

## CHAPTER 4 TYPES OF CHEMICAL REACTIONS and SOLUTION STOICHIOMETRY

### 4.1- Water, the Common Solvent (pp.116-119)

1. **Bonding in H<sub>2</sub>O**—the two O—H bonds are polar covalent since oxygen has a higher electronegativity and thus the electrons are more attracted to the oxygen.
2. This creates a **partial** charge indicated by the Greek lower case letter delta,  $\delta$  (this unequal charge distribution makes the molecule **polar**).
3. Also notice the  $104.5^\circ$  bond angle. The two unshared electron pairs require more space than the shared pairs thus the usual  $109.5^\circ$  bond angle is reduced to about  $104.5^\circ$ .

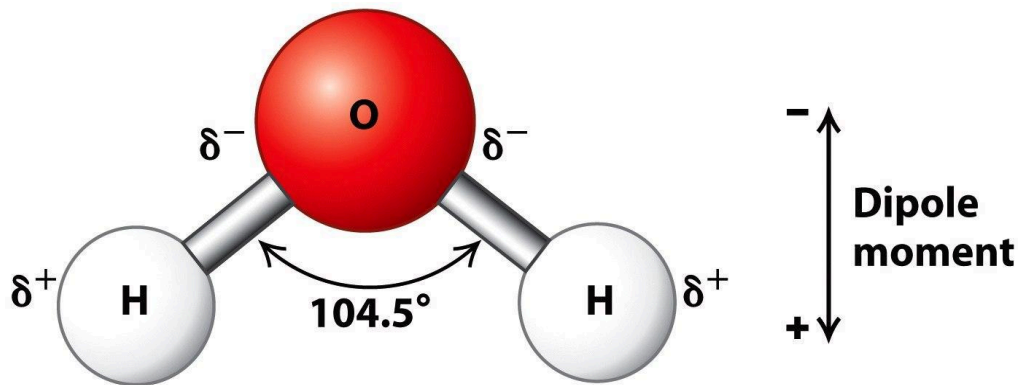
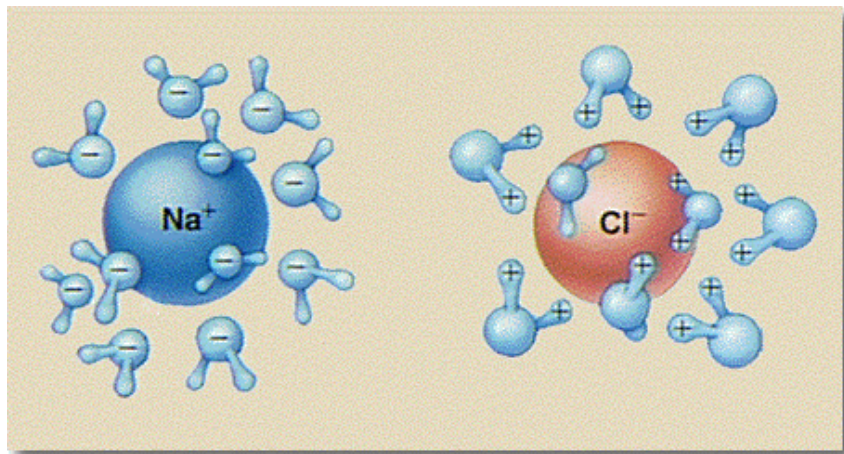
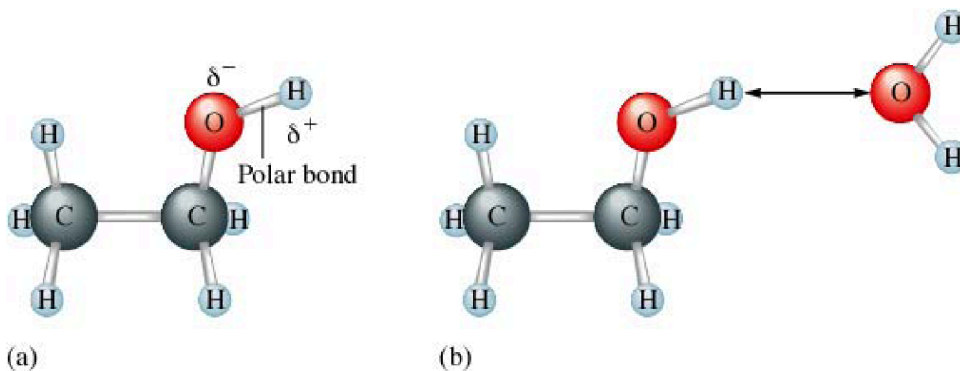


Figure 2-5  
Molecular Cell Biology, Sixth Edition  
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4. **Solubility and Hydration**—Since opposites attract, the positive ends of water are greatly attracted to the negative ions in an **ionic salt crystal** structure. The converse of this is also true. Solubility of ionic substances in water depends on the relative attraction of the ions for the water molecule.
5. In general, the principle of “like dissolves like” (in terms of bonding) is a useful guideline for predicting solute and solvent interaction



- a. Many ionic salts are soluble in water because of **molecule-ion attractions**.
- b. Water can also dissolve nonionic substances such as alcohols and sugars among others.  
If the carbon chain has more than 4 carbons the molecule is only slightly soluble.
- i- Alcohols and sugars contain O—H bonds that are polar just as the O—H bond in water. This polarity makes the molecule soluble.



(a) ethanol

(b) ethanol attracted to water molecule

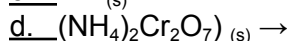
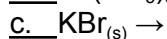
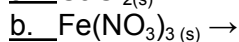
**c. Nonpolar molecules**, such as fats, do not dissolve in water since they are nonpolar and are not attracted by the polarity of the water molecule.

#### Example 4.1- Will the substances mix?

- Sodium nitrate and water
- Hexane(C<sub>6</sub>H<sub>14</sub>) and water
- Iodine and hexane
- Iodine and water

#### Example 4.2 Practice with Equations

Dissolve each of the solids in H<sub>2</sub>O



## 4.2- The Nature of Solutions: Strong and Weak Electrolytes vs. Non Electrolytes (pp.119-123)

1. A **solution** is a homogeneous mixture where a **solute** is dissolved in a **solvent**. **Aqueous** solutions are solutions where the solvent is water.

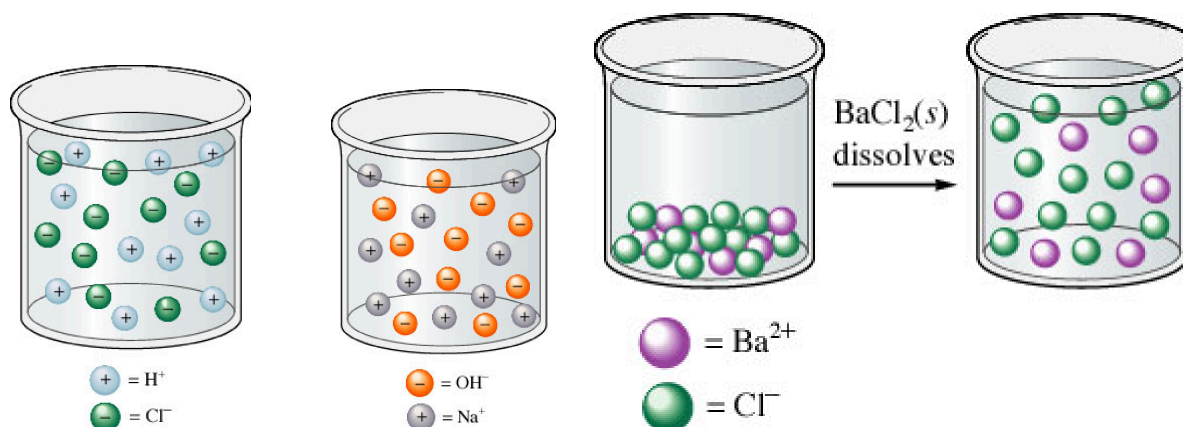
a. **solute**- it is usually the one of a lesser amount; if is the same phase of matter as the solvent it is the one that changes phase; it is the one that dissolves into the solvent.

b. **solvent** – it is usually the one in the greater amount; it is the one that retains its phase of matter; it is the one into which the solute dissolves.

