} + Cl^{1-} MgCl_2(s) \rightarrow Mg^{2+} + 2 Cl^{1-} K_2S(s) \rightarrow 2 K^{1+} + S^{2-}$$

A solution of NaCl contains only Na^{+1} and Cl^{1-} ions; there are no NaCl molecules. Note that the chemical equation for the dissociation must have the same stoichiometry as the substance. Thus, the formula MgCl₂ indicates that there are two Cl^{1-} ions for every one Mg²⁺ ion, so the dissociation must express the same stoichiometry. Many ionic compounds contain polyatomic ions, but the bonds that hold the atoms in polyatomic ions are covalent and do not dissociate in water, so polyatomic ions enter solution intact.

$$NaNO_3(s) \rightarrow Na^{1+} + NO_3^{1-} MgSO_4(s) \rightarrow Mg^{2+} + SO_4^{2-} K_3PO_4 \rightarrow 3 K^{1+} + PO_4^{3-}$$

10.5-3. Acids and Bases as Electrolytes

Ionic compounds are not the only class of compounds that are electrolytes; acids and bases are electrolytes as well. The first chemical definition of acids and bases was made by Svante Arrhenius.

An **Arrhenius acid** is a substance that produces H^{1+} ions when dissolved in water, and an **Arrhenius base** is a substance that produces OH^{1-} ions when dissolved in water.

Acids can be identified because the acidic protons are usually written first in their chemical formulas. For example, H_2S is an acid, so the protons appear first in its formula, but NH_3 is not, so the protons do not appear first in its formula. In Arrhenius theory, acids ionize in water in a manner similar to ionic substances, but only strong acids ionize completely. The common strong acids are HCl, HBr, HI, HNO₃, HClO₄, and H₂SO₄. For example, the following chemical equations represent the Arrhenius view of dissolving three strong acids in water.

$$\operatorname{HCl}(g) \to \operatorname{H}^{1+} + \operatorname{Cl}^{1-} \operatorname{HNO}_3(l) \to \operatorname{H}^{1+} + \operatorname{NO}_3^{1-} \operatorname{HClO}_4(l) \to \operatorname{H}^{1+} + \operatorname{ClO}_4^{1-}$$

Most acids dissociate only partially in water, so they are weak acids. Weak acids are weak electrolytes because they produce only small amounts of H^{1+} and the anion in water. HF, HNO₂, and HClO₂ are examples of weak acids. The light bulb glows only dimly in a 0.1 M solution of a weak electrolyte because there are far fewer ions to conduct the electricity. Hydrofluoric acid is a weak acid as less than 10% of the HF molecules in a typical solution dissociate into their ions. To emphasize the fact that there are many more molecules than ions in a solution of a weak acid, the solution process is written with equilibrium arrows.

$$\mathrm{HF}(aq) \rightleftharpoons \mathrm{H}^{1+} + \mathrm{F}^{1-} \quad \mathrm{HNO}_2(aq) \rightleftharpoons \mathrm{H}^{1+} + \mathrm{NO}_2^{1-} \quad \mathrm{HClO}_2(aq) \rightleftharpoons \mathrm{H}^{1+} + \mathrm{ClO}_2^{1-}$$

Metal hydroxides are the most common strong bases.

$$\operatorname{NaOH}(s) \to \operatorname{Na}^{1+} + \operatorname{OH}^{1-} \operatorname{Ba}(\operatorname{OH})_2(s) \to \operatorname{Ba}^{2+} + 2 \operatorname{OH}^{1-}$$

Most weak bases are also ionic and produce OH^{1-} ions as the result of the reaction of the anion with water. For example, F^{1-} and NO_2^{1-} ions are weak bases.

$$F^{1-} + H_2O \rightleftharpoons HF(aq) + OH^{1-} NO_2^{1-} + H_2O \rightleftharpoons HNO_2(aq) + OH^{1-}$$

Ammonia is the most common example of a molecular substance that is a weak base.

 $\mathrm{NH}_3(aq) + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{NH}_4^{1+} + \mathrm{OH}^{1-}$

10.5-4. Nonelectrolytes

Nonelectrolytes retain their molecular identity in solution.

