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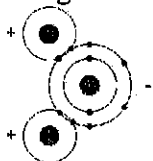
## Chapter 4- Types of Chemical Reactions and Solution Stoichiometry

### Study Guide

#### 4.1 Water, the common solvent

This section introduces you to the nature of interactions between atoms and electrons in the water molecule. Please pay special attention to the following ideas:

- Water is not a linear molecule.** It is bent at an angle of about  $105^\circ$ .
- Electrons are not evenly distributed around the atoms in water. Notice the position of the partial charges on the molecule. The molecule is *polar* because the charges are not distributed symmetrically.



- Like dissolves like. The following classes of molecules, in general, are miscible (they will dissolve):
  - Polar and ionic
  - Polar and polar
  - Nonpolar and nonpolar

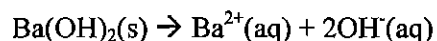
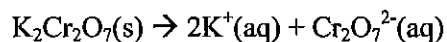
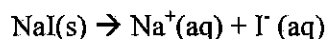
Ionic salts dissolve in water. Compounds that contain *only* carbon and hydrogen are nonpolar. Given that information, please try the following example.

#### Example 4.1A Will the substance mix?

Predict whether each pair of substances are miscible. State why or why not.

- $\text{NaNO}_3$  and  $\text{H}_2\text{O}$  - miscible - ionic + polar
- $\text{C}_6\text{H}_{14}$  and  $\text{H}_2\text{O}$  - immiscible - non polar + polar
- $\text{I}_2$  and  $\text{C}_6\text{H}_{14}$  - miscible - non polar + non polar
- $\text{I}_2$  and  $\text{H}_2\text{O}$  - immiscible - non polar + polar

The dissociation of simple ionic salts in water is often written as shown in the following equations. Each ionic solid is dissolved in  $\text{H}_2\text{O}(\text{l})$ :



#### Example 4.1B Practice with Equations

Complete each of the following dissociation equations:

- $\text{CaCl}_2(\text{s}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$
- $\text{Fe}(\text{NO}_3)_3(\text{s}) \rightarrow \text{Fe}^{3+}(\text{aq}) + 3\text{NO}_3^-(\text{aq})$
- $\text{KBr}(\text{s}) \rightarrow \text{K}^+(\text{aq}) + \text{Br}^-(\text{aq})$
- $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow 2\text{NH}_4^+(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq})$

## 4.2 The Nature of Aqueous Solutions: Strong and Weak Electrolytes

As you read the textbook material in this section, pay particular attention to the **terms and definitions** given. You will use these for as long as you are involved with the study of chemistry. Let's review, and add to, the definitions of the key terms of this section.

- **Solute**
  1. If it and the solvent are present in the same phase, it is the one in lesser amount.
  2. If it and the solute are present in different phases, it is the one that changes phase.
  3. Your book puts it in more general terms by saying that it is the one that dissolves into the solvent.
- **Solvent**
  1. If it and the solute are present in the same phase, it is the one in greater amount.
  2. If it and the solute are present in different phases, it is the one that retains its phase.
  3. Your book says that it is the one into which the solute dissolves.

Figure 4.4 in your book shows the effect of strong, weak and nonelectrolytes on the ability to pass a current (conductivity) in an aqueous solution.

**An aqueous solution means that water is the solvent.**

Electrolyte	Conductivity	Degree of Dissociation	Examples
Strong	High	Total	Strong acids, such as HCl; many salts such as NaCl and Sr(NO <sub>3</sub> ) <sub>2</sub> ; strong bases such as NaOH, Ba(OH) <sub>2</sub> , and other group I and II hydroxides
Weak	Low to moderate	Partial	Weak organic acids, such as HCO <sub>2</sub> H and HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ; weak bases such as NH <sub>3</sub>
Non	None	Close to zero	Sugar, AgCl, Fe <sub>2</sub> O <sub>3</sub>

### Example 4.2 Strong, Weak, or Nonelectrolyte

List whether each of the following is a strong, weak or nonelectrolyte

- |  |  |
|--|--|
| a. HClO <sub>4</sub> <i>Strong</i>           | d. NH <sub>3</sub> <i>weak</i>                               |
| b. C <sub>6</sub> H <sub>12</sub> <i>Non</i> | e. CaCl <sub>2</sub> <i>strong</i>                           |
| c. LiOH <i>Strong</i>                        | f. HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <i>weak</i> |

## 4.3 The composition of solutions

There are many ways to measure the strength of a solution, in this section, we will focus on Molarity (M).

**Molarity is defined as moles of solute per liter of solution.**

$$M = \frac{\text{moles of solute}}{\text{Liter of solution}}$$



Keep in mind that moles/liter = millimoles/milliliter = micromoles/microliter, but

Moles/liter DOES NOT EQUAL millimoles/liter or moles/microliter. Be very careful with your units!

### Example 4.3A Calculating Molarity

Calculate the molarity of a solution prepared by dissolving 11.85 g of solid KMnO<sub>4</sub> in enough water to make 750. mL of solution.

$$M = \frac{\text{moles}}{L} = \frac{11.85 \text{ g KMnO}_4}{750 \text{ mL}} \left( \frac{1000 \text{ mL}}{1 \text{ L}} \right) \left( \frac{1 \text{ mole}}{158 \text{ g}} \right) = \boxed{.100 \text{ M KMnO}_4}$$

### Example 4.3B Mass from Molarity

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

$$\text{moles} = M \times L = \left(0.500 \frac{\text{mol NaCl}}{\text{L}}\right) \left(175 \text{ mL}\right) \left(\frac{1 \text{ L}}{1000 \text{ mL}}\right) = 0.0875 \text{ mol NaCl} \left(\frac{58.5 \text{ g}}{1 \text{ mol}}\right) = \boxed{5.12 \text{ g NaCl}}$$

### Example 4.3C Volume from Molarity

How many mL of solution are necessary if we are to have a 2.48 M NaOH solution that contains 31.52 g of the dissolved solid?

$$31.52 \text{ g NaOH} \left(\frac{1 \text{ mol}}{40 \text{ g}}\right) \left(\frac{1 \text{ L}}{2.48 \text{ mol}}\right) \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right) = 317.7 \text{ mL} = 318 \text{ mL}$$

In the previous problems, we calculated the molarity of the solute. However, we have neglected to take into account the fact that each of the solutes,  $\text{KMnO}_4$ ,  $\text{NaCl}$ , and  $\text{NaOH}$  are **strong electrolytes and completely dissociate** in aqueous solution (Sec 4.2). For example,  $\text{KMnO}_4(\text{s}) \rightarrow \text{K}^+(\text{aq}) + \text{MnO}_4^-(\text{aq})$ .

