# Chapter 4

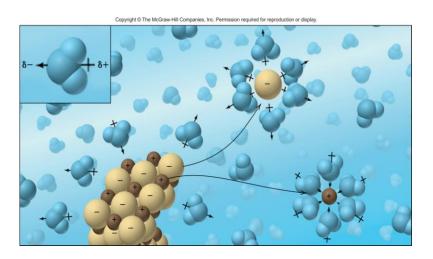
**Solutions** 

# **Determining Amount (mol) of Ions in Solution**

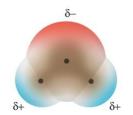
What amount (mol) of each ion is in each solution if 5.0 mol of ammonium sulfate is dissolved in water?

- 1. What happens when an ionic compound dissolves in water?
- 2. Why?

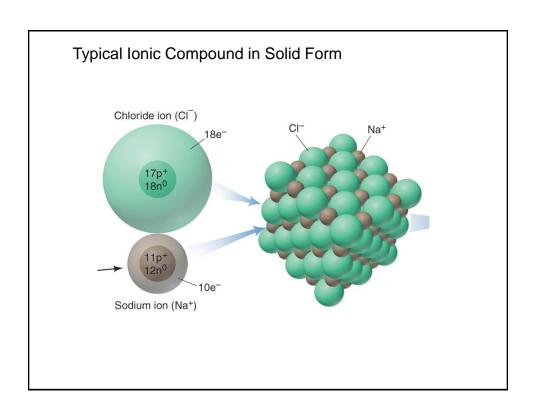
## An ionic compound dissolving in water.

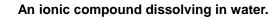


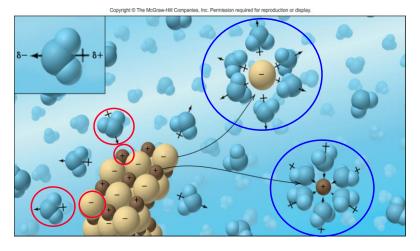
# The Role of Water as a Solvent



- Water is a polar molecule
  - since it has uneven electron distribution
  - and a bent molecular shape.
- · Water readily dissolves a variety of substances.
- Water interacts strongly with its solutes and often plays an active role in aqueous reactions.

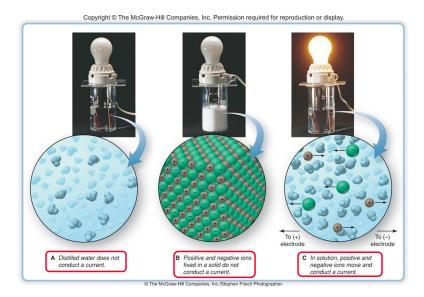






"Electrolyte" describes the species in solution. All ionic compounds are strong electrolytes.

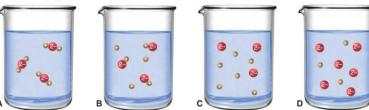
## The electrical conductivity of ionic solutions.



**PROBLEM:** The beakers shown below contain aqueous solutions of the strong electrolyte potassium sulfate.

Which beaker best represents the compound in solution? ( $\rm H_2O$  molecules are not shown).

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Determining Amount (mol) of lons in Solution
What amount (mol) of each ion is in each solution if 5.0 mol of ammonium sulfate is dissolved in water?
Question you MUST be able to answer:
What is the molarity of an aqueous solution that contains 0.715 mole glycine in 495 mL solution?

#### **Fundamentals of Solution Stoichiometry**

**Concentration** – the number of moles present in a certain volume of solution

#### **Expressing Concentration in Terms of Molarity**

A solution consists of a smaller quantity of one substance (the **solute**) dissolved in a larger quantity of another (the **solvent**).

The most important way to express concentration is **molarity (M)** 

Molarity = 
$$\frac{\text{moles solute}}{\text{liters solution}}$$
  $M = \frac{\text{mol solute}}{\text{L soln}}$ 

Note: the term **liters solution** in the denominator is <u>the volume of</u> the solute plus the volume of the solvent.

What is the molarity of an aqueous solution that contains 0.715 mole glycine in 495 mL solution?

# Molarity as a Conversion Factor

If you are given concentration (mol/L),

- To determine volume, you need number of moles
- To determine number of moles, you need volume

How would you prepare 0.80 L of a 0.15 *M* aqueous NaCl solution from a 6.0 *M* aqueous NaCl stock solution?