Sucrose (table sugar) is a nonelectrolyte, so dissolving sucrose in water is represented as

 $C_{12}H_{22}O_{11}(s) \to C_{12}H_{22}O_{11}(aq)$

10.5-5. Distinguishing Strong Electrolytes and Nonelectrolytes Exercise

EXERCISE 10.5:					
Indicate whether each su	ubstance is an electrolyte or	a nonelectrolyte.			
H_2O	$C_{12}H_{22}O_{11}$	NaCl	$egin{array}{c} { m NaNO_3} \\ { m electrolyte} \\ { m nonelectrolyte} \end{array}$		
electrolyte	electrolyte	electrolyte			
nonelectrolyte	nonelectrolyte	nonelectrolyte			
HCl	NaOH	CH_3OH			
electrolyte	electrolyte	electrolyte			
nonelectrolyte	nonelectrolyte	nonelectrolyte			

10.5-6. Distinguishing Strong and Weak Electrolytes Exercise

EXERCISE 10.6:					
Indicate whether eac	ch substance is a strong elec	trolyte or a weak electrolyt	е.		
H_2SO_3	HNO_3	KF	$ m NH_3$		
strong	strong	strong	strong		
weak	weak	weak	weak		

10.5-7. Ion Concentrations in Solutions of Strong Electrolytes

Ionic compounds, such as NaCl, are strong electrolytes because all of the solid NaCl that dissolves dissociates into ions. Thus, a solution labeled 0.10 M NaCl contains Na¹⁺ and Cl¹⁻ ions, but no NaCl molecules. The ions react independently of one another; a chloride ion in a solution of NaCl is the same as one in a solution of KCl or MgCl₂. Thus, it is the concentration of the ion, not the parent compound, that is important in solution chemistry. To convert from the concentration of the parent compound to that of any ion requires the stoichiometry of the chemical equation for the dissociation, which is given by the stoichiometry of the compound.

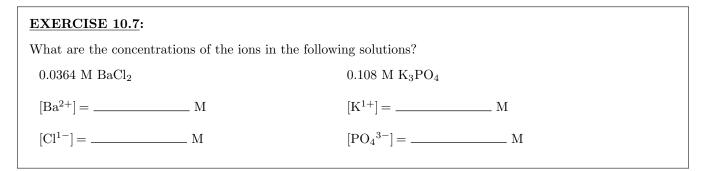
EXAMPLE:

For example, to determine the concentration of chloride ions in a 0.10 M MgCl_2 solution, we recognize that there are two moles of chloride ions for every one mole of MgCl₂ and write the following.

$$[\mathrm{Cl}^{1-}] = \frac{0.10 \text{ mol } \mathrm{MgCl}_2}{1 \text{ L solution}} \times \frac{2 \text{ mol } \mathrm{Cl}^{1-}}{1 \text{ mol } \mathrm{MgCl}_2} = \frac{0.20 \text{ mol } \mathrm{Cl}^{1-}}{1 \text{ L solution}} = 0.20 \text{ M}$$

An aqueous solution that is labeled 0.10 M MgCl₂ is 0.10 M in Mg²⁺ ions and 0.20 M in Cl¹⁻ ions, but it contains no MgCl₂!

10.5-8. Ion Concentration Exercise



10.6 Electrolyte Solutions Introduction

Electrolytes are hydrated in aqueous solution. In this section, you can view an animation showing a crystal of NaCl dissolving in water.

Objectives

• Describe how a crystal of sodium chloride dissolves in water.

10.6-1. The Water Dipole

Ionic bonds must be broken when an ionic substance dissolves, but ionic bonds are strong interactions, so ΔH_{solute} is large and positive. Thus, $\Delta H_{\text{solvation}}$, the enthalpy of solvation (hydration in this case because the solvent is water), must be large and negative for an ionic substance to dissolve in water. In other words, the interaction between the water molecules and the ions must be very strong. This strong interaction arises because water has a strong dipole, which points from the center of the hydrogen atoms toward the electronegative oxygen atom. The large dipole of water also increases its dielectric constant (ϵ in Coulomb's Law), so water effectively shields each ion from the charge of surrounding ions.

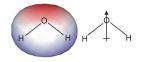


Figure 10.9: Water Dipole

10.6-2. The Solution Process

A video or simulation is available online.