2. Properties of aqueous solutions:

a. **Electrolytes**—substances that dissolve in water to form ions in solutions and thus conduct an electric current.

i- **Strong electrolytes** completely dissociate (strong acids, strong bases, and soluble salts)



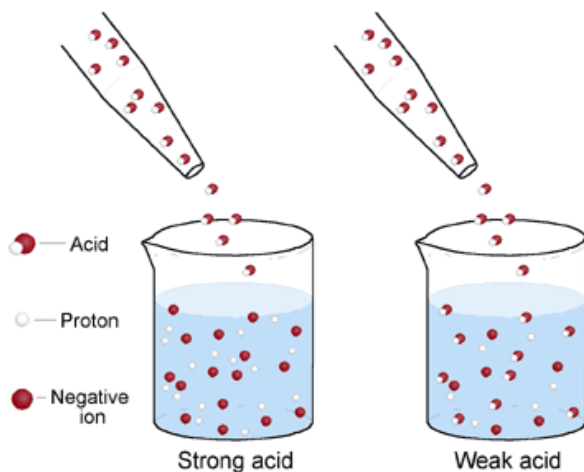
### MEMORIZE!!

• **Six Strong acids:** HClO<sub>4</sub>, HI, HBr, HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>

• **Eight Strong bases:** LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>  
Group 1 + OH<sup>-</sup> and some of Group 2 + OH<sup>-</sup>

• **Solubility Rules for ionic salts:** (See section 4.5)

ii-**Weak electrolytes**- substances that **do not completely ionize** in water; only about 1% dissociation occurs, such that there are mostly un-ionized molecules in the water and only a few ions (weak acids (HF and  $\text{CH}_3\text{COOH}$ ) and weak bases ( $\text{NH}_3$ )). These are poor conductors of electricity.



b. **Nonelectrolytes**--solutions where dissolving has occurred, but the **solute does not make ions** and therefore cannot conduct electricity. (Pure water, sugar, alcohols, antifreeze are a few examples)

**Example 4.2A-** Identify each of the following as a Strong electrolyte, a Weak electrolyte, or a Nonelectrolyte.

a. perchloric acid

d. ammonia

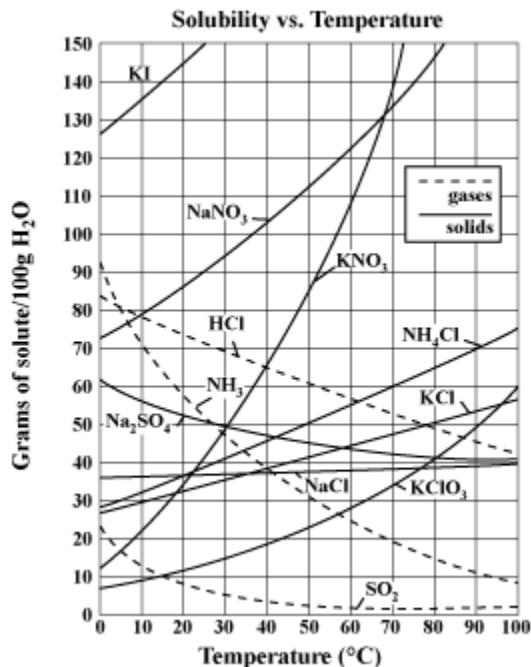
b. hexene

e. calcium chloride

c. lithium hydroxide

f. ethanoic acid

### 3. Solubility Curves



a. Any point on a line indicates the concentration of a saturated solution - the maximum amount of solute that will dissolve at that specific temperature.

b. Values on the graph below a curve represent unsaturated solutions - more solute could be dissolved at that temperature.

c. Values above a curve represent supersaturated solutions, a solution which holds more solute than can normally dissolve in that volume of solvent at a given temperature.

#### Example 4.2C- Solubility Curves – Not in textbook

i- What mass of NaCl solute will dissolve in 100mL of water at 100°C \_\_\_\_\_

ii-Determine the Molarity of a saturated NaCl solution at 100°C. (Assume 1g =1ml.)

iii-What term - saturated, unsaturated, or supersaturated- best describes a solution that contains 70g of NaNO<sub>3</sub> per 100 mL H<sub>2</sub>O at 30°C. \_\_\_\_\_

### 4.3- The Composition of Solutions (pp.123-130)

1. Depending on the type of solutes, a solution may contain only ions (for strong electrolytes), ions and molecules (for weak electrolytes), or only molecules (for nonelectrolytes).

2. The amount of solute dissolved in a solution is expressed in terms of concentrations - the most important is molarity or molar concentration:

$$\text{Molarity (M)} = \frac{\text{Mole of Solute}}{\text{Liters of Solution}} \quad (\text{M} = \text{mol/L})$$

3. If the molar concentration of a solution is known, the mole of solute in a given volume of the solution can be calculated as follows:

$$\text{Mole of solute} = \text{Molarity} \times \text{Liters}_{\text{solution}}$$

4. Concentration may also be expressed as:

$$\text{Percent (by mass)} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 100\%$$

$$\text{Percent (by volume)} = \frac{\text{Volume of Solute}}{\text{Volume of Solution}} \times 100\%$$

$$\text{Mole fraction (X}_i\text{)} = \frac{\text{Moles of Solute}}{\text{Total Moles of Solution}}$$

$$\text{Molality (m)} = \frac{\text{Moles of Solute}}{\text{kg of Solvent (H}_2\text{O)}}$$

$$\text{Parts per Million (PPM)} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^6$$

**Example 4.3A- Calculating Molarity**

What is the molarity of a solution prepared by dissolving 11.85 g of solid potassium permanganate in enough water to make 750. mL of solution?

**Example 4.3B- Mass from Molarity**

Calculate the mass of sodium chloride needed to prepare 175 mL of a 0.500 M NaCl solution.

**Example 4.3C- Volume from Molarity**

How many mL of solution are needed to prepare a 2.48 M sodium hydroxide solution that contains 31.52 g of dissolved solid?

**Example 4.3D.- Calculating Molarity of Ions in Solution**

a. 0.025 M  $\text{Ca}(\text{OCl})_2$

b. 2M  $\text{CrCl}_3$

**Example 4.3E- Calculating Molarity of Ions in Solution**

Calculate the molarity of chloride ions in a solution prepared by dissolving 9.82 g of copper II chloride in enough water to make 600. mL of solution.

**Example 4.3 F- Practice with Ion Concentration**

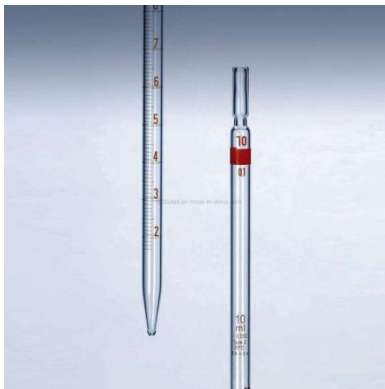
Determine the molarity of  $\text{Fe}^{3+}$  ions and  $\text{SO}_4^{2-}$  ions in a solution prepared by dissolving 48.05 g of  $\text{Fe}_2(\text{SO}_4)_3$  in enough water to make 800 mL of solution.

**Example 4.3- Parts per Million (PPM)**

A 155.3 g sample of pond water is found to have  $1.7 \times 10^{-4}$  g of phosphate in the water. What is the concentration of phosphate in ppm?

5. Preparing Solution by Dilution of Stock Solution(pg 128-129)

- a. A **measuring pipet** is graduated throughout and can be used to measure various volumes of liquid very accurately.
- b. A **volumetric (transfer) pipet** is designed to measure one volume accurately.



- c. When a solution is diluted the number of moles of solute remains constant.

**Mole solute = (initial molarity x initial volume) = (final molarity x final volume)**

$$M_i \times V_i = M_f \times V_f$$

#### **Example 4.3G- Preparing Solution by Dilution of Stock Solution**

- a. What volume of 12 M HCl (aq) must be used to prepare 600 mL of a 0.30 M HCl solution?
- b. The 12 M HCl must be added to how much water?

#### **Example 4.3I- Parts per Million (PPM)**

A 155.3 g sample of pond water is found to have  $1.7 \times 10^{-4}$  g of phosphate in the water. What is the concentration of phosphate in ppm?

#### **Example 4.3J- Molarity to Parts Per Million**

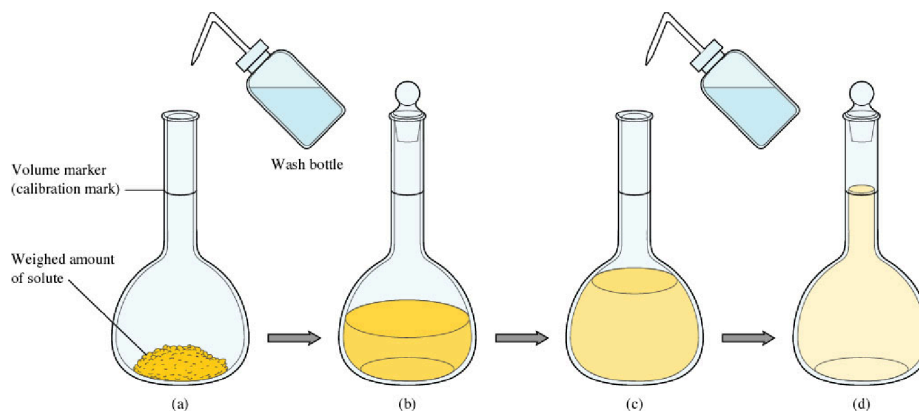
A solution is  $3 \times 10^{-7}$  in manganese (VII) ion. What is the  $Mn^{7+}$  concentration in ppm?