This means that while it is generally acceptable to discuss your solution concentration as "molarity of  $\text{KMnO}_4$ ," it is more chemically correct to discuss "molarity of  $\text{K}^+$  ions and molarity of  $\text{MnO}_4^-$  ions."

A solution that is 0.85 M in  $\text{KMnO}_4$  is really 0.85 M in  $\text{K}^+$  ion and 0.85 M in  $\text{MnO}_4^-$  ion, because  $\text{KMnO}_4$  completely dissociates, and the dissociation is a 1 to 1 to 1 ratio, that is, one mole of  $\text{KMnO}_4$  dissociates into one mole of  $\text{K}^+$  ions and one mole of  $\text{MnO}_4^-$  ion.

### Example 4.3D Molarity of Ions in Solution

Calculate the molarity of all of the ions in each of the following solutions.

a. 0.25 M  $\text{Ca}(\text{OCl})_2$

$$0.25 \frac{\text{mol Ca}(\text{OCl})_2}{\text{L}} \left(\frac{1 \text{ mol Ca}^{2+}}{1 \text{ mol Ca}(\text{OCl})_2}\right) = 0.25 \text{ M Ca}^{2+}$$

$$0.25 \frac{\text{mol Ca}(\text{OCl})_2}{\text{L}} \left(\frac{2 \text{ mol OCl}^-}{1 \text{ mol Ca}(\text{OCl})_2}\right) = 0.50 \text{ M OCl}^-$$

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

$$2 \frac{\text{mol CrCl}_3}{\text{L}} \left(\frac{1 \text{ mol Cr}^{3+}}{1 \text{ mol CrCl}_3}\right) = 2 \text{ M Cr}^{3+}$$

$$2 \frac{\text{mol CrCl}_3}{\text{L}} \left(\frac{3 \text{ mol Cl}^-}{1 \text{ mol CrCl}_3}\right) = 6 \text{ M Cl}^-$$

### Example 4.3E Molarity of Ions in Solution

Determine the molarity of  $\text{Cl}^-$  ion in a solution prepared by dissolving 9.82 g of  $\text{CuCl}_2$  in enough water to make 600. mL of solution.

$$9.82 \text{ g CuCl}_2 \left(\frac{1 \text{ mol CuCl}_2}{134.5 \text{ g}}\right) \left(\frac{2 \text{ mol Cl}^-}{1 \text{ mol CuCl}_2}\right) = \frac{0.146 \text{ mol Cl}^-}{0.600 \text{ L}} = \boxed{0.243 \text{ M Cl}^-}$$

### Example 4.3F 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 Iron(III) Sulfate in enough water to make 800. mL of solution.

$$48.05 \text{ g Fe}_2(\text{SO}_4)_3 \left(\frac{1 \text{ mol}}{335.7 \text{ g}}\right) = \frac{0.1431 \text{ mol Fe}_2(\text{SO}_4)_3}{0.8 \text{ L}} = 0.1789 \text{ M Fe}_2(\text{SO}_4)_3 \rightarrow \begin{cases} 0.3578 \text{ M Fe}^{3+} \\ 0.5368 \text{ M SO}_4^{2-} \end{cases}$$

As important part of your chemistry experience is to be able to prepare *dilute solutions from more concentrated ("stock") solutions*. Your book points out that the most important idea in diluting solutions is that:

**Moles of solute after dilution = moles of solute before dilution**

If molarity = moles of solute/liter of solution, then

$$\text{Moles of solute} = (\text{moles of solute/liter of solution}) \times \text{liters of solution} = M \times V$$

If the **moles of solute remain identical** before and after dilution (only the amount of water changes), then

$$M_1 V_1 = M_2 V_2$$

Where  $M_1$  = molarity of concentrated (initial) solution

$V_1$  = volume of concentrated solution that you add water to dilute...this will often be your "unknown vol."

$M_2$  = molarity of dilute (final) solution

$V_2$  = total volume of your dilute solution

**Example 4.3G Preparation of a Dilute Solution**

What volume of 12 M hydrochloric acid must be used to prepare 600. mL of a 0.30 M HCl solution?

$$M_1 V_1 = M_2 V_2$$

$$(12 M)(V_1) = (0.30 M)(600 \text{ mL})$$

$$V_1 = 15.0 \text{ mL}$$

**Example 4.3H More practice on Preparing Dilute Solutions**

What volume of 9.0 M sodium hydroxide must be used to prepare 1.2 L of a 1.0 M NaOH solution?

$$M_1 V_1 = M_2 V_2$$

$$(9.0 M)(V_1) = (1.0 M)(1.2 \text{ L})$$

$$V_1 = 0.133 \text{ L} = 133 \text{ mL}$$

Although not discussed in chapter 4 of your book, some of the challenge problems in your text use the term **parts per million (ppm)**. 1 part per million of "X" = 1 part X / 1 x 10<sup>6</sup> parts solution

$$= 1 \text{ g X} / 1 \times 10^6 \text{ g soln}$$

$$= 1 \mu\text{g X} / 1 \text{ g soln}$$

If the solution is water (whose density = 1.00 g/mL), 1 ppm X = 1 μg X / 1 mL soln = 1 mg X / 1 L soln.

Note that this differs from molarity in that the units are mass per volume, not moles per volume. To set the stage for your work with the challenging problems, consider the following problem.

$$\text{ppm} = \frac{1 \text{ mg}}{\text{L}}$$

### Example 4.3I Parts Per Million

$$\text{ppm} = \frac{\text{mg}}{\text{L}}$$

An aqueous solution with a total volume of 750. mL contains 14.38 mg of  $\text{Cu}^{2+}$ . What is the concentration of  $\text{Cu}^{2+}$  in parts per million?

$$\frac{14.38 \text{ mg } \text{Cu}^{2+}}{750 \text{ L}} = 19.2 \text{ mg/L} = \boxed{19.2 \text{ ppm}}$$

### Example 4.3 J Molarity to Parts Per Million

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

$$3 \times 10^{-7} \frac{\text{mol Mn}^{7+}}{\text{L}} \left( \frac{54.94 \text{ g}}{1 \text{ mol Mn}} \right) \left( \frac{1000 \text{ mg}}{1 \text{ g}} \right) = .0164 \frac{\text{mg}}{\text{L}} = \boxed{.0164 \text{ ppm}}$$

## 4.4 Types of Chemical Reactions

This section points out that reactions are divided into precipitation reactions, acid-base reactions, and oxidation-reduction reactions. The remainder of the chapter considers reactions that fall into these classes.