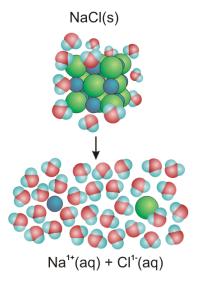


Figure 10.10: Dissolving Sodium Chloride in Water

- The sodium and chloride ions in a crystal adopt the sodium chloride structure with each sodium ion (represented by the blue spheres) surrounded by six chloride ions (represented by the green spheres) and each chloride ion surrounded by six sodium ions. Water is a very polar molecule with the center of positive charge residing between the two hydrogen atoms, and the negative charge centered on the oxygen atom. Only a small fraction of the water molecules are shown. There would be hundreds of water molecules for each ion in a typical solution, and the water molecules would be in contact with each other.
- The positive ends of the water dipoles interact with the chloride anions (green) on the surface of the crystal, while the negative ends interact with the sodium cations (blue) at the surface. The interactions are sufficiently strong to pull the ions on the surface of the crystal out into the solution.
- Six strongly interacting water molecules solvate (or hydrate in this case) each chloride ion in solution. There are many layers of water molecules around each ion. Note that the positive end of the dipole of each water molecule faces the chloride ion.
- The sodium ion is hydrated in the same manner as the chloride ion, except that it is the negative end of the water dipole that faces the cation. As in the case of the anion, the cation is surrounded by several layers of water molecules. The two oppositely charged ions do not recombine because the dipoles of the intervening water molecules arrange themselves in such a way as to insulate the two charges.

10.7 Dissolution of Ionic Substances

Introduction

Not all ionic substances are soluble in water. Indeed, most are not. In this section, we examine the factors that dictate the solubility of ionic substances in water and develop some simple rules to help us predict solubilities.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law (Describe the factors that dictate the force of attraction of two opposite charges suspended in some medium.)
- 4.5 Polyatomic Ions (Identify polyatomic ions.)

Objectives

• Relate solubility to the charge on the ions.

10.7-1. Dissolution and Coulomb's Law

The process whereby an ionic substance dissolves in water is called **dissolution**. The chemical equation for the dissolution of calcium carbonate is $CaCO_3(s) \rightarrow Ca^{2+} + CO_3^{2-}$. As an approximation, we assume that an ionic substance is soluble when the force of attraction between its ions in solution is small enough that the ions can exist separately in solution, i.e., the force is not great enough that the separated ions attract one another to reverse the dissolution process. The force of attraction is described by Coulomb's Law.

$$F = \frac{kq_1q_2}{\epsilon r^2}$$

Although the solubility of ionic compounds is more complicated than a simple Coulombic attraction of the ions, we can still use Coulomb's Law to understand the process qualitatively by examining the factors that dictate the strength of the force of attraction. Thus, an ionic compound is likely soluble in water if the following are true.

- **r** is very large. r is a property of the solution because it is the distance between the ions in the solution. r depends only upon concentration; ions in concentrated solutions are closer than ions in dilute solutions. If a substance is soluble, then the force of attraction cannot be great even at moderate concentration, so r cannot be very large.
- ϵ is large. ϵ is the dielectric constant of the solvent and measures how well the solvent screens the charges in solution. The dielectric constant of water is about 40 times greater than that of a nonpolar solvent such as hexane (C₆H₁₄). This means that the force of attraction of two oppositely charged ions separated by the same distance is 40 times greater in C₆H₁₄ than in water, so the ions are much less likely to recombine in water. The dielectric constants of several common solvents are given in Table 10.5.
- q_1q_2 is small. The product of the charges on the ions is the only factor that is a property of the ionic solute. Recall that the charges on ions typically fall in the range of -3 to +3; thus, q_1q_2 lies between 1 and 9. If the magnitude of the charge on either ion is 1, the magnitude of q_1q_2 cannot exceed 3, but if neither charge is 1, then the magnitude of q_1q_2 cannot be less than 4. Consequently, we expect that ionic compounds containing highly charged ions will not be as soluble in water as those containing +1 and -1 ions because the force of attraction between highly charged ions is too strong.