#### **6. Preparing a Standard Solution from a Pure Solid Substance**



a. **Standard solution**—is a solution whose **concentration is accurately known**.

b. **Volumetric flask**—contains an **exact total volume of solution**.



c. **Steps involved in the preparation of a standard solution.**

i- An analytical balance is used to mass amount a substance (the solute) and is then put into the volumetric flask, and a small quantity of water is added.

ii- The solid is dissolved in the water by gently swirling the flask (with the stopper in place).

iii- More water is added, until the level of the solution just reaches the mark etched on the neck of the flask (in (d) above).

iv- To prepare a standard solution from a pure solid, the amount of solute required is calculated from the volume and molar concentration of the target solution as follows:

d. Thus:      **Mole of solute = (Liter of solution) x Molarity**  
                    **grams of solute needed = (mol of solute) x (molar mass)**

**Example 4.3G- Preparing a Standard Solution from a Pure Solid Substance**

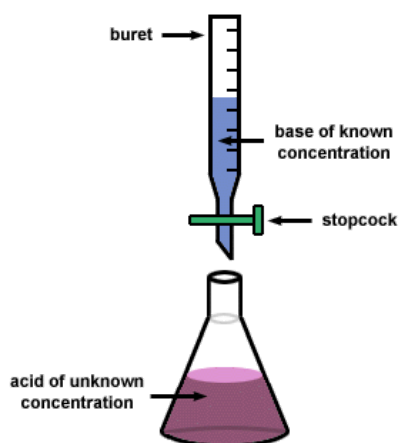
To analyze the alcohol content of a certain wine, a chemist needs 1.00 L of an aqueous 0.200 M  $K_2Cr_2O_7$  (potassium dichromate) solution. How much solid  $K_2Cr_2O_7$  must be weighed out to make this solution? [FYI—this was initially the “stuff” used for breathalyzers]

**4.4 Types of Reactions in Aqueous Solutions- overview (p.130)**

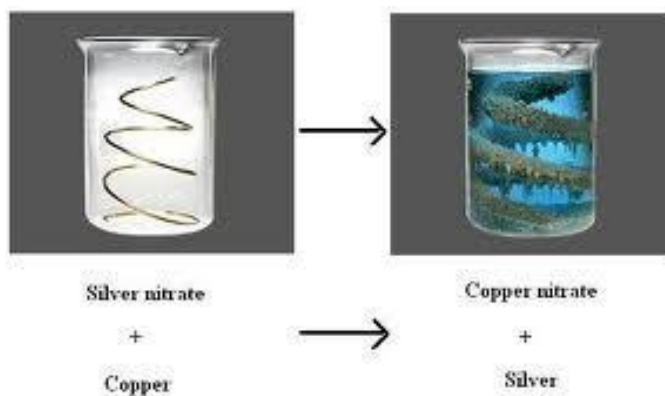
1. Precipitation Reactions (4.5-4.7)



2. Acid-Base (Neutralization) Reactions (4.8)



3. Oxidation-Reduction Reactions (REDOX) (4.9)



#### **4.5 Precipitation Reactions (pp.131-136)**

1. The solubility rules for ionic compounds are useful for predicting precipitation reactions.

#### **Solubility Rules for Ionic Compounds – AP Only responsible for the bold**

- 1. Most salts containing alkali metals and ammonium ( $\text{NH}_4^+$ ) are soluble.**
  - 2. Most compounds of nitrate ( $\text{NO}_3^-$ ), acetate ( $\text{CH}_3\text{COO}^-$ ), hydrogen carbonate ( $\text{HCO}_3^-$ ), perchlorates ( $\text{ClO}_4^-$ ) and chlorates ( $\text{ClO}_3^-$ ) are soluble.**
  3. Most salts containing halides  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions are soluble, except when combined with  $\text{Ag}^+$ ,  $\text{Pb}^{+2}$  and  $\text{Hg}_2^{+2}$ . Note most fluorides  $\text{F}^-$  (except those of alkali metals and ammonium) are insoluble
  4. Most sulfate salts are soluble, except  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{Hg}_2\text{SO}_4$ ,  $\text{SrSO}_4$ , and  $\text{CaSO}_4$ .
  5. Most hydroxides ( $\text{OH}^-$ ) are only slightly soluble, except to the hydroxides of the alkali metals,  $\text{NH}_4\text{OH}$ , warm  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ .
  6. Most sulfide ( $\text{S}^{2-}$ ), carbonate ( $\text{CO}_3^{2-}$ ), chromate ( $\text{CrO}_4^{2-}$ ), and phosphate ( $\text{PO}_4^{3-}$ ) salts are only slightly soluble, except those compounds that apply to Rule #1.
2. These are reactions that yield insoluble products (called **precipitates**) when two aqueous solutions are mixed.



#### **4.6 Describing Reactions in Solution (pp.136-138)**

1. Reactions in aqueous solutions may be described using three different types of equations:
  - a. Molecular Equation
  - b. Complete Ionic Equation or Total Ionic Equation
  - c. Net ionic Equation

**2. Note that only the ions that combine to form the precipitate are indicated in the net ionic equation; ions not involved in forming the precipitate are called spectator ions.**

**Acids only lose one  $\text{H}^+$  ion in a reaction for net ionic equation unless it a titration reaction and then they will react all  $\text{H}^+$ s in a titration reaction. Weak acids do not dissociate but do react.**

**Example 4.6A- Molecular, Complete Ionic, and Net Ionic Equations/Predicting Products**

**a. Aqueous potassium iodide reacts with aqueous lead II nitrate.**

**b Aqueous nickel II chloride reacts with aqueous sodium hydroxide.**

**c. Aqueous Calcium hydroxide reacts with Iron III chloride.**

**d. Aqueous Sodium hydroxide reacts with hydrochloric acid.**

#### **4.7 Stoichiometry of Precipitation Reactions (pp.138-140)**

##### **Example 4.7A- Problems Based on Precipitation**

Calculate the mass of  $\text{Ag}_2\text{S}$  produced when 125 mL of 0.200 M  $\text{AgNO}_3$  is added to excess  $\text{Na}_2\text{S}$  solution.

##### **Example 4.7B- Problems Based on Precipitation**

What mass of  $\text{Fe}(\text{OH})_3$  is produced when 35 mL of a 0.250 M  $\text{Fe}(\text{NO}_3)_3$  solution is mixed with 55 mL of a 0.180 M  $\text{KOH}$  solutions?

##### **Example 4.7C- Problems Based on Precipitation**

An ore sample is to be analyzed for sulfur. As part of the procedure, the ore is dissolved and the sulfur is converted to  $\text{SO}_4^{2-}$ . Barium nitrate is added, which causes the sulfate to precipitate out as  $\text{BaSO}_4$ . The original sample has a mass of 3.187g. The dried  $\text{BaSO}_4$  has a mass of 2.005g. What is the percent sulfur in the original ore?

**Example- Extra: Stoichiometry of Precipitation Reactions**

In an experiment, a mixture is prepared by adding 260. mL of 1.20 M Lead (II) nitrate to 300. mL of 1.90 M potassium iodide. Calculate the following:

- The total amount of precipitate formed.
- The final concentrations of the  $K^+$ ,  $NO_3^-$ ,  $Pb^{+2}$ , and  $I^-$  in the solution.
- Describe the change in concentration of the ions  $K^+$  and  $NO_3^-$  as the reaction occurs in the beaker containing KI (aq).
- An important part of the experiment is determining the % yield of solid product formed at the end of the reaction. To insure precise massing of the collected precipitate, the solid is heat dried in an oven before massing. If the solid is not adequately heat dried at the conclusion of the experiment, how would this error affect the calculation of the % yield? (Too high, too low, no change). Defend your answer with a mathematical setup.

