4

Reactions in Aqueous Solutions

I. Solute Concentration – Molarity

A. Definition of molarity: ____

____

B. Units: ____

C. Exercises:

1. How would you prepare 250.0 mL of a 0.01269 M solution of $Ba(OH)_2$?

Solution: The 0.01269 M means you want a solution that contains 0.01269 mol of $Ba(OH)_2$ per liter. Since the mole is not a unit that can be measured or counted, you will have to express it by using another unit that you can deal with in the laboratory. That unit is grams. You can weigh out $Ba(OH)_2$ in a balance that gives a mass in grams. Thus, you have to "convert" moles/liter to grams/liter. The conversion factor is the molar mass of $Ba(OH)_2$, which is 171.3 g/mol (or $\mathcal{M}$ = 171.3 g/mol). Hence we get

$$0.01269\ \frac{\text{mol}}{\text{L}} \times \frac{171.3\ \text{g}}{1\ \text{mol}} = \frac{2.174\ \text{g}}{\text{L}}$$

However, you want to prepare only 250.0 mL of solution. Thus,

$$\frac{2.174\ \text{g}}{\text{L}} \times 0.2500\ \text{L} = 0.5435\ \text{g}$$

2. A student has 2.687 g of $(NH_4)_2SO_4$. What volume of solution does she need to obtain a solution that is 0.200 M? **(E1)**

3. What is the molarity of a solution of glucose ($C_6H_{12}O_6$) prepared by adding 126.3 g of glucose to a volumetric flask and dissolving it in enough water to make 500.0 mL of solution? **(E2)**

D. Molarity of ions in solution

1. The concentration of an ion sometimes differs from that of the ionic compound it comes from.
2. ***Example:***
   When 1.00 mol of $Ba(NO_3)_2$ is dissolved in enough water to make one liter of solution, a 1.00 M solution of $Ba(NO_3)_2$ is obtained. However, when $Ba(NO_3)_2$ dissolves, the following takes place:

$$Ba(NO_3)_2\ (s) \rightarrow Ba^{2+}\ (aq) + 2\,NO_3^-\ (aq)$$

   Since 1 mol of $Ba(NO_3)_2$ yields 1 mol of Ba^{2+} and 2 mol of NO_3^-, it follows that a 1.00 M solution of $Ba(NO_3)_2$ is 1.00 M in Ba^{2+} and 2.00 M in NO_3^-.

3. *Exercises*

a. Give the concentration in M of each ion in 0.0238 M $Al_2(SO_4)_3$.

Solution: First we write the equation for the dissociation of the solid into ions. In this case

$$Al_2(SO_4)_3\,(s) \rightarrow 2\,Al^{3+}\,(aq) + 3\,SO_4^{2-}\,(aq)$$

Thus 1 mole of $Al_2(SO_4)_3$ yields 2 moles of Al^{3+} and 3 moles of SO_4^{2-}. The following conversion factors can be used.

$$\frac{1\text{ mol }Al_2(SO_4)_3}{2\text{ mol }Al^{3+}} \quad \text{and} \quad \frac{3\text{ mol }SO_4^{2-}}{1\text{ mol }Al_2(SO_4)_3}$$

Using these conversion factors, we obtain

$$\frac{0.0238\text{ mol }Al_2(SO_4)_3}{1\text{ L}} \times \frac{2\text{ mol }Al^{3+}}{1\text{ mol }Al_2(SO_4)_3} = 0.0476\text{ M }Al^{3+}$$

and

$$\frac{0.0238\text{ mol }Al_2(SO_4)_3}{1\text{ L}} \times \frac{3\text{ mol }SO_4^{2-}}{1\text{ mol }Al_2(SO_4)_3} = 0.0714\text{ M }SO_4^{2-}$$

b. Give the concentration, in moles per liter, of each ion in 0.0304 M Na_3N and 0.128 M $ScCl_3$. **(E3)**

II. Precipitation Reactions

A. Solubilities of ionic compounds

1. Anions whose compounds are generally soluble:

a. All ______________________ are soluble.

b. Chlorides are soluble except: ______________________

c. Sulfates are soluble except: ______________________

2. Anions whose compounds are generally insoluble:

a. Hydroxides are insoluble except: ______________________

b. Carbonates are insoluble except: ______________________

c. Phosphates are insoluble except: ______________________

Memorize these rules. In order to do well in this chapter, you need to master these rules.

