

# CHAPTER 4: AQUEOUS REACTIONS AND SOLUTION STOICHIOMETRY

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# SECTION 4.1 – GENERAL PROPERTIES OF AQUEOUS SOLUTIONS

• A solution is a homogeneous mixture of two or more substances.

• A solution in which water is the dissolving medium is called an aqueous solution.



# SOLUTE VS. SOLVENT

- The substance present in the greatest quantity is called the solvent.
- Water is considered the universal solvent because of its ability to dissolve many substances.
- The other dissolved substances are called the solutes.
- A solvent dissolves a solute.



#### Electrolytes

• A substance whose aqueous solutions contain ions is called an electrolyte because it will allow electric current to flow through it. Ex. NaCl

• A substance that does not form ions in solution is called a nonelectrolyte. Ex. C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>



# IONIC COMPOUNDS IN WATER

- When ionic compounds dissolve in water the ions separate and are surrounded by water molecules.
- Once the ions have separated, they can move and conduct electricity. In the crystalline form they cannot move or conduct electricity.
- The solvation process helps stabilize the ions in solution and prevents the cations and anions from recombining.



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# IONIC COMPOUND IN WATER

- OWater molecules are polar and have a  $\delta$ + and  $\delta$ -side.
- The more electronegative oxygen atoms are attracted to the positive ions.
- The less electronegative hydrogen atoms are attracted to the negative ions.



# MOLECULAR COMPOUNDS IN WATER

- When a molecular compound dissolves in water, the solution usually consists of intact molecules (neutral) dispersed throughout the system.
- •Consequently, most molecular compounds are nonelectrolytes. A few exceptions include strong acids like HCl.





Ionic vs. Molecular None

# STRONG AND WEAK ELECTROLYTES

- Strong electrolytes are those solutes that exist in solution completely or nearly completely as ions.
- Weak electrolytes are those solutes that exist in solution mostly in the form of molecules with only a small fraction in the form of ions.



(a) Nonelectrolyte

(b) Weak electrolyte

(c) Strong electrolyte

### CHEMICAL EQUILIBRIUM

- Chemical equilibrium is the state of balance in which the relative numbers of each type of ion or molecule in the reaction are constant over time.
- Equilibrium is represented by a double arrow for the yield sign. This shows that the reaction is occurring in both directions.





#### STRONG ELECTROLYTES

- Remember that soluble ionic compounds are strong electrolytes.
- We consider ionic compounds as those composed of metals and nonmetals – such as NaCl, FeSO<sub>4</sub> and Al(NO<sub>3</sub>)<sub>3</sub> – or compounds containing the ammonium ions, NH<sub>4</sub>+ - such as NH<sub>4</sub>Br and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>.



SAMPLE EXERCISE 4.1

• The diagram below represents an aqueous solution of one of the following compounds: MgCl<sub>2</sub>, KCl, or K<sub>2</sub>SO<sub>4</sub>. Which solution does the drawing best represent?

# PRACTICE EXERCISE

• If you were to draw diagrams like the previous one representing aqueous solutions of each of the following ionic compounds, how many anions would you show if the diagram contained six cations?

#### a. NiSO<sub>4</sub>

- b. Ca(NO<sub>3</sub>)<sub>2</sub>
- c.  $Na_3PO_4$
- d.  $Al_2(SO_4)_3$

## Section 4.2 - Precipitation Reactions

- Reactions that result in the formation of an insoluble product are called precipitate reactions.
- •A precipitate is an insoluble solid formed by a reaction in solution.





## Solubility

• The solubility of a substance at a given temperature is the amount of substance that can be dissolved in a given quantity of solvent at a given temperature.

•Most important solubility rule: Alkali metal ions and ammonium ions are soluble in water.



### SAMPLE EXERCISE 4.2

• Classify the following ionic compounds as soluble or insoluble in water:

a. Sodium carbonate

b. Lead (II) sulfate

### PRACTICE EXERCISE

•Classify the following compounds as soluble or insoluble in water:

a. Cobalt (II) hydroxide

b. Barium nitrate

c. Ammonium phosphate

# EXCHANGE REACTIONS

• Reactions in which positive ions and negative ions appear to exchange partners conform to the following generic equation:

#### $AX + BY \rightarrow AY + BX$

Such reactions are called exchange reactions, double displacement reactions, or metathesis reactions.