## 4.8 Acid-Base Reactions (pp.140-147)

### 1. ACID-BASE THEORIES

#### a. ARRHENIUS DEFINITION

- **acid**--donates a hydrogen ion (H<sup>+</sup>) in water.
- **base**--donates a hydroxide ion in water (OH<sup>-</sup>)
- 

#### b. BRONSTED-LOWRY DEFINITION

- **acid**--donates a proton in water.
- **base**--accepts a proton in water.
- This theory is better; it explains ammonia as a base. This is the main theory that we will use for our acid/base discussion.
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#### c. LEWIS DEFINITION

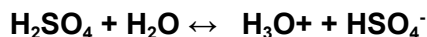
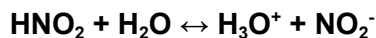
- **acid**--accepts an electron pair.
- **base**--donates an electron pair
- This theory explains **all** traditional acids and bases plus a host of coordination compounds and are used widely in organic chemistry. Uses coordinate covalent bonds.

### 2. THE BRONSTED-LOWRY CONCEPT OF ACIDS AND BASES (our focus!!)

- Using this theory, you should be able to write weak acid/base dissociation equations and identify acids, bases, conjugate acid and conjugate base pairs.
- **conjugate acid-base pair**--A pair of compounds that differ by the presence of one H<sup>+</sup> unit. This idea is critical when it comes to understanding buffer systems.

#### Example 4.8A- Bronsted-Lowry conjugate acid/base pairs.

Identify the acid, base, conjugate acid, conjugate base in each reaction.



#### Example 4.8B- Neutralization of a Strong Acid

How many mL of a 0.800 M NaOH solution is needed to just neutralize 40.00 mL of a 0.600 M HCl.

### 3. Old Table L-Relative Strengths of Acids in Aqueous Solutions

L

**RELATIVE STRENGTHS OF ACIDS IN AQUEOUS SOLUTION AT 1 atm AND 298 K**

Conjugate Pairs		$K_a$
ACID	BASE	
HI	$\text{H}^+ + \text{I}^-$	very large
HBr	$\text{H}^+ + \text{Br}^-$	very large
HCl	$\text{H}^+ + \text{Cl}^-$	very large
$\text{HNO}_3$	$\text{H}^+ + \text{NO}_3^-$	very large
$\text{H}_2\text{SO}_4$	$\text{H}^+ + \text{HSO}_4^-$	large
$\text{H}_2\text{O} + \text{SO}_2$	$\text{H}^+ + \text{HSO}_3^-$	$1.5 \times 10^{-2}$
$\text{HSO}_4^-$	$\text{H}^+ + \text{SO}_4^{2-}$	$1.2 \times 10^{-2}$
$\text{H}_3\text{PO}_4$	$\text{H}^+ + \text{H}_2\text{PO}_4^-$	$7.5 \times 10^{-3}$
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	$\text{H}^+ + \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$8.9 \times 10^{-4}$
$\text{HNO}_2$	$\text{H}^+ + \text{NO}_2^-$	$4.6 \times 10^{-4}$
HF	$\text{H}^+ + \text{F}^-$	$3.5 \times 10^{-4}$
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	$\text{H}^+ + \text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$1.0 \times 10^{-4}$
$\text{CH}_3\text{COOH}$	$\text{H}^+ + \text{CH}_3\text{COO}^-$	$1.8 \times 10^{-5}$
$\text{Al}(\text{H}_2\text{O})_6^{3+}$	$\text{H}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$1.1 \times 10^{-5}$
$\text{H}_2\text{O} + \text{CO}_2$	$\text{H}^+ + \text{HCO}_3^-$	$4.3 \times 10^{-7}$
$\text{HSO}_3^-$	$\text{H}^+ + \text{SO}_3^{2-}$	$1.1 \times 10^{-7}$
$\text{H}_2\text{S}$	$\text{H}^+ + \text{HS}^-$	$9.5 \times 10^{-8}$
$\text{H}_2\text{PO}_4^-$	$\text{H}^+ + \text{HPO}_4^{2-}$	$6.2 \times 10^{-8}$
$\text{NH}_4^+$	$\text{H}^+ + \text{NH}_3$	$5.7 \times 10^{-10}$
$\text{HCO}_3^-$	$\text{H}^+ + \text{CO}_3^{2-}$	$5.6 \times 10^{-11}$
$\text{HPO}_4^{2-}$	$\text{H}^+ + \text{PO}_4^{3-}$	$2.2 \times 10^{-13}$
$\text{HS}^-$	$\text{H}^+ + \text{S}^{2-}$	$1.3 \times 10^{-14}$
$\text{H}_2\text{O}$	$\text{H}^+ + \text{OH}^-$	$1.0 \times 10^{-14}$
$\text{OH}^-$	$\text{H}^+ + \text{O}^{2-}$	$< 10^{-36}$
$\text{NH}_3$	$\text{H}^+ + \text{NH}_2^-$	very small

Note:  $\text{H}^+(\text{aq}) = \text{H}_3\text{O}^+$   
 Sample equation:  $\text{HI} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{I}^-$

**4. Stoichiometry of Acid-Base Reactions\Neutralization Reaction of an Acid**



a. Example of molecular, complete ionic, total ionic, and net ionic equations for strong acid-strong base reactions:



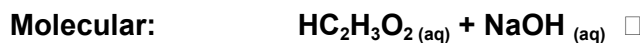
**Complete ionic:**

**Net ionic:**

**Spectator ions:**

**For all strong acid-strong base reactions, the net ionic equations are the same.**

b. Weak acids and weak bases only ionize partially. In fact, most remain in their molecular form in solution. Therefore, they should NOT be written in the ionized forms, even when writing the ionic equations. For example, the equations for the reaction between acetic acid (a weak acid) and sodium hydroxide (a strong base) are as follows:



**Complete ionic:**

**Net ionic:**

**Spectator ion:**

## 5. Acid-Base Titration

a. Titration is an important technique in **volumetric analysis**. It involves adding an exact amount of one reactant (called titrant) from a buret to another reactant (called analyte) in a flask.

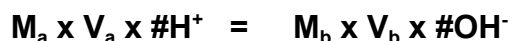
**b. The primary objective of titration is to determine the molar concentration of one solution using the volume and concentration of another solution.**

c. In the process, the titrant is carefully added to the flask from a buret until the **equivalence point** is reached. This is the point in the titration **where enough titrant has been added to react exactly with the analyte**.

d. In a good titration, the equivalence point should match the **end-point** – a point marked by the **change in the color of the indicator**- a substance that changes color when a solution changes from being acidic to slightly basic.

e. A commonly used indicator in acid-base titration is **phenolphthalein**, which changes from colorless in acid solution to pinkish-violet in basic solution.

**f- Neutralization/Titration Equation:**



g. Titration video: <http://www.youtube.com/watch?v=i7jnSaf1Muc>

Notes:

**Example 4.8A- The Stoichiometry of Acid-Base Reactions**

How many mL of a 0.800 M NaOH solution is needed to just neutralize 40.00 mL of a 0.600 M HCl.

**Example 4.8B- Acid-Base titration**

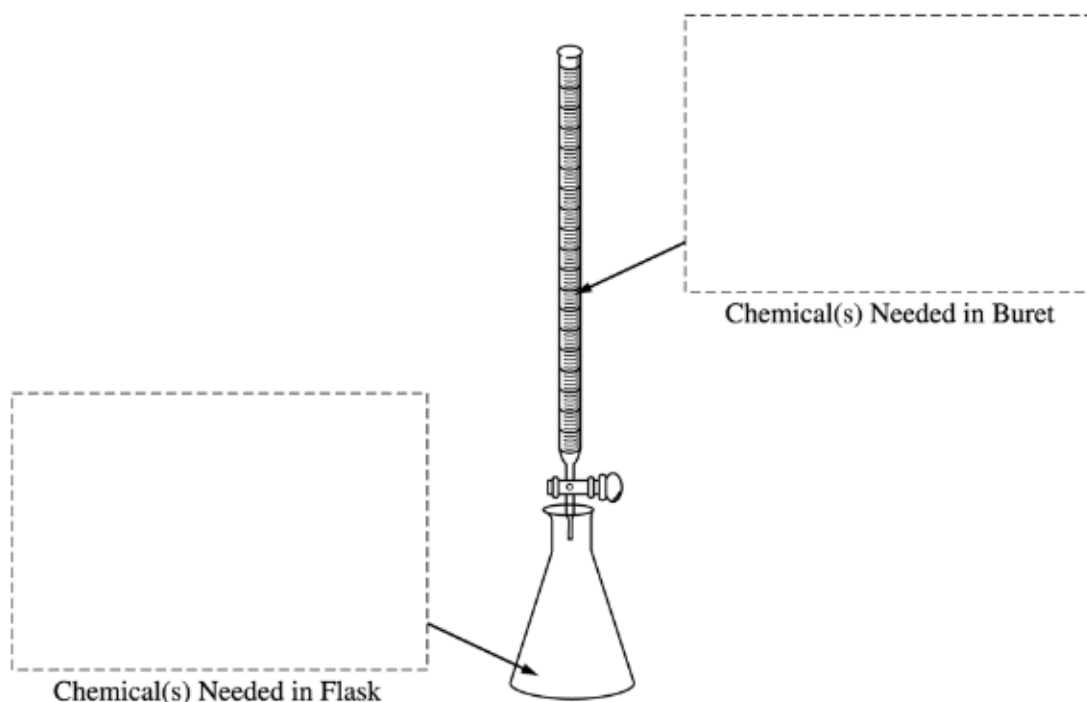
You wish to determine the molarity of a solution of sodium hydroxide. To do this you titrate a 25.00 mL aliquot of your sample, which has had 3 drops of phenolphthalein added so that it is pink, with 0.1067 M HCl. The sample turns clear, indicating that the NaOH has been neutralized, after the addition of 42.95 mL of the HCl. Calculate the molarity of your NaOH solution.