3. *Exercises*
   a. Using the solubility rules shown in Figure 4.3 of your text, predict what will happen when aqueous solutions of silver nitrate and sodium phosphate are mixed.
      Solution: An aqueous solution of silver nitrate, $AgNO_3$, contains Ag^+ and NO_3^- ions; a solution of sodium phosphate, Na_3PO_4, contains Na^+ and PO_4^{3-} ions. Since an ionic compound is made up of an anion and a cation, two different ionic solids could be formed. They are

      $$Ag_3PO_4 \quad \text{and} \quad NaNO_3$$

      From Figure 4.4, we see that $NaNO_3$ is soluble while Ag_3PO_4 is not. Thus, when the solutions are mixed, Ag_3PO_4 will precipitate.
   b. Predict what will happen when the following pairs of aqueous solutions are mixed: **(E4)**
      (1) solutions of copper sulfate and barium chloride.

      (2) solutions of ammonium phosphate and sodium hydroxide.

B. Equations for precipitation reactions
1. Nomenclature
   Give the definition of
   a. Precipitate: ______________________________

   ____
   b. Precipitation reaction: ______________________________

   ____
   c. Net ionic equation: ______________________________

   ____
   d. Spectator ions: ______________________________

   ____
2. Rules for writing net ionic equations
   a. Split up the ionic compounds into their respective ions. These are ions in solution.
   b. Combine a cation with an anion from the ions in solution. There are two possible combinations. These are the possible products.
   c. Check the solubility rules to determine which of the possible products is not soluble. This is the precipitate. There may be one, two, or no precipitates.

d. Write the reaction by putting the precipitate (from part **c**) on the product side first, and then the ions that make it up on the reactant side.

Note: You will not be able to follow these steps if you still have not memorized the charges of metals and polyatomic ions (Chapter 2). Do so now!

3. ***Exercises***

a. Write the net ionic equation for the reaction that occurs when aqueous solutions of potassium carbonate and nickel(II) nitrate are mixed.

Solution: We follow the steps outlined above.

(1) Ions in solution: K^+, CO_3^{2-} (from potassium carbonate); and Ni^{2+}, NO_3^- (from nickel(II) nitrate).

(2) Possible products: KNO_3; $NiCO_3$

(3) Precipitate: The solubility rules indicate that only $NiCO_3$ is insoluble.

(4) Equation: We first write the precipitate on the product side

$$\rightarrow NiCO_3\ (s)$$

Then, we complete the reaction by writing the ions that make up the precipitate on the reactant side. Their subscripts are now coefficients.

$$Ni^{2+}\ (aq) + CO_3^{2-}\ (aq) \rightarrow NiCO_3\ (s)$$

Remember: Always balance your net ionic equations.

b. Write the net ionic equation for the precipitation reaction that occurs when aqueous solutions of ammonium phosphate and zinc nitrate are mixed. **(E5)**

C. Stoichiometry

1. General notes on solving problems in solution stoichiometry

a. Distinguish between the moles of reagent and the moles of reacting species. The reagent is the chemical you obtain from a bottle. The reacting species is most often an ion that is part of the reagent. For example, if 10.0 mL of 0.100 M $Ba(OH)_2$ are used in a reaction, then the data given allows you to calculate that 1.00×10^{-3} moles of $Ba(OH)_2$ are used. The reacting species, however is *not* $Ba(OH)_2$, but either Ba^{2+} or OH^- depending on the reaction. The number of moles of Ba^{2+} is equal to the number of moles of $Ba(OH)_2$ because there is one mole of Ba^{2+} in one mole of $Ba(OH)_2$. However, the number of moles of OH^- is not equal to the number of moles of $Ba(OH)_2$. There are 2 moles of OH^- for every mole of $Ba(OH)_2$, so in this case there are 2.00×10^{-3} moles of OH^- for the reaction.