STEPS FOR WRITING DOUBLE DISPLACEMENT REACTIONS

- 1. Write the formulas for the reactants (balance charges).
- 2. Write the formulas for the products by switching the cations of the two reactants (balance charges).
- 3. Balance the equation.
- 4. Include states of matter when needed.



 $AX + BY \longrightarrow AY + BX$  $Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2KNO_3$ 

### SAMPLE EXERCISE 4.3

a. Predict the identity of the precipitate that forms when solutions of  $BaCl_2$  and  $K_2SO_4$  are mixed.

b. Write the balanced chemical equation for the reaction.

#### PRACTICE EXERCISE

a. What compound precipitates when solutions of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and LiOH are mixed?

b. Write a balanced equation for the reaction.

c. Will a precipitate form when solutions of Ba(NO<sub>3</sub>)<sub>2</sub> and KOH are mixed?

## COMPLETE IONIC EQUATIONS

A molecular equation is an equation showing the complete chemical formulas of the reactants and products without showing dissociated ions.
 Ex:

 $Pb(NO_3)_{2(aq)} + 2KI_{(aq)} \rightarrow PbI_{2(s)} + 2KNO_{3(aq)}$ 

A complete ionic equations is an equation that shows all soluble strong electrolytes as ions.
Ex:

 $\begin{array}{l} \mathrm{Pb}_{2^{+}(\mathrm{aq})} + 2\mathrm{NO}_{3^{-}(\mathrm{aq})} + 2\mathrm{K}_{+}(\mathrm{aq}) + 2\mathrm{I}_{-}(\mathrm{aq}) \xrightarrow{\phantom{aa}} \mathrm{PbI}_{2(\mathrm{s})} + \\ 2\mathrm{K}_{+}(\mathrm{aq}) + 2\mathrm{NO}_{3^{-}(\mathrm{aq})} \end{array}$ 



# NET IONIC EQUATIONS

• Ions that appear in identical forms on both sides of the yield sign are called spectator ions because they do not actually react.

• A net ionic equation is an equation in which the spectator ions have been removed.

**O**Complete Ionic Equation

 $Pb^{2+}(aq) + 2NO_{3^{-}(aq)} + 2K^{+}(aq) + 2I^{-}(aq) \rightarrow PbI_{2(s)} + 2K^{+}(aq) + 2NO_{3^{-}(aq)}$ 

• Net Ionic Equation  $Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_{2(s)}$ 



### **NET IONIC EQUATIONS**

In a net ionic equation, the numbers of atoms and the charges are conserved in the reaction.
If every ion in a complete ionic equation is a spectator, then no reaction occurs.



# STEPS FOR WRITING NET IONIC EQUATIONS

- 1. Write the balanced equation.
- 2. Write the complete ionic equation which shows strong electrolytes (ionic compounds and strong acids) written as ions.
- 3. Identify and cancel spectator ions.



### SAMPLE EXERCISE 4.4

• Write the net ionic equation for the precipitation reaction that occurs when solutions of calcium chloride and sodium carbonate are mixed.

#### PRACTICE EXERCISE

• Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of silver (I) nitrate and potassium phosphate are mixed. SECTION 4.3: ACID-BASE REACTIONS

• Acids and bases are also common electrolytes.

- Acids are substances that ionize in aqueous solutions to form hydrogen ions.
- •Since hydrogen ions consist of only 1 proton, acids are often called proton donors.





# Acids

- OMonoprotic acids contain one ionizable hydrogen. Ex: HCl
- ODiprotic acids contain two ionizable hydrogens. Ex: H<sub>2</sub>SO<sub>4</sub>
- Triprotic acids contain three ionizable hydrogens. Ex: H<sub>3</sub>PO<sub>4</sub>
- Most multiprotic acids only lose one hydrogen to a reasonable extent. HCI HC2H3O2



# Acids



• Acids taste sour.

- •Some acids also contain hydrogens that will not ionize.
- •Normally the hydrogen(s) that will ionize are listed at the from of the chemical formula.
- $\circ$ Ex: HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>
- •Sometimes the hydrogen that will ionize is listed at the end of a COOH group.
- OEx: CH<sub>3</sub>COOH

 $H_2SO_4$ 

# Bases



•Bases taste bitter.

- •Bases are substances that accept (react with ) hydrogen ions.
- •Bases produce hydroxide ions (OH-) when they dissolve in water.
- •Bases do not have to contain the hydroxide ion.



# Strong vs. Weak

• Strong acids and bases are strong electrolytes so they fully ionize in solution.