**Example 4.8C- Molar Mass of an Acid**

A student is trying to determine the molar mass of a monoprotic acid. A 2.879 g sample of the pure solid acid is massed using an electronic balance and dissolved in distilled water. Three drops of phenolphthalein indicator are added to the solution. The sample is titrated with a standardized solution of 0.1704 M NaOH<sub>(aq)</sub>. The pink endpoint is reached after the addition of 42.55 mL of the base. Calculate the molar mass of the monoprotic acid.

An experiment is performed to determine the molar mass of an unknown solid monoprotic acid, HA, by titration with a standardized NaOH solution.

- What measurement(s) must be made to determine the number of moles of NaOH used in the titration?
- Write a mathematical expression that can be used to determine the number of moles of NaOH used to reach the endpoint of the titration.
- How can the number of moles of HA consumed in the titration be determined?
- In addition to the measurement(s) made in part (a), what other measurement(s) must be made to determine the molar mass of the acid, HA?
- Write the mathematical expression that is used to determine the molar mass of HA.
- The following diagram represents the setup for the titration. In the appropriate boxes below, list the chemical(s) needed to perform the titration.

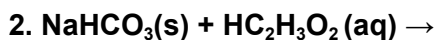
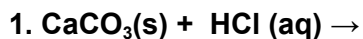


- Explain what effect each of the following would have on the calculated molar mass of HA. Justify your answers.
  - The original solid acid, HA, was not completely dry at the beginning of the experiment.
  - The procedure called for 25 mL of H<sub>2</sub>O in the Erlenmeyer flask, but a student used 35 mL of H<sub>2</sub>O.

**More space on next page**

## 6. Acid-Base Reactions that Produces Gases and Related Reactions

a. Some substances produce gaseous product when reacted with acid solution. For example, all carbonate and bicarbonates produce carbon dioxide gas when reacted with dilute acid solution.



b. Metallic oxides and water form bases (metallic hydroxides):

1. Solid sodium oxide is added to water

2. Solid magnesium oxide is added to water

c. Nonmetallic oxides and water form acids. The nonmetal retains its oxidation number:

1. Dinitrogen pentoxide is bubbled into water

2. Dichlorine trioxide is bubbled into water

d. Metallic oxides and nonmetallic oxides form salts:

1. Solid sodium oxide is added to carbon dioxide

2. Solid calcium oxide is added to sulfur trioxide

1. An oxidation-reduction (REDOX) reaction is an electron transfer reaction.

- a. Oxidation- loss of electrons and an increase in oxidation number. “OIL”
- b. Reduction - the gain of electrons and a decrease in oxidation number. “RIG”
- c. Oxidizing agent- reactant that gains electrons; it contains the element being reduced.
- d. Reducing agent - reactant that loses electrons; it contains the element being oxidized.

2. Determining Oxidation-Reduction Reactions

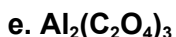
- a. The **oxidation state (or oxidation number)** is the charge that an atom has or appears to have whether it is in free elemental form, a compound, or a polyatomic ion.
- b. The following guidelines are used to determine the oxidation numbers (o.n.) of elements.

3. **Guidelines for Determining Oxidation Numbers-** *(Rules are listed in order of preference. Whenever two rules contradict one another, the one listed first takes precedence)*

- a. Atoms in free elemental forms are assigned an oxidation number 0.
- b. The sum of o.n. of atoms in a neutral molecule or formula unit is 0; the sum of o.n. of atoms in a polyatomic ion is equal to the net charge of the ion (in magnitude and sign).
- c. In their compounds, each element of Group 1 metals has an o.n. +1, each element of Group 2 metals has an o.n. +2, boron and aluminum each have an o.n. +3, silver has an o.n. +1, zinc has an o.n. +2, and fluorine has an o.n. -1.
- d. The o.n. of hydrogen is +1, except in metal hydrides, in which its o.n. is -1.
- e. The o.n. of oxygen is -2, except in peroxides, in which its o.n. is -1 or +2 in  $\text{OF}_2$ .
- f. In binary compounds with metals, chlorine, bromine, and iodine each has an o.n. of -1; sulfur, selenium, and tellurium each has an o.n. of -2. Nitrogen is usually -3 when found as an anion in a compound

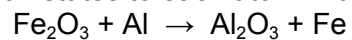
#### Example 4.9A- Assigning Oxidation Numbers

Assign oxidation #'s to each element in the following species:



#### Example 4.9B- Practice with Oxidation States

Assign oxidation states to each atom in the equation.



### Example 4.9C- Oxidation and Reduction

Identify the reduction half reaction, oxidation half reaction, the substance being oxidized, the substance being reduced, balance the equation, and determine the total number of electrons transferred in the process.

- a.  $\text{H}_{2(\text{g})} + \text{O}_2 \rightarrow \text{H}_2\text{O}$
- b.  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
- c.  $\text{AgCl} + \text{H}_2 \rightarrow \text{H}^+ + \text{Ag} + \text{Cl}^-$
- d.  $\text{MnO}_4^- + \text{H}^+ + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$

### 4.10 Balancing Oxidation-Reduction Reactions (pp.152-158)

## **Rules for Balancing REDOX Equations (Half-Reaction Method)**

### **A. Acidic, or Neutral, Solution**

1. Divide the “skeleton” equation into two separate reduction and oxidation “half-reactions”.
2. For **each** half-reaction:
  - a. Balance all elements **except** hydrogen and oxygen.
  - b. Balance oxygen by adding water ( $\text{H}_2\text{O}(l)$ ).
  - c. Balance hydrogen by adding  $\text{H}^+(aq)$  ion.
  - d. Balance charge by adding electrons.
3. If required, multiply each balanced half-reaction by the smallest whole number necessary to equalize the number of electrons in the two half reactions.
4. Sum the two half-reactions to obtain the overall equation. If possible, simplify the overall equation by canceling like species.
5. Check that the elements and charges balance on both sides of the equation.

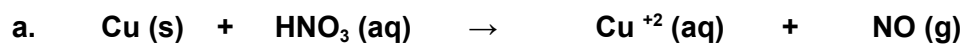
### **B. Basic Solution**

1. Complete steps 1-5 described above for an acidic solution.
2. Add one  $\text{OH}^-(aq)$  ion to both sides of the overall equation for every  $\text{H}^+(aq)$  ion present.
  - a. The  $\text{H}^+(aq)$  ions on one side combine with the added  $\text{OH}^-(aq)$  ions to form  $\text{H}_2\text{O}(l)$ , and  $\text{OH}^-(aq)$  ions appear on the other side of the equation.  $\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$
3. If possible, simplify the resulting overall equation by canceling like species.
4. Check that the elements and charges balance on both sides of the equation.

### **Example 4.10A- Balancing REDOX Practice-acidic solution**

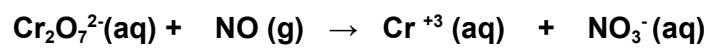


Balance the following REDOX reactions in acid solution:



Example 4.10B- Balancing REDOX Practice-basic solution

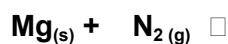
Balance the following REDOX reactions in basic solution:



#### 4.11 Types of Oxidation-Reduction Reactions

### 1. Reactions between Metals and Nonmetals to form binary salts

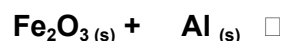
**Examples:**



**In reactions between metals and nonmetals, the metals are reducing agents, which are oxidized to cations, and the nonmetals are oxidizing agents, which are reduced to anions.**

### 2. Single-Replacement Reactions-active metals and nonmetals replace less active metals and nonmetals.

**Examples:**



**In these reactions, free metals such as Al, and Cu, are reducing agents; each loses one or more electrons. In the other reaction, F<sub>2</sub> is reduced as it replaces Cl<sup>-</sup> in KCl.**

### 3. Oxidation-Reduction Reactions in Aqueous Solutions

**Examples:**



**Many oxidation-reduction reactions in aqueous solutions occur under acidic or basic conditions: MnO<sub>4</sub><sup>-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> are strong oxidizing agents; in acidic solutions they are reduced to Mn<sup>2+</sup> and Cr<sup>3+</sup>, respectively.**

## **Simple Oxidation-Reduction Titrations**

1. Titration Involving Oxidation-Reduction Reactions:

a.  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  are the most commonly used oxidizing agents in REDOX titration. **This is because the solutions change color as they are being reduced and this color change serves as the titration indicator.** For example:

i- For  $\text{KMnO}_4$  its purple color changes to colorless when  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$ .