b. If you are asked to determine the concentration of ions after a reaction, you have to divide the number of moles of ions by the *total volume.* Total volume is the sum of the volumes of the solutions mixed together. We assume that for dilute aqueous solutions, volumes are additive.

c. The general procedure that should be followed is:
   (1) Write a balanced net ionic equation for the reaction.
   (2) Calculate the number of moles of reagent and relate it to the number of moles of reacting species.
   (3) Relate the number of moles of one reacting species to the number of moles of the other reacting species using the balanced net ionic equation.
   (4) Calculate the number of moles of product and convert it to the unit asked for.

2. Calculating the amount of product formed
   a. In this type of problem, complete information is usually given about both reactants, one of which is in excess. To determine what quantity or concentration of product is obtained, you must determine the limiting reactant. Do this by calculating the number of moles of each reacting species, and then calculating the moles of product assuming each reactant to be the limiting one.
   b. *Exercises*
      (1) When 200.0 mL of a 0.600 M solution of iron(III) chloride are mixed with 150.0 mL of a 0.100 M solution of barium hydroxide, a precipitate forms. How many grams of precipitate are formed?
      Solution: Using the steps described earlier, we solve the problem.
      — A precipitation reaction is involved.
      Ions in solution: Fe^{3+}; Cl^-; Ba^{2+}; OH^-
      Possible precipitates: $Fe(OH)_3$, $BaCl_2$
      Precipitate formed: $Fe(OH)_3$
      Net ionic equation: $Fe^{3+}(aq) + 3\,OH^-(aq) \rightarrow Fe(OH)_3(s)$
      — *moles* Fe^{3+}: Since Fe^{3+} comes from $FeCl_3$, we start with the information given about $FeCl_3$.

$$0.2000\text{ L} \times \frac{0.600\text{ mol FeCl}_3}{1\text{ L}} \times \frac{1\text{ mol Fe}^{3+}}{1\text{ mol FeCl}_3} = 0.120\text{ mol Fe}^{3+}$$

      moles OH^-: The hydroxide ion is contributed by $Ba(OH)_2$, so we use the information given about it.

$$0.1500\text{ L} \times \frac{0.100\text{ mol Ba(OH)}_2}{1\text{ L}} \times \frac{2\text{ mol OH}^-}{1\text{ mol Ba(OH)}_2}$$

$$= 0.0300\text{ mol OH}^-$$

      — We now calculate the moles of $Fe(OH)_3$ obtained. Since we are mixing given amounts of both reactants, we must first find the limiting reactant.
      If all the Fe^{3+} is consumed:

$$0.120\text{ mol Fe}^{3+} \times \frac{1\text{ mol Fe(OH)}_3}{1\text{ mol Fe}^{3+}} = 0.120\text{ mol Fe(OH)}_3$$

If all the OH^- is consumed:

$$0.0300 \text{ mol } OH^- \times \frac{1 \text{ mol } Fe(OH)_3}{3 \text{ mol } OH^-} = 0.0100 \text{ mol } Fe(OH)_3$$

Since less $Fe(OH)_3$ is made using up OH^-, it is the limiting reactant, and the amount of $Fe(OH)_3$ produced is 0.0100 mol.

— We now calculate the mass of product formed.

$$0.0100 \text{ mol } Fe(OH)_3 \times \frac{106.9 \text{ g } Fe(OH)_3}{1 \text{ mol } Fe(OH)_3} = 1.07 \text{ g } Fe(OH)_3$$

(2) When 300.0 mL of a 0.500 M solution of calcium nitrate is combined with 200.0 mL of a 0.500 M solution of sodium carbonate, a precipitate forms. How many grams of precipitate are obtained? **(E6)**

3. Calculating how much of one reactant is required

a. In this type of calculation, it is not necessary to determine the limiting reactant. Proceed using the steps described above, omitting the limiting reactant step.

b. It is essential that you write out the net ionic equation before you start your calculations.