• Weak acids and bases are weak electrolytes so they only partially ionize in solution.



# Strong Acids

#### •You need to memorize the strong acids.

- HCl hydrochloric acid
- HBr hydrobromic acid
- HI hydroiodic acid
- HClO<sub>3</sub> chloric acid
- HClO<sub>4</sub> perchloric acid
- HNO<sub>3</sub> nitric acid
- $H_2SO_4$  sulfuric acid



#### STRONG BASES

•You need to memorize the strong bases.

Group 1 metal hydroxides: LiOH, NaOH, KOH, RbOH, and CsOH

Heavy Group 2 metal hydroxides: Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>



#### SAMPLE EXERCISE 4.5

• The following diagrams represent aqueous solutions of three acids (HX, HY, and HZ) with water molecules omitted for clarity. Rank them from strongest to weakest.



# PRACTICE EXERCISE

○Imagine a diagram showing 10 Na<sup>+</sup> ions and 10 OH<sup>-</sup> ions. If this solution were mixed with the one pictured on the previous question for HY, what would the diagram look like that represents the solution after any possible reaction? (H<sup>+</sup> ions will reaction with OH<sup>-</sup> ions to form H<sub>2</sub>O.)



### STRONG VS. WEAK ELECTROLYTE

	Strong Electrolyte	Weak Electrolyte	Non- electrolyte
Ionic	All	None	None
Molecular	Strong Acids	Weak acids and weak bases	All other compounds


Classify the following substances as a strong electrolyte, weak electrolyte, or nonelectrolyte: CaCl<sub>2</sub>, HNO<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH (ethanol), HCOOH (formic acid), KOH.

Consider solutions in which 0.1 mol of each of the following compounds is dissolved in 1L of water: Ca(NO<sub>3</sub>)<sub>2</sub>, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> (glucose), CH<sub>3</sub>COONa (sodium acetate), and CH<sub>3</sub>COOH (acetic acid). Rank the solutions in order of increasing electrical conductivity based on the fact that the greater the number of ions in solution the greater the conductivity.

#### **NEUTRALIZATION REACTIONS**

OWhen a solution of an acid and a solution of a base are mixed, a neutralization reaction occurs.
OThe products of the reaction are water and a salt.
OA salt is any ionic compound whose cation comes from a base and whose anion comes from an acid.



a. Write a balanced equation for the reaction between aqueous solutions of acetic acid (CH<sub>3</sub>COOH) and barium hydroxide.

b. Write the net ionic equation for this reaction.

a. Write a balanced equation for the reaction of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) and potassium hydroxide.

b. Write the net ionic equation for this reaction.

#### GAS FORMATION

• The sulfide ion and the carbonate ion will react with acids to form gases.



 $\circ$ Ex: S<sup>2-</sup>

 $2HCl_{(aq)} + Na_2S_{(aq)} \rightarrow H_2S_{(g)} + 2NaCl_{(aq)}$ 

○ Ex:  $CO_3^{2-}$ HCl<sub>(aq)</sub> + NaHCO<sub>3(aq)</sub> → NaCl<sub>(aq)</sub> + H<sub>2</sub>CO<sub>3(aq)</sub> H<sub>2</sub>CO<sub>3(aq)</sub> → H<sub>2</sub>O<sub>(l)</sub> + CO<sub>2(g)</sub> So ... HCl<sub>(aq)</sub> + NaHCO<sub>3(aq)</sub> → NaCl<sub>(aq)</sub> + H<sub>2</sub>O<sub>(l)</sub> + CO<sub>2(g)</sub>

#### SECTION 4.4 – OXIDATION-REDUCTION REACTIONS

•Oxidation-reduction reactions (redox reactions) are reactions in which electrons are transferred between reactants.

- •Oxidation is loss of electrons.
- Reduction is gain of electrons.

•Oxidation and reduction always occur together.



#### RULES FOR OXIDATION NUMBERS

1. For an atom in its elemental form, the oxidation number is always zero.

Ex: Na = 0  $F_2 = 0$ 

2. For any monatomic ion the oxidation number equals the charge on the ion.

Ex:  $Mg_2N_3 - Mg = +2$ , N = -3

3. The oxidation number of hydrogen is usually +1 when bonded to nonmetals and -1 when bonded to metals

> Ex: HCl H = +1LiH H = -1

#### **RULES FOR OXIDATION NUMBERS**

4. The oxidation number of oxygen is usually -2 (except in peroxide,  $O_{2^{2}}$ , where it is -1).

Ex: 
$$CO_2$$
  $O = -2$   
 $H_2O_2$   $O = -1$ 

5. The oxidation number of fluorine is -1 in all compounds. The other halogens have an oxidation number of -1 except when combined with oxygen in oxyanions.