#### **Preparing and Diluting Molar Solutions**

The correct preparation of a solution containing a solid solute consists of four steps. Let's consider the preparation of 0.500 L of 0.350 M nickel (II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, *M* 290.82 g/mol)

- 1. Determine mass of solid needed.
- 2. Carefully transfer the calculated mass of solute to a volumetric flask filled halfway with solvent.
- 3. Dissolve completely by swirling.
- 4. Add enough solvent to reach final volume.

#### **Diluting a Solution**

It is common practice to prepare a concentrated (stock) solution from which dilute (i.e., less concentrated) solutions are then made.

How would you prepare 0.80 L of a 0.15 *M* aqueous NaCl solution from a 6.0 *M* aqueous NaCl stock solution?

As a government chemist testing commercial antacids, you use 0.10 M HCl to simulate that acid concentration in stomach acid. How many liters of 'stomach acid' react with a tablet containing 0.10 g of Mg(OH)<sub>2</sub>?

$$Mg(OH)_2$$
 (s) + 2HCl (aq)  $\rightarrow$   $MgCl_2$  (aq) + 2H<sub>2</sub>O (l)

#### **Stoichiometry of Reactions in Solution**

We solve stoichiometry problems for reactions occurring in solution using the same approach as described before. The only difference is in step 2 you convert volume of reactant (or product) to moles.

#### Approach for solving ANY stoichiometric problem

- 1. Write the balanced equation.
- 2. Find the amount (mol) of one substance from the volume and molarity.
- 3. Select appropriate equivalent molar ratio.
- 4. Convert moles given to moles desired substance.
- 5. Convert to mass or number of entities (if required).

As a government chemist testing commercial antacids, you use 0.10 M HCl to simulate that acid concentration in stomach acid. How many liters of 'stomach acid' react with a tablet containing 0.10 g of Mg(OH)<sub>2</sub>?

$$Mg(OH)_2$$
 (s) + 2HCl (aq)  $\rightarrow$   $MgCl_2$  (aq) + 2H<sub>2</sub>O (l)

# Chapter 4

Reactions

$$2AgNO_3(aq) + Na_2CrO_4(aq) \rightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$$

- · What is happening in this reaction?
- How do we predict what the products are?

Start with the reactants.

· What does (aq) mean?



# **Writing Equations for Aqueous Ionic Reactions**

 $2AgNO_3(aq) + Na_2CrO_4(aq) \rightarrow Ag_2CrO_4(s) + 2NaNO_3(aq)$ 

The **molecular equation** shows all reactants and products as if they were *intact, undissociated compounds*.

This gives the least information about the species in solution.

The total ionic equation shows all soluble ionic substances dissociated into ions.

This gives the most accurate information about species in solution.

$$2Ag^{+}(aq) + 2NO_{3}^{-}(aq) \rightarrow Ag_{2}CrO_{4}(s) + 2Na^{+}(aq) + CrO_{4}^{2-}(aq) + 2Na^{+}(aq) + 2NO_{3}^{-}(aq)$$

Spectator ions are ions that are not involved in the actual chemical change. Spectator ions appear unchanged on both sides of the total ionic equation.

$$2Ag^{+}(aq) + 2NO_{3}^{-}(aq) \rightarrow Ag_{2}CrO_{4}(s) + 2Na^{+}(aq) + CrO_{4}^{2-}(aq) + 2Na^{+}(aq) + 2NO_{3}^{-}(aq)$$

The **net ionic equation** eliminates the **spectator ions** and shows only the actual chemical change.

$$2\mathsf{Ag^+} \ (aq) + \mathsf{CrO_4}^{2^-} \ (aq) \quad \longrightarrow \quad \mathsf{Ag_2CrO_4} \ (s)$$

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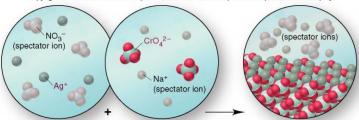


Figure 4.4 An aqueous ionic reaction and the three types of equations.

Select the precipitate that forms when the following reactants are mixed.

$$Na_2CO_3(aq) + BaCl_2(aq) \rightarrow$$

# **Precipitation Reactions**

- In a precipitation reaction, two soluble ionic compounds react to give an insoluble product, called a precipitate.
- The precipitate forms through the net removal of ions from solution.
- It is possible for more than one precipitate to form in such a reaction.