## 4.5 Precipitation Reactions

The major ideas in this section are that:

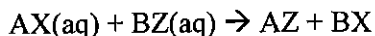
1. Many salts dissociate into ions in aqueous solution.
2. If a solid forms from a combination of selected ions in solution, the solid must contain an anion part and a cation part, and the net charge on the solid must be zero.
3. There are some simple solubility rules you can use that can help you predict the products of reactions in aqueous solutions.

Table 4.1 in your book lists solubility rules for salts in water. The information is important enough to reprint below.

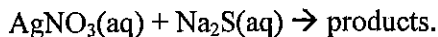
### Simple Rules for the Solubility of Salts in Water:

1. Most nitrate ( $\text{NO}_3^-$ ) salts are soluble.
2. Most salts containing the alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$ ) and the ammonium ion ( $\text{NH}_4^+$ ) are soluble.
3. Most chloride, bromide and iodide salts are soluble. Notable exceptions are salts containing the ions  $\text{Ag}^+$ ,  $\text{Pb}^+$  and  $\text{Hg}_2^{2+}$ .
4. Most sulfate salts are soluble. Notable exceptions are  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ ,  $\text{HgSO}_4$  and  $\text{CaSO}_4$ .
5. Most hydroxide salts are only slightly soluble. The important soluble hydroxides are NaOH and KOH. The compounds  $\text{Ba}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  are marginally soluble.
6. Most sulfide ( $\text{S}^{2-}$ ), carbonate ( $\text{CO}_3^{2-}$ ) and phosphate ( $\text{PO}_4^{3-}$ ) salts are only slightly soluble.

If two soluble substances (call them AX and BZ) are combined, you can assume that the products will be AZ and BX.

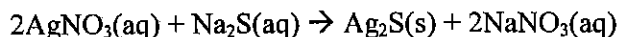


Your goal is to determine, based on your knowledge of solubility rules, whether AZ or BX will form a solid (precipitate). Let's look at the following reaction.



The reactants are electrolytes that will dissociate to form the ions ( $Ag^+ + NO_3^- + 2Na^+ + S^{2-}$ ) all aqueous.

If a solid forms, and if it is to have zero charge, it can be either  $Ag_2S$  or  $NaNO_3$ . According to solubility rule #1,  $NaNO_3$  is soluble. According to solubility rule #6,  $Ag_2S$  is insoluble, and will therefore precipitate. The correct (balanced) reaction therefore, is



### Example 4.5 Predicting Precipitates

Complete and balance the following reactions, determining, in each case, if a precipitate is formed. Assume all reactants are in aqueous solution.

- a.  $2KCl + Pb(NO_3)_2 \rightarrow 2KNO_3(aq) + PbCl_2(s)$
- b.  $2AgNO_3 + MgBr_2 \rightarrow 2AgBr(s) + Mg(NO_3)_2(aq)$
- c.  $3Ca(OH)_2 + 2FeCl_3 \rightarrow 3CaCl_2(aq) + 2Fe(OH)_3(s)$
- d.  $NaOH + HCl \rightarrow NaCl(aq) + H_2O(l)$

## 4.6 Describing Reactions in Solution

This section discusses the three kinds of equations that are used to describe reactions in aqueous solution. Specific definitions for the **molecular**, **complete ionic** and **net ionic equations** are given in your textbook. Let's look how the aqueous reaction of silver nitrate with sodium sulfide can be expressed with each type of equation.

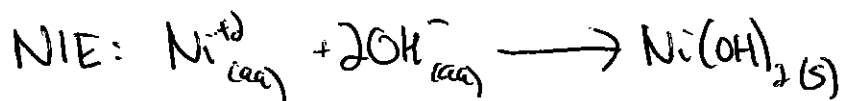
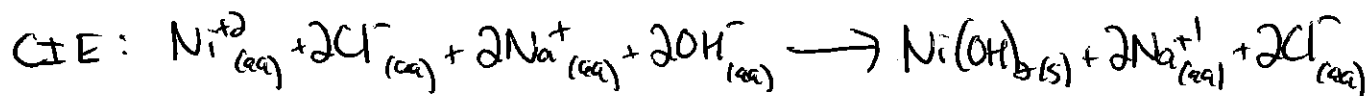
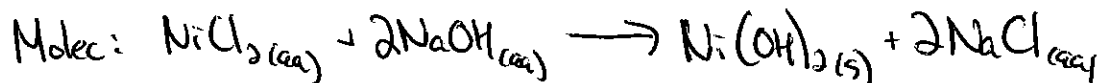
- a. **Molecular:** This gives the overall reaction. While it does give information on stoichiometry, it gives no information on whether or not compounds really exist as ions in solution. Molecular form:  
$$2AgNO_3(aq) + Na_2S(aq) \rightarrow Ag_2S(s) + 2NaNO_3(aq)$$
- b. **Complete Ionic:** This gives information including all ions in solution. Because all compounds and ions are present, some information may be redundant. Complete ionic form:  
$$2Ag^+(aq) + 2NO_3^-(aq) + 2Na^+(aq) + S^{2-}(aq) \rightarrow Ag_2S(s) + 2Na^+(aq) + 2NO_3^-(aq)$$
- c. **Net ionic:** This only gives information on those species that undergo a chemical change. Ions that appear in the same form on both sides of the complete ionic equation are called **spectator ions** and are not included in the net ionic equation. In our sample equations,  $Na^+$  and  $NO_3^-$  are unaltered during the reaction. They are therefore omitted from the net ionic equations. Net ionic form:  
$$2Ag^+(aq) + S^{2-}(aq) \rightarrow Ag_2S(s)$$

The **molecular** and **net ionic** forms of equations are most commonly used. The **complete ionic** form helps us to determine the net ionic form.