Ex: NaF 
$$F = -1$$
  
HBr  $Br = -1$   
ClO-  $Cl = +1$ 

#### **RULES FOR OXIDATION NUMBERS**

6. The sum of the oxidation numbers of all atoms in a neutral compound is zero. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.

> Ex:  $P_2O_5$  O = -2, so P = +5 $CO_{3^{2-}}$  O = -2, so C = +4

• Determine the oxidation number of sulfur in each of the following:

a.  $H_2S$ 

b.  $S_8$ 

c.  $SCl_2$ 

d.  $Na_2SO_3$ 

e.  $SO_{4^{2}}$ 

• What is the oxidation state of each element in the following:
 a. P<sub>2</sub>O<sub>5</sub>

#### b. NaH

c.  $Cr_2O_7^{2}$ -

d. SnBr<sub>4</sub>

#### e. BaO<sub>2</sub>



 $OXIDATION \ OF \ METALS$ 

• Many metals undergo displacement reactions with acids to form salts and hydrogen gas.

 $\frac{\text{Mg}(s) + 2\text{HCl}(aq)}{0} \rightarrow \frac{\text{MgCl}_{2(aq)} + \text{H}_{2(g)}}{+1 - 1} \rightarrow \frac{1}{2} - 1 \qquad 0$ 

- Write the oxidation numbers for each element to determine which element is oxidized and which is reduced.
- OSince Mg goes from 0 to +2, it is oxidized. Since H goes from +1 to 0, it is reduced.



• Write the balance equation and net ionic equation for the reaction of aluminum with hydrobromic acid.

a. Write a balanced equation and net ionic equation for the reaction between magnesium and cobalt (II) sulfate.

b. What is oxidized and what is reduced in the reaction?

#### THE ACTIVITY SERIES

- A list of metals arranged in order of decreasing ease of oxidation is called an activity series.
- Active metals are at the top of the series and are most easily oxidized.
- •Noble metals are at the bottom of the series are not very reactive.
- •Any metal on the list can be oxidized by the ions of elements below it.



#### ACTIVITY SERIES

Metal	Oxidation Reaction	
Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$	
Potassium	$K(s) \longrightarrow K^+(aq) + e^-$	1
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^{-}$	
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^{-}$	
Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$	
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$	
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}$	
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^{-}$	
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$	
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^{-}$	
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^{-}$	
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^{-}$	
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^{-1}$	
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^{-}$	
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^{-}$	
Hydrogen	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$	
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^{-}$	
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$	
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^{-}$	
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^{-}$	
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^{-}$	

• Will an aqueous solution of iron (II) chloride oxidize magnesium metal? If so, write the balanced equation and net ionic equation for the reaction.

OWhich of the following metals will be oxidized by Pb(NO<sub>3</sub>)<sub>2</sub>: Zn, Cu, Fe?

# $\begin{array}{c} \text{Section 4.5-Concentrations of} \\ \text{Solutions} \end{array}$

- Scientists use the term concentration to designate the amount of solute dissolved in a given quantity of solvent or solution.
- Molarity (M) expresses the concentration of a solution as the number of moles of solute in a liter of solution.



Molarity (M) = L solution

• Calculate the molarity of a solution made by dissolving 23.4g of sodium sulfate in enough water to form 125mL of solution.

• Calculate the molarity of a solution made by dissolving 5.00g of glucose in sufficient water to form exactly 100mL of solution.

#### IONIC COMPOUNDS

 OWhen calculating concentration, remember that ionic compounds break into ions in solutions.
 OEx: MgCl<sub>2</sub> breaks into Mg<sup>2+</sup> and 2Cl<sup>-</sup>



• What are the molar concentrations of each of the ions present in a 0.025M aqueous solution of calcium nitrate?

• What is the molar concentration of K<sup>+</sup> ions in a 0.015M solution of potassium carbonate?

#### MOLARITY

## •Since molarity equals mol/L, it can be used as a conversion factor.



OHow many grams of Na<sub>2</sub>SO<sub>4</sub> are required to make 0.350L of 0.500M Na<sub>2</sub>SO<sub>4</sub>?

a. How many grams of Na<sub>2</sub>SO<sub>4</sub> are there in 15mL of 0.50M Na<sub>2</sub>SO<sub>4</sub>?

b. How many milliliters of 0.50M Na<sub>2</sub>SO<sub>4</sub> solution are needed to provide 0.038 mol of this salt?