# **Predicting Whether a Precipitate Will Form**

- Note the ions present in the reactants.
- Consider all possible cation-anion combinations.
- Use the **solubility rules** to decide whether any of the ion combinations is insoluble.
  - An insoluble combination identifies the precipitate that will form.

$$Na_2CO_3(aq) + BaCl_2(aq) \rightarrow$$

#### Table 4.1 Solubility Rules for Ionic Compounds in Water

#### Soluble Ionic Compounds

- All common compounds of Group 1A(1) ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, etc.) and ammonium ion (NH<sub>4</sub><sup>+</sup>) are soluble.
- 2. All common nitrates (NO $_3$ <sup>-</sup>), acetates (CH $_3$ COO $^-$  or C $_2$ H $_3$ O $_2$ <sup>-</sup>) and most perchlorates (ClO $_4$ <sup>-</sup>) are soluble.
- 3. All common chlorides (Cl<sup>-</sup>), bromides (Br<sup>-</sup>) and iodides (l<sup>-</sup>) are soluble, *except* those of Ag<sup>+</sup>, Pb<sup>2+</sup>, Cu<sup>+</sup>, and Hg<sub>2</sub><sup>2+</sup>. All common fluorides (F<sup>-</sup>) are soluble *except* those of Pb<sup>2+</sup> and Group 2A(2).
- All common sulfates (SO<sub>2</sub><sup>2-</sup>) are soluble, except those of Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Ag<sup>+</sup>, and Pb<sup>2+</sup>.

#### **Insoluble Ionic Compounds**

- All common metal hydroxides are insoluble, except those of Group 1A(1) and the larger members of Group 2A(2)(beginning with Ca<sup>2+</sup>).
- All common carbonates (CO<sub>3</sub><sup>2-</sup>) and phosphates (PO<sub>4</sub><sup>3-</sup>) are insoluble, except those of Group 1A(1) and NH<sub>4</sub><sup>+</sup>.
- All common sulfides are insoluble except those of Group 1A(1), Group 2A(2) and NH<sub>4</sub>+.

Select the precipitate that forms when the following reactants are mixed.

$$Na_2CO_3(aq) + BaCl_2(aq) \rightarrow$$

What are the products for the following reaction?  $Ba(OH)_2(aq) + HNO_3(aq) \rightarrow$ 

# **Acid-Base Reactions**

An **acid** is a substance that produces  $H^+$  ions when dissolved in  $H_2O$ .

$$HX \stackrel{H_2O}{\longrightarrow} H^+(aq) + X^-(aq)$$

A **base** is a substance that produces  $OH^-$  ions when dissolved in  $H_2O$ .

$$MOH \stackrel{H_2O}{\longrightarrow} M^+(aq) + OH^-(aq)$$

#### Table 4.2 Strong and Weak Acids and Bases

#### **Acids**

#### Strong

hydrochloric acid, HCI hydrobromic acid, HBr hydriodic acid, HI nitric acid, HNO<sub>3</sub> sulfuric acid, H<sub>2</sub>SO<sub>4</sub> perchloric acid, HClO<sub>4</sub>

#### Weak

hydrofluoric acid, HF phosphoric acid, H<sub>3</sub>PO<sub>4</sub>

acetic acid,  $CH_3COOH$  (or  $HC_2H_3O_2$ ) Weak

#### **Bases**

#### Strong

Group 1A(1) hydroxides: lithium hydroxide, LiOH sodium hydroxide, NaOH potassium hydroxide, KOH rubidium hydroxide, RbOH cesium hydroxide, CsOH Heavy Group 2A(2) hydroxides: calcium hydroxide, Ca(OH)<sub>2</sub> strontium hydroxide, Sr(OH)<sub>2</sub> barium hydroxide, Ba(OH)<sub>2</sub>

ammonia, NH<sub>3</sub>

#### STRONG ACIDS and BASES

- •Have one or more H atoms or OH ions as part of their structure
- •Acids completely release H atoms as protons in water

$$\mathsf{HX} \ \stackrel{\mathsf{H}_2\mathsf{O}}{\longrightarrow} \ \mathsf{H}^+(aq) + \mathsf{X}^-(aq) \ \longrightarrow \ \mathsf{H}_3\mathsf{O}^+(aq) + \mathsf{X}^-(aq)$$

•Bases completely release OH- ions in water

$$MOH \stackrel{H_2O}{\longrightarrow} M^+(aq) + OH^-(aq)$$

#### **WEAK ACIDS and BASES**

- Have one or more H atoms or OH<sup>-</sup> ions as part of their structure
- $\bullet$  Acids partially release H atoms as protons in water  $${\rm H}_2{\rm O}$$

$$HX = H^+(aq) + X^-(aq)$$

• Bases partially release OH- ions in water

$$H_2O$$
  $H_2O$   $H_2O$ 

Reaction is continuously occurring in both directions. Achieves a state of *equilibrium*.