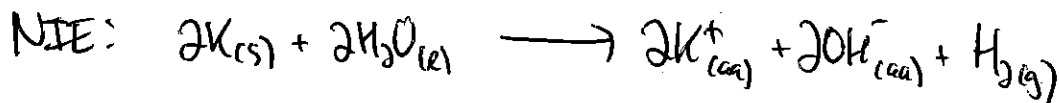
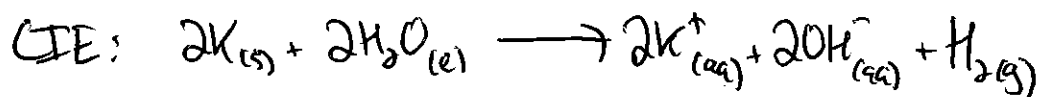
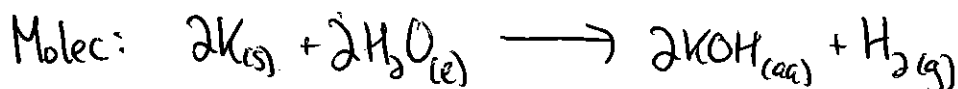
**Example 4.6 Molecular, Complete Ionic and Net Ionic Equations**

Write the molecular, complete ionic and net ionic forms for each of the following equations.

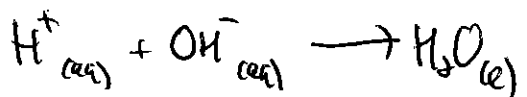
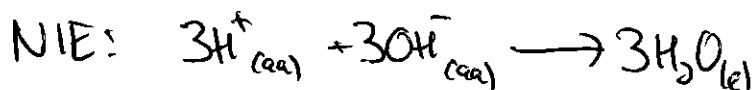
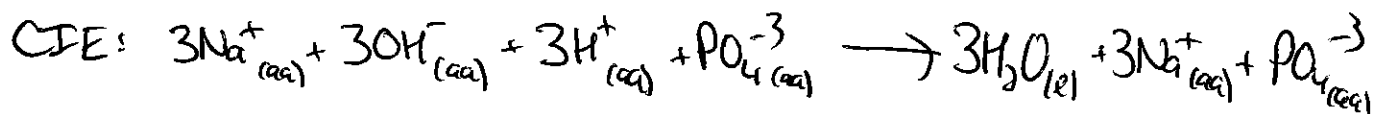
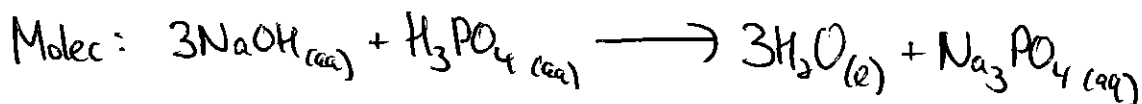
- a. Aqueous nickel (II) chloride reacts with aqueous sodium hydroxide to give a nickel (II) hydroxide precipitate and aqueous sodium chloride.



- b. Solid potassium metal reacts with water to give aqueous potassium hydroxide and hydrogen gas.



- c. Aqueous sodium hydroxide reacts with phosphoric acid to give water and aqueous sodium phosphate.



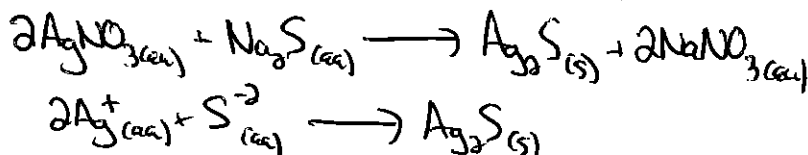
## 4.7 Stoichiometry of Precipitation reactions

The material in this section is very important because it combines most of the previous chemical ideas that you have learned up to now. Solving problems involving precipitates from solution makes use of *molarity*, *solubility rules*, *balancing equations*, and *limiting reactant calculations*.

The problems can be quite "wordy," but wordy problems are not necessarily hard. They are just wordy. Each sentence contains some chemical information, and it is useful to jot down information as it appears. Keep in mind that although no two examples are exactly alike, the approach to solving problems will be similar.

### Example 4.7A An Introduction to Problems based on Precipitation Reactions

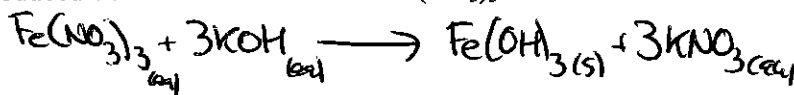
Calculate the mass of  $\text{Ag}_2\text{S}$  produced when 125 mL of 0.200 M  $\text{AgNO}_3$  is added to excess  $\text{Na}_2\text{S}$  solution.



$$.125 \cancel{\text{L}} \text{AgNO}_3 \left( \frac{.200 \text{ mol AgNO}_3}{\cancel{\text{L}}} \right) \left( \frac{2 \text{ mol Ag}^+}{1 \text{ mol AgNO}_3} \right) \left( \frac{1 \text{ mol Ag}_2\text{S}}{2 \text{ mol Ag}^+} \right) \left( \frac{248 \text{ g}}{1 \text{ mol Ag}_2\text{S}} \right) = \boxed{3.10 \text{ g Ag}_2\text{S}}$$

### Example 4.7 B Practice with precipitation problems

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



$$.035 \cancel{\text{L}} \text{Fe}(\text{NO}_3)_3 \left( \frac{.250 \text{ mol}}{\cancel{\text{L}}} \right) \left( \frac{1 \text{ mol Fe}(\text{OH})_3}{1 \text{ mol Fe}(\text{NO}_3)_3} \right) \left( \frac{106.85 \text{ g}}{1 \text{ mol Fe}(\text{OH})_3} \right) = .935 \text{ g Fe}(\text{OH})_3$$

$$.055 \cancel{\text{L}} \text{KOH} \left( \frac{.180 \text{ mol}}{\cancel{\text{L}}} \right) \left( \frac{1 \text{ mol Fe}(\text{OH})_3}{3 \text{ mol KOH}} \right) \left( \frac{106.85 \text{ g}}{1 \text{ mol Fe}(\text{OH})_3} \right) = \boxed{.353 \text{ g Fe}(\text{OH})_3} \quad \text{KOH is LP.}$$

### Example 4.7 C Gravimetric Analysis

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

$$2.005 \text{ g BaSO}_4 \left( \frac{1 \text{ mol BaSO}_4}{233.33 \text{ g}} \right) \left( \frac{1 \text{ mol S}}{1 \text{ mol BaSO}_4} \right) \left( \frac{32 \text{ g}}{1 \text{ mol S}} \right) = 0.2750 \text{ g S}$$

$$\% \text{ S in ore} = \frac{\text{mass S}}{\text{mass ore}} \times 100 = \frac{.2750 \text{ g S}}{3.187 \text{ g ore}} \times 100 =$$

$$\boxed{8.628\% \text{ S}}$$



## 4.8 Acid-Base Reactions

The key to solving acid-base problems is to know that they **require the same strategy** as most other types of problems in this chapter. **Writing down balanced chemical equations is always your first, and most important, step.**