Solvent	Formula	ϵ	Solvent	Formula	ϵ
acetic acid	CH ₃ COOH	6.20	acetone	$(CH_3)_2C=O$	21.0
benzene	C_6H_6	2.28	carbon disulfide	CS_2	2.63
carbon tetrachloride	CCl ₄	2.24	dimethyl sulfoxide	$(CH_3)_2S=O$	47.2
ether	$(C_2H_5)_2O$	4.27	ethanol	C_2H_5OH	25.3
hexane	C_6H_{14}	1.89	methanol	CH ₃ OH	33.0
water	H ₂ O	80.10			

In general, ionic substances that contain a +1 and/or a -1 ion are more soluble than those that do not.

Table 10.5: Dielectric Constants of Selected Solvents at 20 °C

10.7-2. Dissolution and Coulomb's Law Exercise

EXERCISE 10.8:

Use the rule that compounds with lower q_1q_2 products are more soluble than those with high q_1q_2 products to select the more soluble compound in each pair.

CsI	CaS	CaCl_2	
$AlPO_4$	$ m NH_4NO_3$	Al_2O_3	

10.7-3. Solubility Rules

The solubility rules offer only a rough guideline to the solubility of ionic compounds; there are many exceptions.

We have seen that the solubility of simple ionic compounds in water can be related in a simple way to the charge on the ions. The magnitude of q_1q_2 ranges from 1 (1 × 1) to 9 (3 × 3) if ions with charges greater than 3 are neglected. In addition, if the magnitude of either charge is 1, then the product ranges from 1 to 3. However, the magnitude of the charge product ranges from 4 to 9 if neither charge is 1. Thus, the attraction between charges is much smaller if the magnitude of one of the charges is only 1, and as a rough first approximation, ionic substances that contain a +1 or a -1 ion are soluble, while those that contain no +1 or -1 ions are not. This generalization is given by the solubility rules shown in Table 10.6.

Rule 1	Compounds of NH_4^{1+} and Group	Compounds containing a $+1$ and/or -1 ion are probably soluble.
	1A ions are soluble.	Hydroxides (OH^{1-}) are insoluble except by Rule 1, so they are a
		common exception.
Rule 2	Compounds of NO_3^{1-} , ClO_4^{1-} ,	
	ClO_3^{1-} , and $C_2H_3O_2^{1-}$ are sol-	
	uble.	
Rule 3	Compounds of Cl^{1-} , Br^{1-} , and I^{1-} are soluble <i>except</i> those of Ag ¹⁺ , Cu ¹⁺ , Tl ¹⁺ , Hg ₂ ²⁺ , and Pb ²⁺ .	The insoluble halides appear to violate the $+1/-1$ rule for solubil- ity, but these metals are late metals that are fairly electronegative, so their halides are not very ionic. For example, the Ag–Cl bond is only 30% ionic, and the Pb–Cl bond is only 15% ionic (see Chap-
		ter 5.2-5 Exceptions). Consequently, Coulomb's Law doesn't really apply here.
Rule 4	Compounds of SO_4^{2-} are soluble except those of Ca^{2+} , Sr^{2+} , Ba^{2+} , and Pb^{2+} .	Sulfates are the only soluble compounds that do not have to contain an $+1$ or -1 ion.
Rule 5	Most others are NOT soluble in water.	If an ionic substance is not soluble by Rules 1 through 4, then it is probably not soluble in water.

Table 10.6: Solubility Rules for Ionic Substances in Water

10.7-4. Solubility is a Matter of Degree

Solubilities vary from very soluble to very insoluble, but no ionic solid is completely soluble in water and none is completely insoluble. As is usually the case in chemistry, it is a matter of degree. Consider the following solubilities of some sulfates.

Compound	Molar Solubility
$BaSO_4$	0.000013
$PbSO_4$	0.00014
$SrSO_4$	0.00073
Hg_2SO_4	0.00010
$CaSO_4$	0.015
Ag_2SO_4	0.027
$Al_2(SO_4)_4$	1.1
FeSO_4	1.9
$MgSO_4$	3.0
MnSO ₄	4.2

Table 10.7

In general, the solubilities in Table 10.7 are consistent with the solubility rules. However, our definition of soluble was that the solubility of the substance had to be at least 0.1 M, and a slightly soluble substance had to have a solubility between 0.01 and 0.1 M, so the following are inconsistencies in the solubility rules.

- CaSO₄ is slightly soluble, not insoluble.
- Ag₂SO₄ is slightly soluble, not soluble.
- Hg_2SO_4 is insoluble, not soluble.