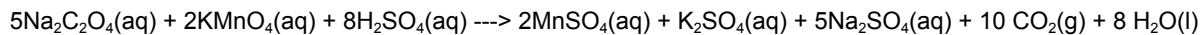
ii- For  $\text{K}_2\text{Cr}_2\text{O}_7$ , its color changes from bright orange to purplish-blue when  $\text{Cr}_2\text{O}_7^{2-}$  is reduced to  $\text{Cr}^{3+}$ .

**b. Summary of steps in a REDOX titration:**

### **Example 4.11 A REDOX Titrations**

0.2640 g of sodium oxalate is dissolved in a flask and requires 30.74 mL of potassium permanganate (from a buret) to titrate it and cause it to turn pink (the end point).

The equation for this reaction is:

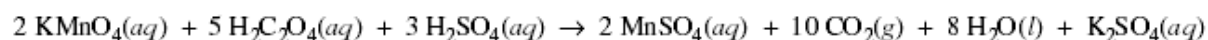


- (a) How many moles of sodium oxalate are present in the flask?
- (b) How many moles of potassium permanganate have been titrated into the flask to reach the end point?
- (c) What is the molarity of the potassium permanganate?

#### Example 4.11B REDOX Titrations

A 0.0483 M  $\text{KMnO}_4$  solution was used to titrate a solution containing 0.8329 g of impure  $\text{CaC}_2\text{O}_4$ . If 30.25 mL of  $\text{KMnO}_4$  solution was required to reach the titration endpoint, calculate the mass percent of the  $\text{CaC}_2\text{O}_4$ .

Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is a primary standard used to determine the concentration of potassium permanganate,  $\text{KMnO}_4$ , in solution. The equation for the reaction is as follows.



A student dissolves a sample of oxalic acid in a flask with 30 mL of water and 2.00 mL of 3.00 M  $\text{H}_2\text{SO}_4$ . The  $\text{KMnO}_4$  solution of unknown concentration is in a 25.0 mL buret. In the titration, the  $\text{KMnO}_4$  solution is added to the solution containing oxalic acid.

- What chemical species is being oxidized in the reaction?
- What substance indicates the observable endpoint of the titration? Describe the observation that shows the endpoint has been reached.
- What data must be collected in the titration in order to determine the molar concentration of the unknown  $\text{KMnO}_4$  solution?
- Without doing any calculations, explain how to determine the molarity of the unknown  $\text{KMnO}_4$  solution.
- How would the calculated concentration of the  $\text{KMnO}_4$  solution be affected if 40 mL of water was added to the oxalic acid initially instead of 30 mL? Explain your reasoning.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.



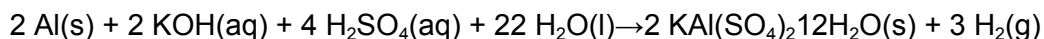
The mass percent of iron in a soluble iron(II) compound is measured using a titration based on the balanced equation above.

(a) What is the oxidation number of manganese in the permanganate ion,  $\text{MnO}_4^{-}(\text{aq})$ ?

(b) Identify the reducing agent in the reaction represented above.

The mass of a sample of the iron (II) compound is carefully measured before the sample is dissolved in distilled water. The resulting solution is acidified with  $\text{H}_2\text{SO}_4(\text{aq})$ . The solution is then titrated with  $\text{MnO}_4^{-}(\text{aq})$  until the end point is reached.

(c) Describe the color change that occurs in the flask when the end point of the titration has been reached. Explain why the color of the solution changes at the end point.



In an experiment, a student synthesizes alum,  $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O(s)}$ , by reacting aluminum metal with potassium hydroxide and sulfuric acid, as represented in the balanced equation above.

(a) In order to synthesize alum, the student must prepare a 5.0M solution of sulfuric acid. Describe the procedure for preparing 50.0 mL of 5.0 M  $\text{H}_2\text{SO}_4$  using any of the chemicals and equipment listed below. Indicate specific amounts and equipment where appropriate.

10.0 M  $\text{H}_2\text{SO}_4$

50.0 mL volumetric flask

Distilled water 50.0 mL buret

100 mL graduated cylinder 25.0 mL pipet

100 mL beaker 50 mL beaker

(b) Calculate the minimum volume of 5.0 M  $\text{H}_2\text{SO}_4$  that the student must use to react completely with 2.7 g of aluminum metal.

(c) As the reaction solution cools, alum crystals precipitate. The student filters the mixture and dries the crystals, then measures their mass.

(i) If the student weighs the crystals before they are completely dry, would the calculated percent yield be greater than, less than, or equal to the actual percent yield? Explain.

(ii) Cooling the reaction solution in an ice bath improves the percent yield obtained. Explain.

(d) The student heats crystals of pure alum,  $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O(s)}$ , in an open crucible to a constant mass. The mass of the sample after heating is less than the mass before heating. Explain.



Answer the following questions that relate to laboratory observations and procedures.

(a) An unknown gas is one of three possible gases: nitrogen, hydrogen, or oxygen. For each of the three possibilities, describe the result expected when the gas is tested using a glowing splint (a wooden stick with one end that has been ignited and extinguished, but still contains hot, glowing, partially burned wood).

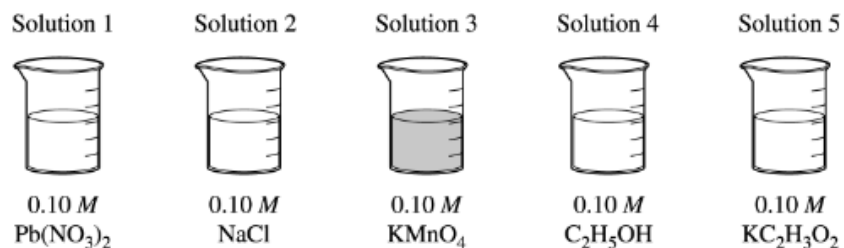
(b) The following three mixtures have been prepared: CaO plus water, SiO<sub>2</sub> plus water, and CO<sub>2</sub> plus water. For each mixture, predict whether the pH is less than 7, equal to 7, or greater than 7. Justify your answers.

(c) Each of three beakers contains a 0.1M solution of one of the following solutes: potassium chloride, silver nitrate, or sodium sulfide. The three beakers are labeled randomly as solution 1, solution 2, and solution 3. Shown below is a partially completed table of observations made of the results of combining small amounts of different pairs of the solutions.

<b>Solution</b>	<b>1</b>	<b>2</b>	<b>3</b>
<b>1</b>	xxxxxxxxxxxxxxxxxxxx	<b>Black Precipitate</b>	
<b>2</b>		xxxxxxxxxxxxxxxxxxxx	<b>No Reaction</b>
<b>3</b>			xxxxxxxxxxxxxxxxxxxx

- (i) Write the chemical formula of the black precipitate.
- (ii) Describe the expected results of mixing solution 1 with solution 3.
- (iii) Identify each of the solutions 1, 2, and 3.





5. Answer the questions below that relate to the five aqueous solutions at 25°C shown above.

- Which solution has the highest boiling point? Explain.
- Which solution has the highest pH? Explain.
- Identify a pair of the solutions that would produce a precipitate when mixed together. Write the formula of the precipitate.
- Which solution could be used to oxidize the  $\text{Cl}^-$  (aq) ion? Identify the product of the oxidation.
- Which solution would be the least effective conductor of electricity? Explain.

Answers:

In each part, one point is earned for the correct solution or solutions, and one point is earned for the correct explanation (in parts a, b, and e), precipitate (in part c), or product (in part d).

(a)  $\text{Pb}(\text{NO}_3)_2$  (Solution 1) **1 point**

$\text{Pb}(\text{NO}_3)_2$  has the largest value of  $i$ , the van't Hoff factor, so the solution has the highest number of solute particles (it dissociates into the most particles). **1 point**

- Student must address the relative number of particles.