**AN ACID IS A PROTON DONOR.**

**A BASE IS A PROTON ACCEPTOR.**

**Strong Acids**- 100% dissociation between hydrogen ion and anion. 6 types- Hydrochloric Acid (HCl), Hydrobromic Acid (HBr), Hydroiodic Acid (HI), Nitric Acid (HNO<sub>3</sub>), Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) and Perchloric Acid (HClO<sub>4</sub>)

**Weak Acids**- molecules containing an ionizable hydrogen ion. There are thousands of weak acids, most of them organic in nature. Examples- phosphoric acid, pyruvic acid, hydrofluoric acid, nitrous acid, lactic acid, acetic acid, carbonic acid, hydrogen sulfide, hypochlorous acid, hydrogen cyanide.

**Strong Bases**- 100% dissociation between positive cation (Group I and heavier Group II metals) and the hydroxide ion. 8 types- Lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), rubidium hydroxide (RbOH), cesium hydroxide (CsOH), calcium hydroxide (Ca(OH)<sub>2</sub>), strontium hydroxide (Sr(OH)<sub>2</sub>), and barium hydroxide (Ba(OH)<sub>2</sub>).

**Weak Bases**- Weak bases do not furnish OH<sup>-</sup> ions directly by dissociation. Rather, the hydroxide ions are generated by the reaction of a weak base and water. Ammonia (NH<sub>3</sub>) is a common weak base that reacts with water as follows: NH<sub>3</sub>(aq) + H<sub>2</sub>O(l) ↔ NH<sub>4</sub><sup>+</sup>(aq) + OH<sup>-</sup>(aq)

You may assume that the acid-base reactions used in this section go to completion. The steps for solving acid-base problems are listed below. Try on the following examples.

### Performing Calculations for Acid-Base Reactions

1. List the species present in solution before reaction.
2. Write the balanced net ionic reaction.
3. Calculate the moles of reactants. For reactants in solution, use the volumes of original solutions and their molarities.
4. Determine the limiting reactant where appropriate.
5. Calculate the moles of the required reactant or product.
6. Convert to grams or volume (of solution) as required.
7. You should double check to make sure that the moles of acid equals the moles of base.

neutralization:  
moles acid = moles base  
 $M_A V_A = M_B V_B$

#### *Example 4.8A 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 sol'n?

$$\begin{array}{ccc} V_B & M_B & \\ M_A V_A = M_B V_B & & \\ (.600M)(40.00mL) = (.800M)(V_B) & & \end{array}$$

$$\boxed{V_B = 30.00 \text{ mL}}$$

The remainder of this section deals with **VOLUMETRIC ANALYSIS**. This kind of analysis use **precisely measured amounts of liquid** to carry out an analysis. There are several new terms introduced such as **titration, buret, equivalence point, indicator and endpoint**. When solving volumetric analysis problems, the same chemical rules apply as with most other acid-base problems.

### 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 indicator added so that it is pink, with 0.1067 M HCl. The sample turns clear (indicating that the NaOH has been precisely neutralized by the HCl solution) after the addition of 42.95 mL of HCl. Calculate the molarity of your NaOH solution.

$$M_A V_A = M_B V_B \Rightarrow (0.1067 \text{ M HCl})(42.95 \text{ mL}) = M_B (25.00 \text{ mL})$$
$$M_B = 0.1833 \text{ M NaOH}$$

### Example 4.8C Molar Mass of an Acid

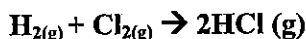
You want to determine the molar mass of an acid. The acid contains one acidic hydrogen per molecule. You weigh out 2.879 g sample of the pure acid and dissolve it, along with 3 drops of phenolphthalein indicator, in distilled water. You titrate the sample with 0.1704 M NaOH. The pink endpoint is reached after the addition of 42.55 mL of the base. Calculate the molar mass of the acid.

$$MM_{\text{acid}} = \frac{\text{mass acid}}{\text{mols acid}} = \frac{2.879 \text{ g}}{0.05735} = 397.9 \text{ g/mol}$$
$$0.1704 \frac{\text{mol Base}}{\text{L}} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) (42.55 \text{ mL}) \left( \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} \right) \left( \frac{1 \text{ mol H}^+}{1 \text{ mol OH}^-} \right) \left( \frac{1 \text{ mol Acid}}{1 \text{ mol H}^+} \right) = 0.05735 \text{ mol Acid}$$

## 4.9 Oxidation-Reduction Reactions

This section deals with definitions and assignments relating to **electron charge**, and the next deals with balancing such equations. You need these skills before you do the electrochemical problems, because you need to know how to deal with electron exchange before you can manipulate values to solve problems.

Your book defines **oxidation-reduction reactions** as being those in which **one or more electrons are transferred**.



In this case, electrons are transferred from the hydrogen to the chlorine.

Below are the rules for defining oxidation states (the grandfather to ionic charge).

### VALENCE AND OXIDATION NUMBER (PSEUDOVALNCE)

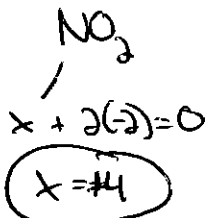
In the case of an ionic compound such as sodium chloride, NaCl, we assign the Na valence of +1 because it has lost an electron to the Cl which then has a valence of -1. However, this will not work with molecular compounds such as SO<sub>2</sub> or H<sub>2</sub>O where there is no complete transfer of electrons but rather a sharing. We cannot use the term valence in these cases because it refers to the term electrovalence, so we use the term oxidation number. This is the number that we arrive at by using the following rules:

1. The oxidation number of a free, uncombined element (including elements in the molecular state) is zero.
2. Oxygen always has an oxidation number of -2 in any compound except in peroxides where it is -1.
3. Hydrogen has an oxidation number of +1 except when combined with a metal in a simple binary compound where it is -1.
4. The algebraic sum of all valences and/or oxidation numbers in any compound must equal zero.
5. The algebraic sum of all the valences and/or oxidation numbers in a polyatomic ion must add up to the charge carried by that ion.