Thus, Ag^{1+} and Hg_2^{2+} should be added to the list of ions that form insoluble sulfates if Ca^{2+} is included. We conclude that care must be taken when using the solubility rules too literally. They are only very rough guidelines.

10.7-5. Predicting Solubility Exercise

 $\begin{array}{l} \hline \textbf{EXERCISE 10.9:} \\ \mbox{Which of the following compounds can be used to make a solution that is 0.1 M in Pb^{2+} ions?} \\ \mbox{PbSO}_4 \\ \mbox{Pb(NO}_3)_2 \\ \mbox{PbI}_2 \\ \mbox{Pb(OH)}_2 \\ \end{array} \\ \begin{array}{l} \mbox{Which of the following compounds can be used to make a solution that is 0.1 M in <math>\mbox{CrO}_4^{2-} \mbox{ ions}? \\ \mbox{K}_2\mbox{CrO}_4 \\ \mbox{BaCrO}_4 \\ \mbox{FeCrO}_4 \\ \mbox{Ag}_2\mbox{CrO}_4 \end{array}$

10.8 Precipitation of Ionic Substances Introduction

Most reactions between ionic compounds take place in aqueous solutions, but not all of the species present in the solutions necessarily take part in the reactions. A *net ionic equation*, or simply *net equation*, is one that shows only those ions that are involved in the reaction. In this section, we learn how to predict which ions are involved in precipitation reactions and how to write net ionic equations for their reaction.

Prerequisites

• 1.8 Electromagnetism and Coulomb's Law

Objectives

- Write the net ionic equation for a simple precipitation reaction.
- Use the solubility rules to predict whether an ionic compound is expected to be soluble in water.
- Write a net ionic equation for the precipitation of an ionic compound from solution.
- Use the solubility rules to predict whether mixing two solutions will produce a precipitate.

10.8-1. Formation of AgCl

A net ionic equation shows only the ions involved in the precipitation. Spectator ions are not included.

It is often the case that when two clear solutions are mixed, a solid called a *precipitate* forms, or a precipitation reaction occurs. The ions that are present in solution but are not involved in the reaction are called *spectator ions*. Spectator ions are present because they were paired with a reacting ion initially. For example, consider the net ionic equation to explain the fact that when solutions of NaCl and AgNO₃ are mixed, a white precipitate forms. First, we determine if the compound formed from each anion-cation combination is soluble (anion-anion and cation-cation interactions are repulsive and can be ignored). The following are possible combinations.

- $Na^{1+} + NO_3^{1-}$
- $Ag^{1+} + Cl^{1-}$

NaNO₃ is soluble from both Rules 1 and 2, so Na¹⁺ + NO₃¹⁻ are spectator ions. AgCl is NOT soluble from Rule 3. Therefore, the white precipitate is AgCl. The net ionic equation is $Ag^{1+} + Cl^{1-} \rightarrow AgCl$.

 $Ag^{1+} + Cl^{1-} \rightarrow AgCl$



SS

The aqueous solution on the right contains Ag^{1+} and NO_3^{1-} ions. The aqueous solution on the left contains Na^{1+} and Cl^{1-} ions.

 $\rightarrow \qquad {\rm NaNO_3\ is\ soluble\ by\ Rules\ 1\ and\ 2,\ and\ AgCl} is\ insoluble\ by\ Rule\ 3. Thus,\ mixing\ the two\ solutions\ produces\ a\ solution\ of\ Na^{1+}\ and NO_3^{1-} ions\ as\ well\ as\ a\ white\ precipitate\ of\ AgCl.}$

10.8-2. Video on the AgCl Precipitation Process

A video or simulation is available online.

The animation shows the addition of $AgNO_3$, which comes in from the top, to a solution of NaCl. Note the hydration of each of the ions. The ions are mobile in solution and do encounter each other. Only a very small fraction of the water molecules are shown for clarity. Recall that there are hundreds of water molecules for each ion.