c. Exercises

(1) A solution of barium chloride is added to a copper(II) sulfate solution. A precipitate forms. What volume of 0.750 M copper(II) sulfate is required to react completely with 25.0 mL of 0.800 M barium chloride solution?
Solution: The net ionic equation for this reaction is

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

We now follow the steps outlined earlier:

— We have complete information (volume and molarity) on barium chloride, so we calculate the number of moles.

$$0.0250\ \text{L} \times \frac{0.800\ \text{mol BaCl}_2}{1\ \text{L}} = 0.0200\ \text{mol BaCl}_2$$

— The reacting species, Ba^{2+}, comes from $BaCl_2$.

$$0.0200\ \text{mol BaCl}_2 \times \frac{1\ \text{mol Ba}^{2+}}{1\ \text{mol BaCl}_2} = 0.0200\ \text{mol Ba}^{2+}$$

— The other reacting species is SO_4^{2-}. According to the net ionic equation we can use the conversion factor

$$\frac{1\ \text{mol Ba}^{2+}}{1\ \text{mol SO}_4^{2-}}$$

Thus

$$0.0200\ \text{mol Ba}^{2+} = 0.0200\ \text{mol SO}_4^{2-}$$

— The reacting species, SO_4^{2-}, comes from $CuSO_4$. Hence

$$0.0200\ \text{mol SO}_4^{2-} \times \frac{1\ \text{mol CuSO}_4}{1\ \text{mol SO}_4^{2-}} = 0.0200\ \text{mol CuSO}_4$$

— We are asked for the volume of $CuSO_4$. We obtain this by using the molarity, 0.750 mol/L, as a conversion factor.

$$0.0200\ \text{mol CuSO}_4 \times \frac{1\ \text{L}}{0.750\ \text{mol CuSO}_4} = 0.0267\ \text{L}$$

We thus need 26.7 mL of 0.750 M $CuSO_4$ to react completely with 25.0 mL of 0.800 M $BaCl_2$.

(2) When 35.25 mL of a 0.125 M magnesium chloride solution react completely with 54.80 mL of potassium hydroxide solution, a precipitate forms. What is the molarity of the potassium hydroxide solution? **(E7)**

III. **Acid-Base Reactions**

A. Working definition of acid and base

1. Acid – a species that supplies H^+ ions to water
2. Base – a species that supplies OH^- ions to water

B. Types of acids

1. Strong acids

a. Definition:

A strong acid is one that completely ionizes in water forming an H^+ ion and an anion.

b. *Example:*

HNO_3 in water ionizes completely to form H^+ and NO_3^-. The reaction is

$$HNO_3\,(aq) \rightarrow H^+\,(aq) + NO_3^-\,(aq)$$

In a solution prepared by adding 0.01 moles of HNO_3 to water there are 0.01 moles of H^+ and 0.01 moles of NO_3^- ions.

c. What are the strong acids? (Name and formula)

(1) ______________________________

(2) ______________________________

(3) ______________________________

(4) ______________________________

(5) ______________________________

(6) ______________________________

Memorize these six strong acids. You will have a lot of trouble with this chapter and subsequent chapters if you do not know them.

Note that for all the strong acids, except H_2SO_4, one mole of acid produces one mole of H^+ ions. Sulfuric acid, in its reactions with bases, effectively produces two moles of H^+ ions per mole of H_2SO_4.

2. Weak acids

a. Definition:

A weak acid is one that only partially ionizes in water to give H^+ and the anion.

b. *Example*

HF partially ionizes in water to give H^+ and F^-. It is a weak acid. Its ionization equation is

$$HF\,(aq) \rightleftharpoons H^+\,(aq) + F^-\,(aq)$$

c. What are the weak acids?

There are thousands of weak acids. The easiest way to determine whether a compound is a weak acid is to see whether ionization of the species yields an H^+ ion. If it does and it is not one of the six strong acids, then the acid must be weak. Any molecule that starts with an H is a prime candidate for a weak acid.

C. Types of bases

1. Strong bases

a. Definition:

____

b. Example of the ionization of a strong base in water

____

c. What are they?

____

Know what the strong bases are. Note that for the hydroxides of Group 2 metals, 2 OH^- are produced for every mole of base that ionizes.