# **Acid-Base Reactions (Neutralization Reaction)**

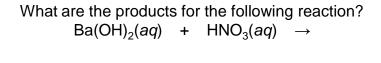
Strong acid + strong base  $\rightarrow$  ionic salt + water

$$HX(aq) + MOH(aq) \rightarrow MX(aq) + H_2O(l)$$
  
acid base salt water

$$H^+(aq) + X^-(aq) + M^+(aq) + OH^-(aq) \rightarrow M^+(aq) + X^-(aq) + H_20(I)$$

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(1)$$

- •Double displacement or metathesis reaction
- Only cation and anion in salt will vary



#### Sample Problem 4.6

# Writing Ionic Equations for Acid-Base Reactions

**PROBLEM:** Write balanced molecular, total ionic, and net ionic equations for the following acid-base reactions and identify the spectator ions.

barium hydroxide (aq) + sulfuric acid (aq)  $\rightarrow$ 

Automobile batteries use 3.0 M H $_2$ SO $_4$  as an electrolyte. How much 1.20 M NaOH will be needed to neutralize 225 mL of battery acid?

# Quantifying Acid-Base Reactions by Titration

- In a *titration*, the concentration of one solution is used to determine the concentration of another.
- In an acid-base titration, a standard solution of base is usually added to a sample of acid of unknown molarity.
- An acid-base indicator has different colors in acid and base, and is used to monitor the reaction progress.
- At the *equivalence point*, the mol of H<sup>+</sup> from the acid equals the mol of OH<sup>-</sup> ion produced by the base.
  - Amount of H+ ion in flask = amount of OH- ion added
- The end point occurs when there is a slight excess of base and the indicator changes color permanently.

Figure 4.9 An acid-base titration.

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Temporary excess of OHT

A Before titration

B Near end point

C At end point

H\*(aq) + X\*(aq) + M\*(aq) + OH\*(aq)

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Permanent slight excess of OH\*

O H\*

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Permanent slight excess of OH\*

O H\*

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Automobile batteries use 3.0  $M\,H_2SO_4$  as an electrolyte. How much 1.20  $M\,NaOH$  will be needed to neutralize 225 mL of battery acid?

What is the oxidizing agent in the following reaction?  $Mg(s) + 2H_2O(g) \rightarrow Mg(OH)_2(s) + H_2(g)$ 

# **Oxidation-Reduction (Redox) Reactions**

Oxidation is the loss of electrons.

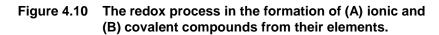
The reducing agent loses electrons and is oxidized.

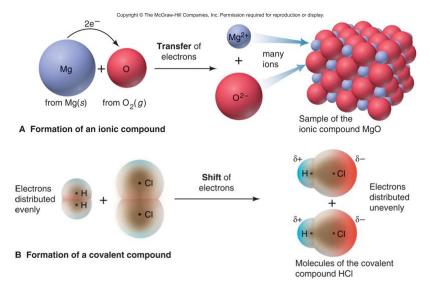
Reduction is the gain of electrons.

The oxidizing agent gains electrons and is reduced.

A redox reaction involves electron transfer

Oxidation and reduction occur together.





#### Table 4.3 Rules for Assigning an Oxidation Number (O.N.)

#### **General rules**

- 1. For an atom in its elemental form (Na, O<sub>2</sub>, Cl<sub>2</sub>, etc.): O.N. = 0
- 2. For a monoatomic ion: O.N. = ion charge
- 3. The sum of O.N. values for the atoms in a compound equals zero. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge.