(b)  $\text{KC}_2\text{H}_3\text{O}_2$  (Solution 5) **1 point**

The acetate ion is the conjugate base of a weak acid, so it is a weak base (**or**  $\text{KC}_2\text{H}_3\text{O}_2$  is the salt of a strong base and a weak acid, so the solution is basic). **1 point**

(c)  $\text{Pb}(\text{NO}_3)_2$  and  $\text{NaCl}$  (Solutions 1 and 2) **1 point**

$\text{PbCl}_2$  would precipitate **1 point**

- Points can also be earned for  $\text{KMnO}_4$  plus one of the other solutions (with the precipitation of  $\text{MnO}_2$ ).
- Points can also be earned for  $\text{KMnO}_4$  plus  $\text{Pb}(\text{NO}_3)_2$  (with the precipitation of  $\text{PbO}_2$  or  $\text{MnO}_2$ ).

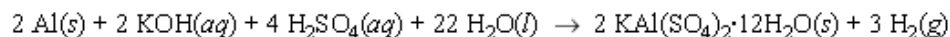
(d)  $\text{KMnO}_4$  (Solution 3) **1 point**

The product of the oxidation is  $\text{Cl}_2$  **1 point**

(e)  $\text{C}_2\text{H}_5\text{OH}$  (Solution 4) **1 point**

Ethanol is the only nonelectrolyte given. It does not readily dissociate into ions, so it would not produce charged species that would conduct a current. **1 point**

- One point can also be earned for explanations using  $i$ , the van't Hoff factor.



In an experiment, a student synthesizes alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(s)$ , by reacting aluminum metal with potassium hydroxide and sulfuric acid, as represented in the balanced equation above.

- (a) In order to synthesize alum, the student must prepare a 5.0 M solution of sulfuric acid. Describe the procedure for preparing 50.0 mL of 5.0 M  $\text{H}_2\text{SO}_4$  using any of the chemicals and equipment listed below. Indicate specific amounts and equipment where appropriate.

10.0 M $\text{H}_2\text{SO}_4$	50.0 mL volumetric flask
Distilled water	50.0 mL buret
100 mL graduated cylinder	25.0 mL pipet
100 mL beaker	50 mL beaker

$(50.0 \text{ mL}) \left( \frac{1 \text{ L}}{1,000 \text{ mL}} \right) \left( \frac{5.0 \text{ mol H}_2\text{SO}_4}{1 \text{ L}} \right) = 0.25 \text{ mol H}_2\text{SO}_4$ $(0.25 \text{ mol H}_2\text{SO}_4) \left( \frac{1 \text{ L}}{10.0 \text{ mol H}_2\text{SO}_4} \right) \left( \frac{1,000 \text{ mL}}{1 \text{ L}} \right) = 25.0 \text{ mL of } 10.0 \text{ M H}_2\text{SO}_4$ <p>Put on goggles. Measure approximately 20 mL of distilled water using the 100 mL graduated cylinder, and add the distilled water to the 50.0 mL volumetric flask. Measure 25.0 mL of the 10.0 M <math>\text{H}_2\text{SO}_4</math> using the 25.0 mL pipet, and transfer the concentrated acid slowly, with occasional swirling, to the 50.0 mL volumetric flask containing the distilled water. After adding all the concentrated acid, carefully add distilled water until the meniscus of the solution is at the 50.0 mL mark on the neck of the flask at 20°C.</p>	<p>One point is earned for the volume of 10.0 M <math>\text{H}_2\text{SO}_4</math>.</p> <p>One point is earned for using a volumetric flask and the pipet.</p> <p>One point is earned for adding the acid to the water.</p> <p>One point is earned for filling to the mark with water.</p>
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- (b) Calculate the minimum volume of 5.0 M  $\text{H}_2\text{SO}_4$  that the student must use to react completely with 2.7 g aluminum metal.

$V_{\text{H}_2\text{SO}_4} = (2.7 \text{ g Al}) \left( \frac{1 \text{ mol Al}}{27.0 \text{ g Al}} \right) \left( \frac{4 \text{ mol H}_2\text{SO}_4}{2 \text{ mol Al}} \right) \left( \frac{1 \text{ L}}{5.0 \text{ mol H}_2\text{SO}_4} \right)$ $V_{\text{H}_2\text{SO}_4} = 0.040 \text{ L}$	<p>One point is earned for the number of moles of Al.</p> <p>One point is earned for the correct stoichiometry.</p> <p>One point is earned for the answer.</p>
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(c) As the reaction solution cools, alum crystals precipitate. The student filters the mixture and dries the crystals, then measures their mass.

(i) If the student weighs the crystals before they are completely dry, would the calculated percent yield be greater than, less than, or equal to the actual percent yield? Explain.

If the  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(s)$  crystals have not been properly dried, there will be excess water present, making the mass of the product greater than it should be and the calculated percent yield too high. Therefore, the calculated percent yield will be greater than the actual percent yield.

One point is earned for the prediction and a correct explanation.

(ii) Cooling the reaction solution in an ice bath improves the percent yield obtained. Explain.

If the solubility of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(s)$  decreases with decreasing temperature, cooling the reaction solution would result in the precipitation of more  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(s)$ .

One point is earned for the correct explanation.

(d) The student heats crystals of pure alum,  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(s)$ , in an open crucible to a constant mass. The mass of the sample after heating is less than the mass before heating. Explain.

$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(s)$  is a hydrate. For the mass of the sample to be less after heating, the water of hydration must be lost. Heating the sample of  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}(s)$  crystals will drive off the water first, decreasing the mass of the sample.

One point is earned for the correct explanation.

- (a) An unknown gas is one of three possible gases: nitrogen, hydrogen, or oxygen. For each of the three possibilities, describe the result expected when the gas is tested using a glowing splint (a wooden stick with one end that has been ignited and extinguished, but still contains hot, glowing, partially burned wood).

<p>Nitrogen: When the glowing splint is inserted into the gas sample, the glowing splint will be extinguished.</p> <p>Hydrogen: When the glowing splint is inserted into the gas sample, a popping sound (explosion) can be heard.</p> <p>Oxygen: When the glowing splint is inserted into the gas sample, the splint will glow brighter or reignite.</p>	<p>One point is earned for each description.</p>
---	--

- (b) The following three mixtures have been prepared: CaO plus water, SiO<sub>2</sub> plus water, and CO<sub>2</sub> plus water. For each mixture, predict whether the pH is less than 7, equal to 7, or greater than 7. Justify your answers.

<p>CaO plus water: The pH of the solution will be greater than 7. CaO in water forms the base Ca(OH)<sub>2</sub> (or metal oxides are basic, or basic anhydrides).</p> <p>SiO<sub>2</sub> plus water: The pH of the solution will be equal to 7. SiO<sub>2</sub> is insoluble in water, so there would not be a change in the pH of the mixture.</p> <p>CO<sub>2</sub> plus water: The pH of the solution will be less than 7. CO<sub>2</sub> in water forms the acid H<sub>2</sub>CO<sub>3</sub> (or nonmetal oxides are acidic, or acidic anhydrides).</p>	<p>One point is earned for each description.</p>
--	--

- (c) Each of three beakers contains a 0.1 M solution of one of the following solutes: potassium chloride, silver nitrate, or sodium sulfide. The three beakers are labeled randomly as solution 1, solution 2, and solution 3. Shown below is a partially completed table of observations made of the results of combining small amounts of different pairs of the solutions.

	Solution 1	Solution 2	Solution 3
Solution 1		black precipitate	
Solution 2			no reaction
Solution 3			

- (i) Write the chemical formula of the black precipitate.

The black precipitate is $\text{Ag}_2\text{S}$ .	One point is earned for the correct formula.
--	--

- (ii) Describe the expected results of mixing solution 1 with solution 3.

A precipitate will be produced when the two solutions are mixed.	One point is earned for the correct observation.
--	--

- (iii) Identify each of the solutions 1, 2, and 3.

Solution 1 is silver nitrate. Solution 2 is sodium sulfide. Solution 3 is potassium chloride.	One point is earned for the correct identification of all three solutions.
---	--



5. An experiment is performed to determine the molar mass of an unknown solid monoprotic acid, HA, by titration with a standardized NaOH solution.

(a) What measurement(s) must be made to determine the number of moles of NaOH used in the titration?

Initial volume of standardized NaOH solution and final volume of standardized NaOH solution (volume at the endpoint of the titration)	1 point for identifying both initial and final volume of base
---	---

(b) Write a mathematical expression that can be used to determine the number of moles of NaOH used to reach the endpoint of the titration.