2. Weak bases

a. Weak bases do not furnish OH^- ions by ionization. They react with water, and the OH^- comes from the water. The remaining H^+ ion from the water attaches itself to the weak base. You may think of it as a two-step reaction:

$$H_2O \rightleftharpoons H^+ (aq) + OH^- (aq)$$
$$\text{weak base} + H^+ (aq) \rightleftharpoons (\text{weak base})H^+ (aq)$$

$$\text{weak base} + H_2O \rightleftharpoons OH^- (aq) + (\text{weak base})H^+ (aq)$$

b. What are the weak bases?
In this chapter, the weak bases we will consider are ammonia, NH_3, and amines.

D. Writing equations for acid-base reactions

1. Reacting species
As we have seen, the species in aqueous solution depend on the type of acid or base (strong or weak). The reacting species are the species in water solution. They are written on the left side of an acid-base reaction. They are

a. strong acid: ______________________________

b. strong base: ______________________________

c. weak acid: ______________________________

d. weak base: ______________________________

2. Net ionic equations

a. Strong acid + strong base

____

b. Strong acid + weak base

____

c. Weak acid + strong base

____

3. *Exercises*

a. Write the net ionic equation for the reaction between $H_3C_6H_5O_7$, citric acid, and sodium hydroxide.

Solution: Citric acid is not one of the strong acids, thus it must be a weak acid. The reacting species is $H_3C_6H_5O_7$. Sodium hydroxide is a strong base. The reacting species is OH^-. The equation will be of the form

$$HB\,(aq) + OH^-\,(aq) \rightarrow B^-\,(aq) + H_2O$$

In this case, HB is $H_3C_6H_5O_7$ and B^- is $H_2C_6H_5O_7^-$. It is $H_3C_6H_5O_7$ minus an H. The net ionic equation is

$$H_3C_6H_5O_7\,(aq) + OH^-\,(aq) \rightarrow H_2C_6H_5O_7^-\,(aq) + H_2O$$

b. Write net ionic equations for the reactions between aqueous solutions of the following acids and bases.

(1) phenylaniline, $C_6H_5NH_2$, and hydriodic acid **(E8)**

(2) potassium hydroxide and perchloric acid **(E9)**

(3) barium hydroxide and ascorbic acid, $HC_6H_7O_6$ **(E10)**

E. Acid-Base Titrations

1. Definitions

a. titration: ______________________________

b. standard solution: ______________________________

c. equivalence point: ______________________________

d. indicator: ______________________________

2. Stoichiometry
   a. Review the general notes and the worked out exercises for the stoichiometry of precipitation reactions.
   b. *Exercises*
      (1) What is the molarity of an aqueous solution of $Ba(OH)_2$ if 45.00 mL are required to react with 12.35 mL of 0.1500 M HCl in order to reach the equivalence point? **(E11)**

      (2) A sample is known to contain only potassium hydroxide and an inert, nonreactive substance. If 29.80 mL of a 0.2513 M solution of perchloric acid reacts completely with the KOH in the sample, how many grams of KOH reacted? **(E12)**

      (3) Citric acid ($C_6H_8O_7$) contains one mole of H^+/mole of citric acid. A sample containing citric acid has a mass of 1.286 g. The sample is dissolved in 100.0 mL of water. The solution is titrated with 0.0150 M NaOH. If 14.93 mL of the base are required to neutralize the acid, then what is the mass percent of citric acid in the sample? **(E13)**

(4) A sample of solid strontium hydroxide is mixed with water at 30°C and allowed to stand. A 100.0-mL sample of the solution is titrated with 59.4 mL of a 0.0400 M solution of hydrobromic acid. What is the concentration of the strontium hydroxide solution? **(E14)**

IV. Oxidation-Reduction Reactions

A. Some facts about redox reactions

1. Oxidation and reduction occur in the same reaction.
2. In a redox reaction the number of electrons (e^-) lost must equal the number of electrons gained.
3. a. In a reduction reaction there is a(n) ______________ of electrons.

   b. The electrons appear on the ______________ side of the equation.
4. a. In an oxidation reaction there is a(n) ______________ of electrons.

   b. The electrons appear on the ______________ side of the equation.