#### DILUTION

- Stock solutions are solutions that are purchased at a specific concentration, but sometimes a different concentration is needed for an experiment.
- Solutions of lower concentration can then be obtained by adding water, a process called dilution.
- When solvent is added to dilute a solution, the number of moles of solute remains the same.

#### $\mathbf{M}_1 \ge \mathbf{V}_1 = \mathbf{M}_2 \ge \mathbf{V}_2$



#### OHow many milliliters of 3.0M H<sub>2</sub>SO<sub>4</sub> are needed to make 450mL of 0.10M H<sub>2</sub>SO<sub>4</sub>?

a. What volume of 2.50M lead (II) nitrate solution contains 0.0500mol of Pb<sup>2+</sup>?

b. How many milliliters of 5.0M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution must be diluted to prepare 250mL of 0.10M solution?

c. If 10.0mL of a 10.0M stock solution of NaOH is diluted to 250mL, what is the concentration of the resulting stock solution?

#### SECTION 4.6 – SOLUTION STOICHIOMETRY AND CHEMICAL ANALYSIS

•You can use molar mass and molarity to solve stoichiometry problems.

### STOICHIOMETRY

 the study of the quantitative aspects of chemical reactions.



OHow many grams of Ca(OH)<sub>2</sub> are needed to neutralize 25.0mL of 0.100M HNO<sub>3</sub>?

a. How many grams of NaOH are needed to neutralize 20.0mL of 0.150M H<sub>2</sub>SO<sub>4</sub> solution?

b. How many liters of 0.500M HCl are needed to react completely with 0.100 mol of Pb(NO<sub>3</sub>)<sub>2</sub>, forming a precipitate of PbCl<sub>2</sub>?

#### TITRATIONS

• To determine the concentration of a particular solute in a solution, chemists often carry out a titration, which involves combining a sample of the solution with a reagent solution of known concentration, called a standard solution.



#### TITRATIONS

- The point at which stoichiometrically equivalent quantities are brought together is known as the equivalence point.
- In acid-base titrations, dyes known as acid-base indicators are used to identify the equivalence point.
- The color change of the indicator signals the end point of the titration, which usually coincides very nearly with the equivalence point.




## SAMPLE EXERCISE 4.16

a. How many grams of chloride ion are in a sample of the water if 20.2mL of 0.100M Ag<sup>+</sup> is needed to react with all the chloride in the sample?

 $Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$ 

a. If the sample has a mass of 10.0g, what percent Cl- does it contain?

## PRACTICE EXERCISE

- a. A solution that contains  $Fe^{2+}$  is titrated with 47.20mL of 0.02240M MnO<sub>4</sub>. How many moles of MnO<sub>4</sub> were added to the solution?
  - $\begin{array}{c} MnO_{4^{\text{-}}(aq)} + 5Fe^{2+}{}_{(aq)} + 8H^{+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + \\ & 4H_2O_{(l)} \end{array}$

b. How many moles of  $Fe^{2+}$  were in the sample?

## PRACTICE EXERCISE

c. How many grams of iron were in the sample?

d. If the sample had a mass of 0.8890g, what is the percentage of iron in the sample?

# SAMPLE EXERCISE 4.17

One commercial method used to peel potatoes is to soak them in a solution of NaOH for a short time, remove them from the NaOH, and spray off the peel. The concentration of NaOH is normally in the range of 3 to 6M. The NaOH is analyzed periodically. In one such analysis, 45.7mL of 0.500M H<sub>2</sub>SO<sub>4</sub> is required to neutralize a 20.0mL sample of NaOH solution. What is the concentration of the NaOH solution? PRACTICE EXERCISE

• What is the molarity of an NaOH solution if 48.0mL is needed to neutralize 35.0mL of 0.144M H<sub>2</sub>SO<sub>4</sub>?

## SAMPLE INTEGRATIVE EXERCISE

A sample of 70.5mg of potassium phosphate is added to 15.0mL of 0.050M silver nitrate, resulting in the formation of a precipitate.
a. Write the molecular equation for the reaction.

b. What is the limiting reagent in the reaction?

SAMPLE INTEGRATIVE EXERCISE

c. Calculate the theoretical yield, in grams, of the precipitate that forms.