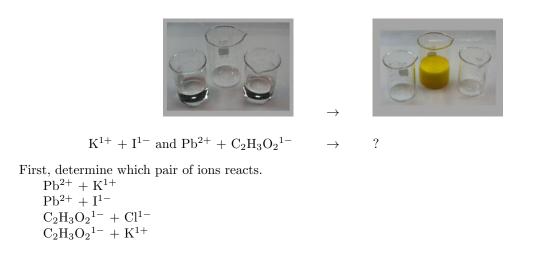
- When the two cations or the two anions encounter one another, the force is repulsive.
- When Ag¹⁺ and NO₃¹⁻ encounter one another, the force of attraction is weak enough that the shielding of the intervening water molecules (dielectric) prevents reaction.
- When Ag¹⁺ encounters Cl¹⁻, the driving force to form a bond (mostly covalent in nature) is sufficient to overcome the shielding from water, and AgCl precipitates from solution.

Note that the Na^{1+} and NO_3^{1-} ions are surrounded only by water molecules at the beginning and end of the reaction, so they are unaffected by the reaction, i.e., they are spectator ions.

10.8-3. Predicting a Precipitate

EXERCISE 10.10:

Write the net ionic equation that describes the formation of a yellow precipitate when solutions of lead acetate and potassium iodide are mixed.



Write the balanced equation (Cation + Anion \rightarrow Precipitate).

10.8-4. Practice

EXERCISE 10.11:

Use the method developed previously and Table 10.6 to determine whether a reaction occurs when aqueous solutions containing the following are mixed. If a reaction does occur, write the balanced equation.



Sodium Phosphate and Silver Nitrate

Select the reacting ions or "no reaction."

_____ + _____

 $\begin{array}{l} {\rm Na^{1+}} + {\rm Ag^{1+}} \\ {\rm Na^{1+}} + {\rm NO_3^{1-}} \\ {\rm PO_4^{3-}} + {\rm Ag^{1+}} \\ {\rm PO_4^{3-}} + {\rm NO_3^{1-}} \\ {\rm no\ reaction} \end{array}$

If there is a reaction, write the balanced equation (Cation + Anion \rightarrow Precipitate).

 \rightarrow



Ammonium Sulfate and Sodium Phosphate

Select the reacting ions or "no reaction."

 $------ + ------ \rightarrow ----$

 $\begin{array}{l} {\rm NH_4^{1+}\,+\,Na^{1+}}\\ {\rm NH_4^{1+}\,+\,PO_4^{3-}}\\ {\rm SO_4^{2-}\,+\,Na^{1+}}\\ {\rm SO_4^{2-}\,+\,PO_4^{3-}}\\ {\rm no\ reaction} \end{array}$

If there is a reaction, write the balanced equation (Cation + Anion \rightarrow Precipitate).

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Potassium Chromate and Lead Nitrate

 $\begin{array}{l} \mbox{Select the reacting ions or "no reaction."} \\ \mbox{Pb}^{2+} + {\rm K}^{1+} \\ \mbox{Pb}^{2+} + {\rm CrO}_4{}^{2-} \\ \mbox{NO}_3{}^{1-} + {\rm K}^{1+} \\ \mbox{NO}_3{}^{1-} + {\rm CrO}_4{}^{2-} \\ \mbox{no reaction} \end{array}$

+

If there is a reaction, write the balanced equation (Cation + Anion \rightarrow Precipitate).



Barium Acetate and Ammonium Sulfate

Select the reacting ions or "no reaction." \mathbb{D}^{2+}

+

 $\begin{array}{l} Ba^{2+} + NH_4{}^{1+} \\ Ba^{2+} + SO_4{}^{2-} \\ C_2H_3O_2{}^{1-} + NH_4{}^{1+} \\ C_2H_3O_2{}^{1-} + SO_4{}^{2-} \\ no \ reaction \end{array}$

If there is a reaction, write the balanced equation (Cation + Anion \rightarrow Precipitate).

 \rightarrow



Cobalt(II) Chloride and Sodium Phosphate

Select the reacting ions or "no reaction."

+ _

 $\begin{array}{l} {\rm Co}^{2+} + {\rm Na}^{1+} \\ {\rm Co}^{2+} + {\rm PO}_4{}^{3-} \\ {\rm Cl}^{1-} + {\rm Na}^{1+} \\ {\rm Cl}^{1-} + {\rm PO}_4{}^{3-} \\ {\rm no\ reaction} \end{array}$

If there is a reaction, write the balanced equation (Cation + Anion \rightarrow Precipitate).