B. Oxidation number

1. Oxidation number refers to the charge of a monatomic ion. In a molecule or polyatomic ion, each element gets a "pseudo-charge", arbitrarily obtained by assigning bonding electrons to the atom with the greater attraction for the electrons.
2. Rules for assigning oxidation number

   a. The oxidation number of an element in an elementary substance is _____.

   b. The oxidation number of an element in a monatomic ion is equal to

   ____.

   c. Group 1 metals always have an oxidation number of ______________ in their compounds.

   d. Group 2 metals always have an oxidation number of ______________ in their compounds.

   e. The sum of the oxidation numbers of all the atoms in a neutral species is

   ____.

f. The sum of the oxidation numbers of all the atoms in an ion is

____.

g. The oxidation number of hydrogen in compounds is almost always ____ . When it is combined with a metal only, then its oxidation number is –1.

h. The oxidation number of oxgen in compounds is almost always ________. When it is combined with a metal in Groups 1 and 2, determine its oxidation number using rules (**c**)–(**f**).
Example: In Na_2O, oxygen has an oxidation number of –2. Since sodium is always +1 and there are two sodium ions, the cationic charge is +2. Hence, the anionic charge (the oxidation number of the oxygen atom) must be –2.
In Na_2O_2, sodium, having always an oxidation number of +1, makes the cationic charge +2. The total anionic charge is –2. There are two atoms of oxygen in the anion, so each atom is assigned an oxidation number of –1.

Note: Memorize these rules. Become adept at assigning oxidation numbers.

3. Exercises

a. What is the oxidation number of each atom in SO_3^{2-}?
Solution: Here, oxygen has oxidation number –2 since it is not combined with a Group 1 or Group 2 metal. Thus, if we assign x as the oxidation number for sulfur, and recognize that the charge for the whole polyatomic ion is –2 (see superscript), we get the equation

$$x + 3(-2) = -2$$

$$x = 4$$

The oxidation number for S in SO_3^{2-} is +4.

b. What are the oxidation numbers for all atoms in NO_2 and NH_4^+? **(E15)**

4. Defining oxidation-reduction on the basis of oxidation numbers

a. Oxidation can be defined as a(n) ______________________________ in oxidation number.

b. Reduction can be defined as a(n) ______________________________ in oxidation number.

c. The reducing agent is the substance being oxidized.

d. The oxidizing agent is the substance being reduced.

e. *Exercises*

(1) For the reaction

$$2\,Cl_2\,(aq) + 2\,H_2O\,(g) \rightarrow 4\,HCl\,(g) + O_2\,(g)$$

identify the oxidizing and reducing agents.

Solution: To do this, we must know which of the species is oxidized and which is reduced. Thus, we determine the oxidation number of each of the atoms in all the compounds. The oxidation numbers are:

$$\text{reactants}: Cl = 0; \quad H = +1; \quad O = -2$$
$$\text{products}: Cl = -1; \quad H = +1; \quad O = 0$$

We see that chlorine goes from an oxidation number of 0 to −1. Since that is reduction (because there is a decrease in oxidation number), chlorine is the species reduced and Cl_2 is the oxidizing agent.

We see that hydrogen's oxidation number stays the same.

We also note that oxygen goes from an oxidation number of −2 to 0. That is an increase in oxidation number, and oxygen is said to be oxidized. Hence H_2O is the reducing agent.

(2) In the unbalanced redox equation

$$MnO_4^-\,(aq) + NO_2^-\,(aq) + H^+\,(aq) \rightarrow Mn^{2+}\,(aq) + NO_3^-\,(aq) + H_2O$$

identify the oxidizing and reducing agents. **(E16)**

C. Balancing half-reactions (oxidation and reduction)

The following steps should be followed in balancing oxidation and reduction half-reactions. Follow them systematically every time you have to balance a half-reaction, so that the process becomes a habit.