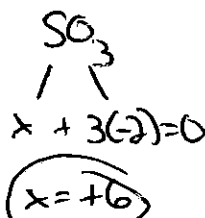
**Example 4.9 A Assigning Oxidation Numbers**

Assign oxidation numbers to each element in:

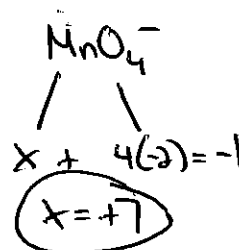
a. Nitrogen dioxide



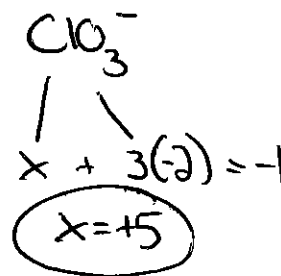
b. sulfur trioxide



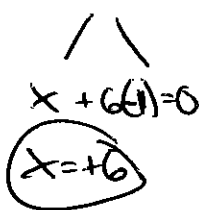
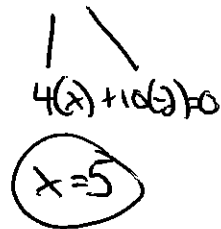
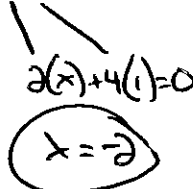
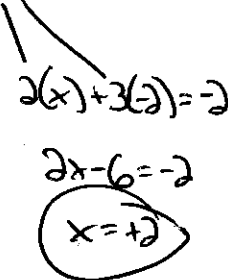
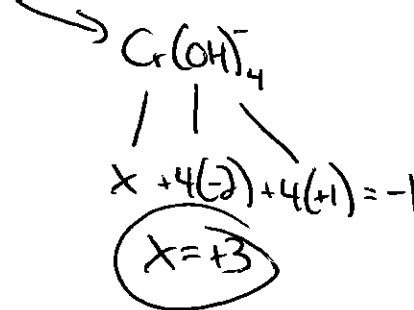
c. permanganate ion



d. chlorate ion

**Example 4.9B More oxidation numbers**

Assign oxidation numbers to each element in:

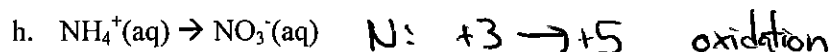
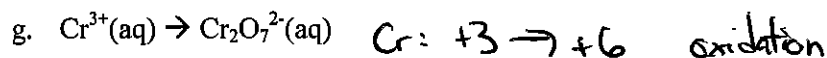
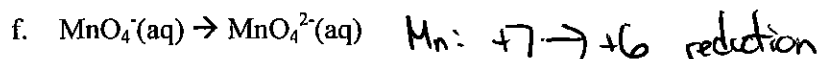
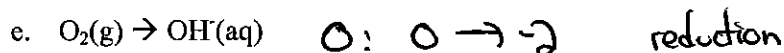
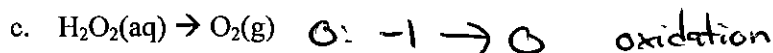
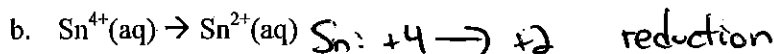
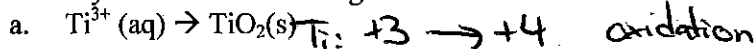
a. SF<sub>6</sub>b. Sb<sub>4</sub>O<sub>10</sub>c. N<sub>2</sub>H<sub>4</sub>d. S<sub>2</sub>O<sub>3</sub><sup>2-</sup>e. Cr(OH)<sub>4</sub><sup>-</sup>

In a reaction, when a species is losing an electron (gaining positive charge), it is being oxidized.

In a reaction, when a species is gaining an electron (losing positive charge), it is being reduced.

Follow the acronym **OIL RIG**. (**O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain).**Example 4.9C Identification of Oxidation or Reduction**

Classify each of the following half-reactions as oxidation or reduction.



#### 4.10 Balancing RedOx Reactions

Balancing redox reactions can be quite confusing, but it is made simpler by following these basic rules below.

##### REDOX REACTIONS IN AQUEOUS SOLUTION- ACIDIC OR BASIC

An alternate method of balancing redox reactions avoids the problem of assigning oxidation numbers. This method is based on splitting the reaction into two parts: an oxidation half and a reduction half. The two half-reactions are balanced separately, showing electrons, and then combined to show the final equation by eliminating electrons. The result is a *net ionic equation* which eliminated spectator ions (those not directly involved in the redox change).

##### Detailed Steps for ACIDIC Solution

1. Separate the change into half-reactions.
2. Balance each half-reaction separately.
  - a. Change coefficients to account for all atoms except H and O.
  - b. Add H<sub>2</sub>O to the side deficient in O.
  - c. Add H<sup>+</sup> to the side deficient in H.
  - d. Add e<sup>-</sup> to the side deficient in negative charge.
3. Determine the least common multiple (LCM) for electrons lost and gained.
4. Multiply half-reactions by appropriate coefficients needed to balance electrons.
5. Add the two balanced half-reactions and subtract duplications on the left and right.

##### Detailed Steps for BASIC Solution

Often we need to balance redox reactions taking place in basic solution. Here, we should not have H<sup>+</sup> ions in the final equation; their concentration in basic solution is exceedingly small. Instead, hydrogen in such equations should be in the form of OH<sup>-</sup> ions or H<sub>2</sub>O molecules. A simple way to accomplish this is to eliminate and H<sup>+</sup> ions appearing in the net reaction, "neutralizing" them by adding an equal number of OH<sup>-</sup> ions to both sides of the equation.