 \rightarrow



Ammonium Sulfate and Silver Nitrate

Select the reacting ions or "no reaction." $NH_4^{1+} + Ag^{1+}$ $NH_4^{1+} + NO_3^{1-}$ $SO_4^{2-} + Ag^{1+}$ $SO_4^{2-} + NO_3^{1-}$ no reaction

If there is a reaction, write the balanced equation (Cation + Anion \rightarrow Precipitate).

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10.9 Solubility Equilibria
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Introduction

A precipitate is in equilibrium with its ions in solution, and, in this section, we show how to treat that equilibrium quantitatively.

Prerequisites

• 9.11 Equilibrium and the Equilibrium Constant (Write the equilibrium constant expression for a reaction involving solids and solutes.)

Objectives

- Write the chemical equation to which the solubility product constant applies and write the solubility product constant expression for a compound.
- Determine the concentration of an ion in equilibrium with another ion of known concentration in a saturated solution of a compound composed of the ions.

10.9-1. Solubility Equilibria

When the amount of solid that is added to water exceeds the amount that is soluble in water at that temperature, the solid reaches equilibrium with the ions. For example, when solid AgCl is added to water, only a small amount of the solid dissolves as it reaches equilibrium with its ions.

$$\operatorname{AgCl}(s) \rightleftharpoons \operatorname{Ag}^{1+} + \operatorname{Cl}^{1-}$$

Recall that pure solids and liquids enter the equilibrium expression as 1 (unity), so the equilibrium constant for the above process would be written as $K = [Ag^{1+}][Cl^{1-}]/1$. Note that the equilibrium concentrations of the ions are determined by the solubility of AgCl and that the equilibrium constant is simply the product of the ion concentrations because the denominator is one. Consequently, the equilibrium constant is called the *solubility product constant* and given the symbol K_{sp} . The solubility product constant of AgCl is

$$K_{\rm sp} = [{\rm Ag}^{1+}][{\rm Cl}^{1-}] = 1.8 \times 10^{-10}$$

The fact that the value of $K_{\rm sp}$ is so small indicates how insoluble AgCl is. The expressions and values of several silver compounds are given in Table 10.8.

Compound	K_{sp} expression	$K_{\mathbf{sp}}$ value
AgCl	$[Ag^{1+}][Cl^{1-}]$	1.8×10^{-10}
Ag_2CrO_4	$[Ag^{1+}]^2[CrO_4^{2-}]$	1.1×10^{-12}
AgI	$[Ag^{1+}][I^{1-}]$	8.3×10^{-17}
Ag ₂ S	$[Ag^{1+}]^2[S^{2-}]$	6.3×10^{-50}
Ag ₃ PO ₄	$[Ag^{1+}]^3[PO_4^{3-}]$	2.6×10^{-18}

Table 10.8: Solubility Product Constant Values and Expressions for Some Compounds of Silver

10.9-2. Exercise

EXERCISE 10.12:

The solubility product constant is given for a substance, but it applies to a process. Check your understanding by answering the following questions.

 $K_{\rm sp}$ of zinc carbonate is 1.0 x 10⁻¹⁰.

Write the process to which this number applies.

_____ + __

Write the expression to which it applies. Specify the cation concentration first in the expression.

 $K_{\rm sp} =$ _____

 $K_{\rm sp}$ of iron(III) hydroxide is 1.6×10^{-39} .

Write the process to which this number applies.

 \rightleftharpoons

Write the expression to which it applies. Specify the cation concentration first in the expression.

 $K_{\rm sp} =$ _____

10.9-3. Determining Equilibrium Concentrations

EXERCISE 10.13:

Solubility product constants can be used to determine the equilibrium concentrations of the ions present. The following example shows how this is done.

What is maximum [Fe³⁺] that can exist in a solution in which $[OH^{1-}] = 1.0 \times 10^{-7} M$?

The $K_{\rm sp}$ of iron(III) hydroxide is 1.6×10^{-39} .

First, write the process to which the solubility product constant applies.

≓ _____ + ____

Next, write the solubility product constant expression for the process with the cation concentration specified first.

 $K_{\rm sp} =$ _____

Substitute the known values for $K_{\rm sp}$ and $[{\rm OH^{1-}}]$ into the solubility product constant expression and solve for $[{\rm Fe^{3+}}]$.

____ M

10.10 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.