1. Write an oxidation half-reaction by picking out the ions and/or compounds that contain the element oxidized (i.e., the one that increases its oxidation number). Do the same for the reduction half-equation, only this time pick out the ions and/or compounds that contain the element reduced (i.e., the one that decreases its oxidation number).
2. Balance the atoms of the element being oxidized or reduced.
3. Add electrons to reflect the change in oxidation number.
   a. Put the electrons on the left side when reduction occurs.
   b. Put the electrons on the right side when oxidation occurs.

c. The number of electrons should reflect the *total* change in oxidation number.
Example: For the reduction half-reaction

$$Cl_2\,(g) \rightarrow 2\,Cl^-\,(aq)$$

the change in oxidation number is from 0 (Cl_2) to −1 (Cl^-). However, since there are two Cl^- ions, each with an oxidation number of −1, the change in oxidation number is 2. Thus the half-reaction should be written

$$Cl_2\,(g) + 2\,e^- \rightarrow 2\,Cl^-\,(aq)$$

4. Balance charge.
   a. Add H^+ ions to the side with the smaller total charge when the reaction is done in acidic medium.
   b. Add OH^- ions to the side with the larger total charge when the reaction is done in basic medium.
5. Balance atoms.
   a. The element that is either oxidized or reduced should already be balanced (Step **1**).
   b. Add H_2O to balance hydrogen.
   c. Check to see that oxygen is balanced. It should be.

All this will make more sense when you see it actually used and when you use it yourself.

6. Exercises

a. Consider the following redox reaction in acidic medium.

$$Cr_2O_7^{2-}\,(aq) + NO_2^-\,(aq) \rightarrow Cr^{3+}\,(aq) + NO_3^-\,(aq)$$

Write balanced oxidation and reduction half-reactions.
Solution: Let's start with the reduction half-reaction.
Step (1) Chromium is the element reduced since it has an oxidation number of +6 as reactant and +3 as product. The half-reaction is

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

Note that $Cr_2O_7^{2-}$ is the reactant. It is the species that has the Cr atom. Do *not* write

$$Cr^{6+} \rightarrow Cr^{3+}$$

as your half-reaction.
Step (2) Since there are 2 Cr atoms on the left and only one on the right, we write

$$Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+}$$

Step (3) The half-reaction is a reduction so electrons (e^-) are put on the left side. The oxidation number goes from 2(+6) = 12 (since there are two chromium on the left each with an oxidation number of +6) to 2(+3) = 6 (again since there are 2 chromium on the right, each with an oxidation number of +3). The change in oxidation number is from +12 to +6 which is $6e^-$.

$$Cr_2O_7^{2-} + 6e^- \rightarrow 2\,Cr^{3+}$$

Step (4) We now balance charge. The charge on the left is –8 [i.e.,–2 + (–6)]. The charge on the right is +6 [i.e., 2 x (+3)]. The smaller charge is on the left (i.e., $-8 < +6$) so we add H^+ to the left side. To figure out how many H^+ you have to add, you can use the algebraic equation

$$-8 + x = +6$$

where –8 is the charge on the left, x is the number of H^+ to be added, and +6 is the charge on the right. We see that x = 14. (If you get a negative number of x, you have chosen the wrong side for x.) Thus, we need 14 H^+, and we write

$$Cr_2O_7^{2-} + 6e^- + 14\,H^+ \rightarrow 2\,Cr^{3+}$$

The charge is now balanced. On the left we have a total charge of +6 [i.e., –6 + (–2) + 14], on the right we have +6 [i.e., 2(+3)].
Step (5) We balance atoms.
(1) Cr was balanced in Step (1).
(2) For hydrogen, we have 14 H on the left and no H on the right. We need to add H_2O, and since we need 14 H on the right, we add 7 H_2O on the right.

$$Cr_2O_7^{2-} + 6e^- + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

(3) We see that oxygen has also been balanced by adding water.
The balanced reduction half-reaction is

$$Cr_2O_7^{2-}\,(aq) + 6e^- + 14\,H^+\,(aq) \rightarrow 2\,Cr^{3+}\,(aq) + 7\,H_2O$$