#### Rules for specific atoms or periodic table groups

1. For Group 1A(1): O.N. = +1 in all compounds

2. For Group 2A(2): O.N. = +2 in all compounds

3. For hydrogen: O.N. = +1 in combination with nonmetals

4. For fluorine: O.N. = -1 in combination with metals and boron

5. For oxygen: O.N. = -1 in peroxides

O.N. = -2 in all other compounds(except with F)

6. For Group 7A(17): O.N. = -1 in combination with metals, nonmetals

(except O), and other halogens lower in the group

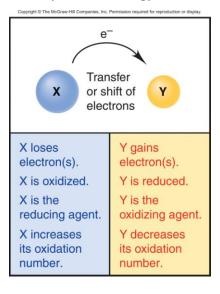
Determine the oxidation number (O.N.) of each element in these species:

(a) zinc chloride

(b) sulfur trioxide

(c) nitric acid





## **Identifying Oxidizing and Reducing Agents**

Identify the oxidizing agent and reducing agent in each of the following reactions:

(a) 
$$2AI(s) + 3H_2SO_4(aq) \rightarrow AI_2(SO_4)_3(aq) + 3H_2(g)$$

(b) PbO (s) + CO (g) 
$$\rightarrow$$
 Pb (s) + CO<sub>2</sub> (g)

What is the oxidizing agent in the following reaction?  $Mg(s) + 2H_2O(g) \rightarrow Mg(OH)_2(s) + H_2(g)$ 

### **Free Elements in Redox Reactions**

- · Combination Reactions
  - Two or more reactants combine to form a new compound:
  - $-X+Y\rightarrow Z$
- Decomposition Reactions
  - A single compound decomposes to form two or more products:
  - $-Z \rightarrow X + Y$
- · Displacement Reactions
  - double diplacement: AB + CD  $\rightarrow$  AD + CB (not redox) [metathesis]
  - single displacement: X + YZ → XZ + Y (redox)
- Combustion
  - the process of combining with O<sub>2</sub>

#### The active metal lithium displaces H<sub>2</sub> from water.

The most active metals displace H<sub>2</sub> from water.

$$2\text{Li}(s) + 2\text{H}_20(l) \rightarrow 2\text{LiOH}(aq) + \text{H}_2(g)$$

O.N. increasing O.N. decreasing

oxidation reduction occurring occurring

reducing agent oxidizing agent

## The displacement of H<sub>2</sub> from acid by nickel.

Less reactive metals need the higher concentrations of  $H^+$  ions in acid solutions to displace  $H_2$ .

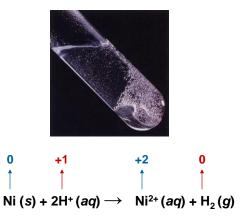


Figure 4.15 A more reactive metal (Cu) displacing the ion of a less reactive metal (Ag+) from solution.

Copper wire

Copper wire

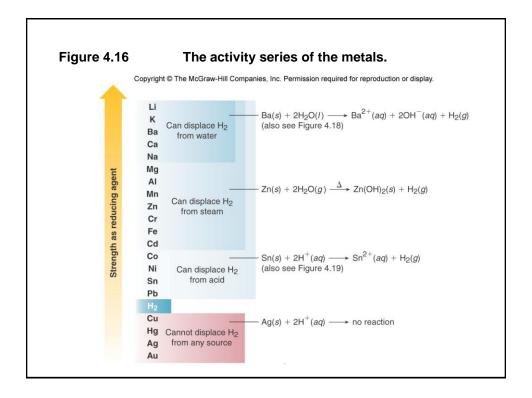
Silver nitrate solution

Cu2+

Ag atoms coating wire

L+1+5-2 0 +2+5-2 0 cu(NO<sub>3</sub>)<sub>2</sub>(aq) + 2Ag(s)

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Classify the following redox reaction as a combination, decomposition, or displacement reaction. Write a balanced molecular equation and identify the oxidizing and reducing agents:

magnesium (s) + nitrogen (g) 
$$\longrightarrow$$
 magnesium nitride (aq)

$$3\mathsf{Mg}\left(s\right)+\mathsf{N}_{2}\left(g\right)\,\longrightarrow\,\mathsf{Mg}_{3}\mathsf{N}_{2}\left(s\right)$$

This is a <u>combination</u> reaction, since Mg and N<sub>2</sub> combine.

Mg is the reducing agent;  $N_2$  is the oxidizing agent.

Classify the following redox reactions as a combination, decomposition, or displacement reaction. Write a balanced molecular equation and identify the oxidizing and reducing agents:

hydrogen peroxide (I)  $\rightarrow$  water (I) + oxygen gas

This is a decomposition reaction, since  $H_2O_2$  breaks down:

$$2 H_2O_2(I) \longrightarrow 2H_2O(I) + O_2(g)$$

 $H_2O_2$  is both the reducing and the oxidizing agent.