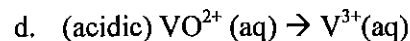
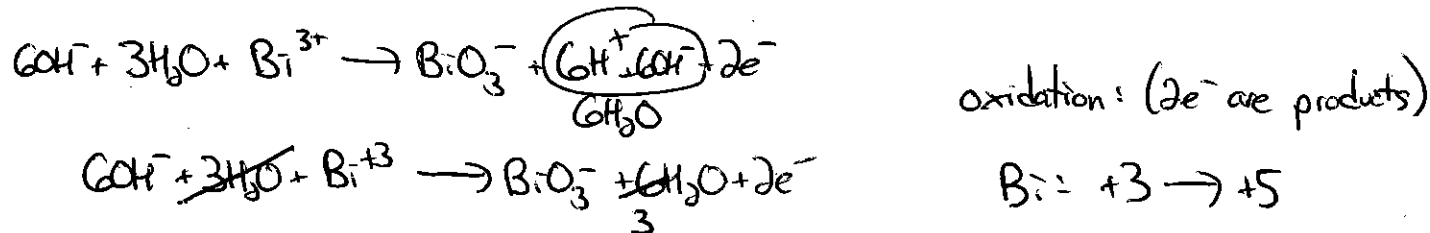
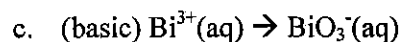
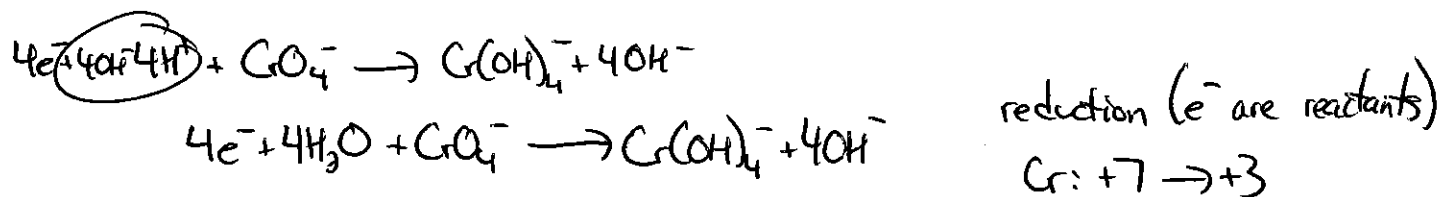
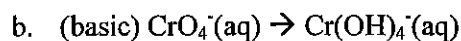
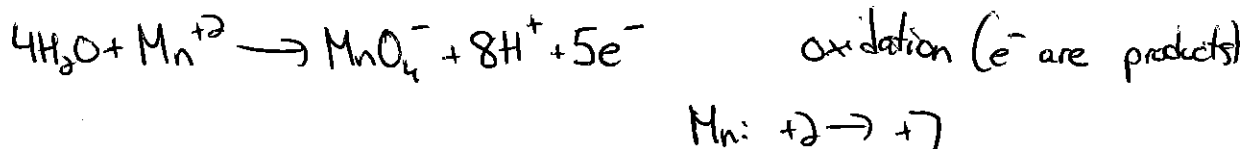
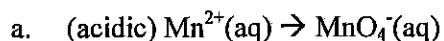
Follow the procedure for balancing in acid solution. Be sure to complete ALL of the steps (1) thru (5).

You now have an equation with H<sup>+</sup><sub>(aq)</sub> ions on one side of the equation. These species must be eliminated using the following modifications.

6. Add OH<sup>-</sup> ions equal to the number of H<sup>+</sup> ions to **BOTH** sides of the equation. The OH<sup>-</sup> ions will neutralize the H<sup>+</sup> ions according to the net ionic equation:  $\text{H}^+_{(aq)} + \text{OH}^-_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)}$
7. You must subtract duplications on the left and right once again.

**Example 4.10A Balancing Redox reactions**

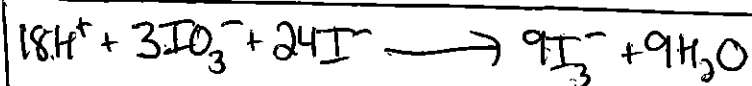
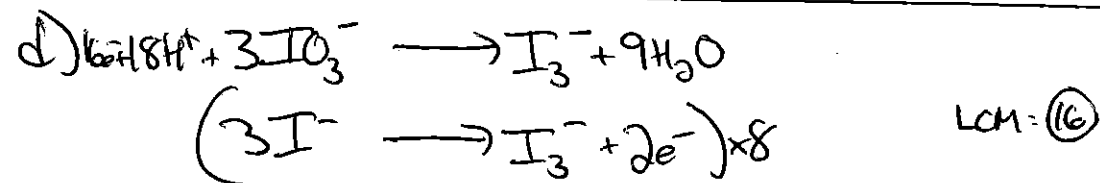
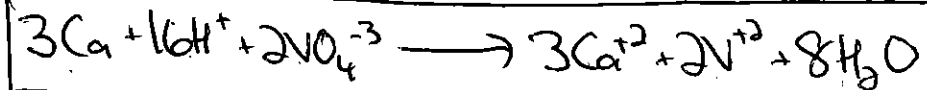
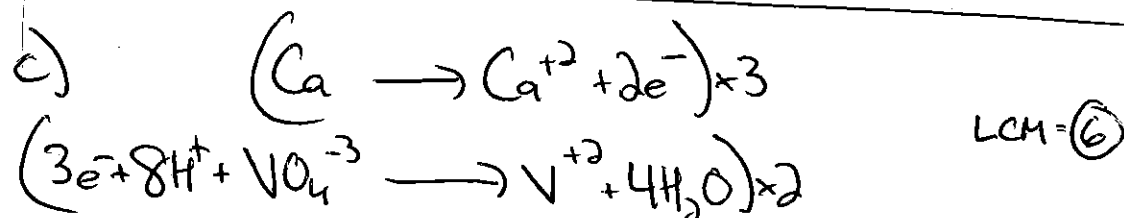
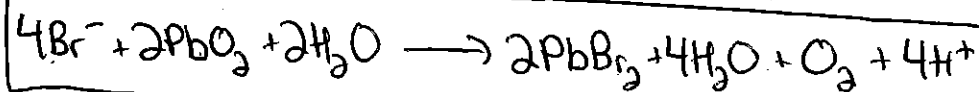
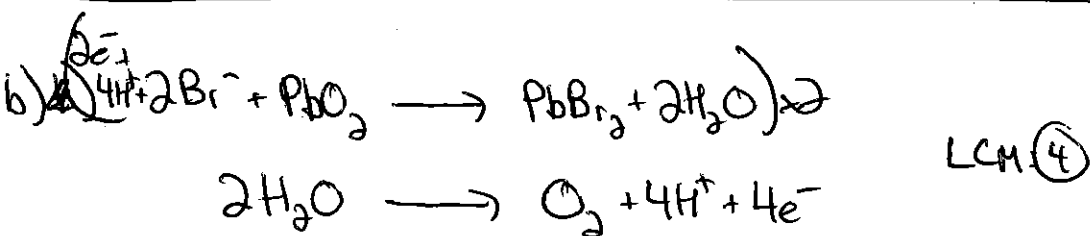
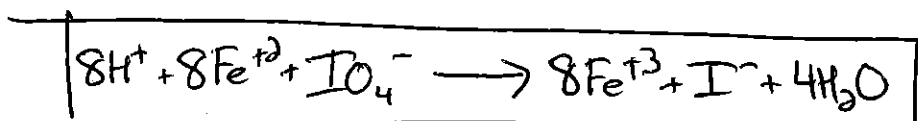
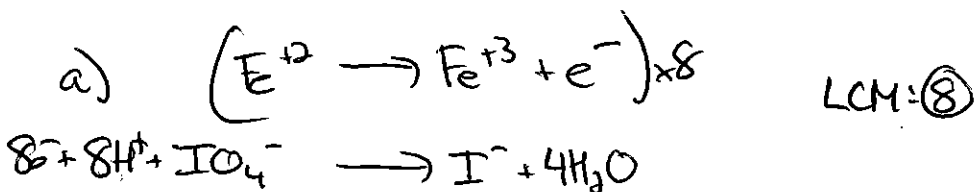
Classify each of the following half-reactions as oxidation or reduction and balance.