$M_{\text{NaOH}} \times V_{\text{NaOH}}$ (Molarity of NaOH solution) times (volume (in L) of NaOH added)	1 point for mathematical expression
---	-------------------------------------

(c) How can the number of moles of HA consumed in the titration be determined?

$\text{HA} + \text{NaOH} \rightarrow \text{NaA} + \text{H}_2\text{O}$ moles HA = moles NaOH moles monoprotic acid = moles NaOH $n_{\text{HA}} = \text{moles NaOH} \left( \frac{1 \text{ mol HA}}{1 \text{ mol NaOH}} \right)$	1 point for showing conversion based on stoichiometry of the neutralization reaction
--	--

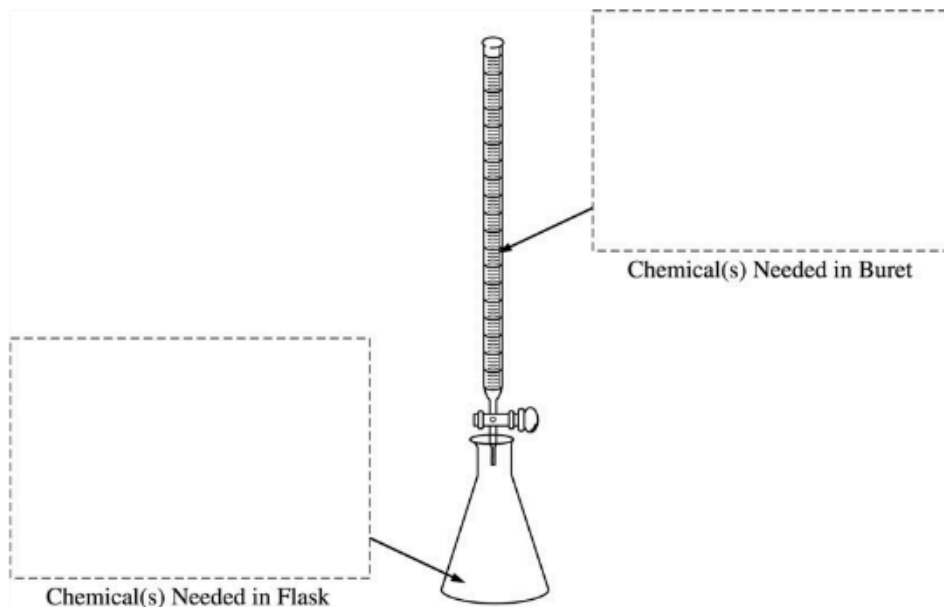
(d) In addition to the measurement(s) made in part (a), what other measurement(s) must be made to determine the molar mass of the acid, HA?

mass of HA	1 point for measurement
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(e) Write the mathematical expression that is used to determine the molar mass of HA.

$\frac{\text{mass HA}}{\text{mol HA}}$ mass of HA measured in part (d) divided by the moles of HA determined in part (c)	1 point for quotient
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- (f) The following diagram represents the setup for the titration. In the appropriate boxes below, list the chemical(s) needed to perform the titration.



Chemicals needed in flask: solid weak monoprotic acid (HA) and an indicator to detect endpoint of titration	1 point for either one of two chemicals in flask, 2 points for both
Chemical in buret: standardized NaOH solution	1 point for NaOH in the buret

Chemicals needed in flask: solid weak monoprotic acid (HA) and an indicator to detect endpoint of titration	1 point for either one of two chemicals in flask, 2 points for both
Chemical in buret: standardized NaOH solution	1 point for NaOH in the buret

(g) Explain what effect each of the following would have on the calculated molar mass of HA. Justify your answers.

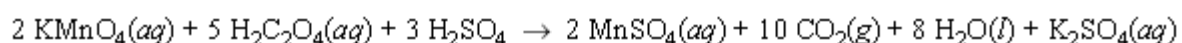
(i) The original solid acid, HA, was not completely dry at the beginning of the experiment.

Measured mass of HA is larger; so, according to expression in part (e), calculated molar mass will be higher than it should.	1 point for the effect on molar mass <u>and</u> explanation.
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(ii) The procedure called for 25 mL of H<sub>2</sub>O in the Erlenmeyer flask, but a student used 35 mL of H<sub>2</sub>O.

No effect on calculated molar mass, because mathematical expression for molar mass does not include amount of water used to dissolve solid HA. Both mass and number of moles of HA are unaffected by the addition of water.	1 point for effect on molar mass <u>and</u> explanation.
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5. Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is a primary standard used to determine the concentration of potassium permanganate,  $\text{KMnO}_4$ , in solution. The equation for the reaction is as follows.



A student dissolves a sample of oxalic acid in a flask with 30 mL of water and 2.00 mL of 3.00 M  $\text{H}_2\text{SO}_4$ . The  $\text{KMnO}_4$  solution of unknown concentration is in a 25.0 mL buret. In the titration, the  $\text{KMnO}_4$  solution is added to the solution containing the oxalic acid.

- (a) What chemical species is being oxidized in the reaction?

<p><math>\text{H}_2\text{C}_2\text{O}_4</math> is the substance being oxidized. The half-reaction is:</p> $\text{H}_2\text{C}_2\text{O}_4(aq) \rightarrow 2 \text{CO}_2(g) + 2 \text{H}^+(aq) + 2 e^-$ <p><b>OR</b></p> <p>The oxidation state of carbon changes from +3 to +4 in <math>\text{CO}_2</math>.</p>	<p>1 point for identifying <math>\text{H}_2\text{C}_2\text{O}_4</math> or <math>\text{C}_2\text{O}_4^{2-}</math> as species oxidized</p>
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- (b) What substance indicates the observable endpoint of the titration? Describe the observation that shows the endpoint has been reached.

<p>In the reaction, the purple <math>\text{KMnO}_4</math> solution in the buret is added to the colorless solution in the flask. <math>\text{KMnO}_4</math> reacts with <math>\text{H}_2\text{C}_2\text{O}_4</math> upon addition, so the purple <math>\text{KMnO}_4</math> color disappears as it is added to the solution in the flask that contains unreacted <math>\text{H}_2\text{C}_2\text{O}_4</math>.</p> <p>As soon as all the <math>\text{H}_2\text{C}_2\text{O}_4</math> has reacted (endpoint), the <math>\text{KMnO}_4</math> is in excess and the solution in the flask will turn pink (pink is the color produced when the more concentrated purple <math>\text{KMnO}_4</math> solution in the buret is diluted in the solution in the flask).</p>	<p>1 point for identifying <math>\text{KMnO}_4</math> as reacting species that indicates the endpoint</p> <p>1 point for indicating color change is from colorless to pink at the endpoint</p>
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- (c) What data must be collected in the titration in order to determine the molar concentration of the unknown  $\text{KMnO}_4$  solution?

<p>The mass of oxalic acid, the initial volume of the <math>\text{KMnO}_4</math> solution in the buret, and the final volume of the <math>\text{KMnO}_4</math> solution in the buret</p>	<p>1 point for the mass of oxalic acid</p> <p>1 point for the initial and final volume <i>or</i> for saying the change in volume of <math>\text{KMnO}_4</math></p>
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- (d) Without doing any calculations, explain how to determine the molarity of the unknown  $\text{KMnO}_4$  solution.

Determine the moles of oxalic acid (by dividing the mass of oxalic acid measured/weighed, by the molar mass of oxalic acid).	1 point for determining moles of $\text{H}_2\text{C}_2\text{O}_4$
Use the stoichiometric ratio of the amount (2 mol) of $\text{KMnO}_4$ to amount (5 mol) of $\text{H}_2\text{C}_2\text{O}_4$ from the balanced chemical equation to convert from amount (in moles) of $\text{H}_2\text{C}_2\text{O}_4$ to amount (in moles) of $\text{KMnO}_4$ .	1 point for using correct stoichiometric factor
Divide the amount (in moles) of $\text{KMnO}_4$ by the volume, expressed in liters, of $\text{KMnO}_4$ needed to reach the endpoint.	1 point for dividing moles of $\text{KMnO}_4$ by liters of $\text{KMnO}_4$ solution

- (e) How would the calculated concentration of the  $\text{KMnO}_4$  solution be affected if 40 mL of water was added to the oxalic acid initially instead of 30 mL? Explain your reasoning.

There would be no effect on the concentration of the $\text{KMnO}_4$ solution. We are only interested in the moles of oxalic acid. Since it is a solid, the moles of oxalic acid are calculated from the mass of oxalic acid. The volume of water used to dissolve the oxalic acid is independent of the moles of oxalic acid.	1 point for effect 1 point for explanation
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