**Example 4.10B Balancing Redox reactions in Acidic Solutions**

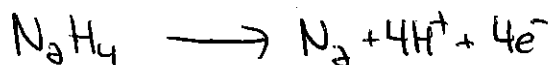
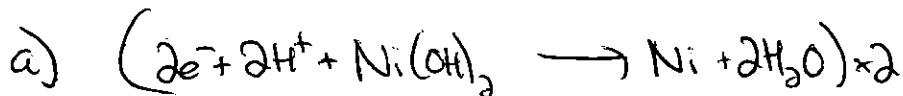
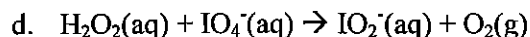
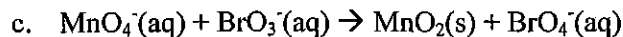
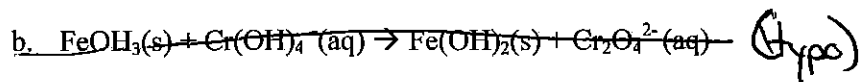
Write balanced equations for the following reactions in acid solution.

- $\text{Fe}^{2+}(\text{aq}) + \text{IO}_4^{-}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{I}^{-}(\text{aq})$
- $\text{PbO}_2(\text{s}) + \text{Br}^{-}(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{PbBr}_2(\text{s}) + \text{O}_2(\text{g})$
- $\text{Ca}(\text{s}) + \text{VO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{V}^{2+}(\text{aq})$
- $\text{IO}_3^{-}(\text{aq}) + \text{I}^{-}(\text{aq}) \rightarrow \text{I}_3^{-}(\text{aq})$

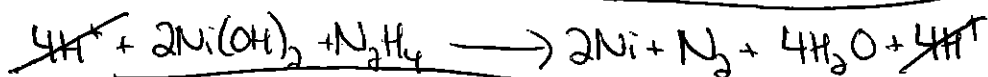


**Example 4.10C Balancing Redox reactions in Basic Solutions**

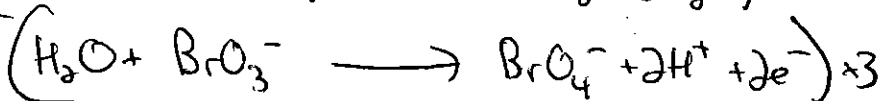
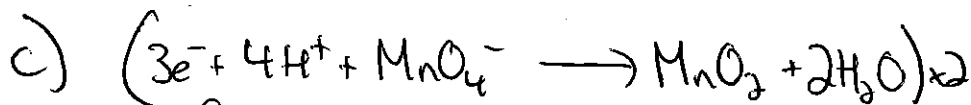
Write balanced equations for the following reactions in basic solution.



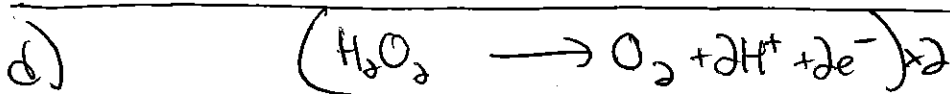
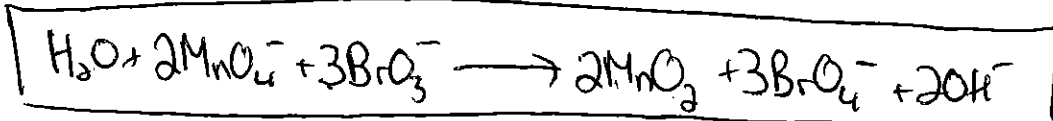
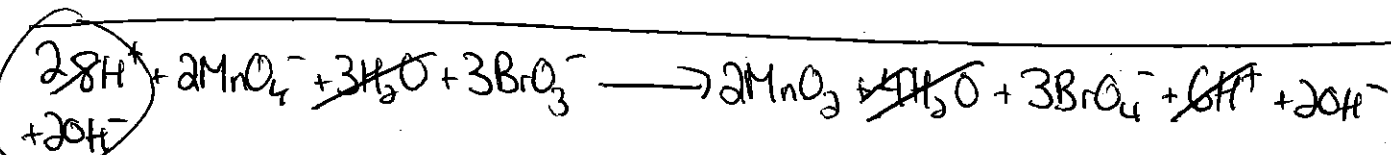
LCM: (4)



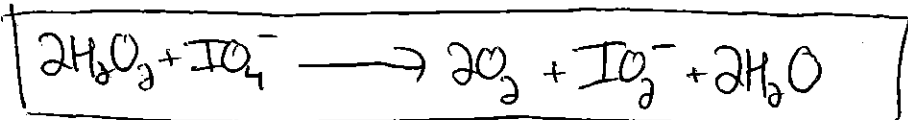
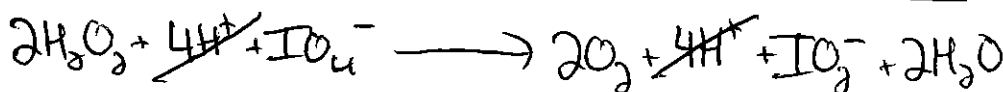
- No  $H^+$  in final reaction, so no need to add  $OH^-$ .



LCM: (6)



LCM: (4)



No  $H^+$  in final reaction, so no need to add  $OH^-$ .