We now write the oxidation half-reaction.
Step (1) Nitrogen is the element oxidized from +3 to +5. NO_2^- has the N atom and is written on the left. NO_3^- also has the N atom, and is written on the right.

$$NO_2^- \rightarrow NO_3^- -$$

Step (2) There is one N on the left and one on the right, so the atom that changes oxidation number is balanced.
Step (3) The oxidation number changes from 1(3) = 3 to 1(5) = 5. The total change in oxidation number is 2. Since this is an oxidation half-reaction, we write $2e^-$ on the right.

$$NO_2^- \rightarrow NO_3^- + 2\,e^-$$

Step (4) We balance charge. The total charge on the left is –1. The total charge on the right is –3. (Do not confuse charge with oxidation number!) The smaller charge is on the right (–3 < –1), so we add H^+ (x) on the right.

$$-1 = -3 + x$$
$$x = 2$$

Thus we add 2 H^+ on the right side.

$$NO_2^- \rightarrow NO_3^- + 2\,e^- + 2\,H^+$$

Step (5) We balance hydrogen atoms. There are 2 H on the right but none on the left. We balance that by adding an H_2O on the left.

$$NO_2^- + H_2O \rightarrow NO_3^- + 2\,e^- + 2\,H^+$$

We see that the oxygen atoms have also been balanced. The oxidation half-reaction is

$$NO_2^-\,(aq) + H_2O \rightarrow NO_3^-\,(aq) + 2\,H^+\,(aq) + 2\,e^-$$

b. For the reaction

$$PbO\,(s) + NH_3\,(g) \rightarrow Pb\,(s) + N_2\,(g) + H_2O\,(g)$$

Write a balanced reduction half-reaction and oxidation half-reaction in basic medium. **(E17)**

D. Balancing redox reactions

1. Steps to balance overall redox reactions

   a. *Step 1:* Split the equation and write a balanced oxidation half-reaction and a balanced reduction half-reaction.
   This process was just explained.

   b. *Step 2:* Multiply the two half-reactions by coefficients so that the two half-reactions have the same number of electrons on opposite sides.

   c. *Step 3:* Add the two equations making sure that
   (1) electrons cancel out.
   (2) H^+, OH^-, and/or H_2O appear on only one side of the overall equation.

2. *Exercises*

   a. Write a balanced net ionic equation for the following redox reaction in acidic medium.

$$Cr_2O_7^{2-}\ (aq) + NO_2^-\ (aq) \rightarrow Cr^{3+}\ (aq) + NO_3^-\ (aq)$$

Solution:

Step (1): The balanced half-reactions (explained earlier) are

$$Cr_2O_7^{2-}\ (aq) + 6\,e^- + 14\,H^+\ (aq) \rightarrow 2\,Cr^{3+}\ (aq) + 7\,H_2O$$

$$NO_2^-\ (aq) + H_2O \rightarrow NO_3^-\ (aq) + 2\,H^+\ (aq) + 2\,e^-$$

Step (2): Since both half-reactions must have the same number of electrons, we multiply the oxidation half-reaction (NO_2^- (aq) $\rightarrow$ NO_3^- (aq)) by 3. We leave the reduction half-reaction alone. Doing that we get

$$Cr_2O_7^{2-}\ (aq) + 6\,e^- + 14\,H^+\ (aq) \rightarrow 2\,Cr^{3+}\ (aq) + 7\,H_2O$$

$$3\,NO_2^-\ (aq) + 3\,H_2O \rightarrow 3\,NO_3^-\ (aq) + 6\,H^+\ (aq) + 6\,e^-$$

Step (3): We add both half-reactions, cancelling the 6 electrons appearing on both sides.

$$Cr_2O_7^{2-}\ (aq) + 3\,NO_2^-\ (aq) + 14\,H^+\ (aq) + 3\,H_2O \rightarrow$$
$$2\,Cr^{3+}\ (aq) + 7\,H_2O + 3\,NO_3^-\ (aq) + 6\,H^+\ (aq)$$

Note that

(1) 14 H^+ appear on the left and 6 H^+ appear on the right. Net H^+ is 8 H^+ on the left. (Subtract 6 H^+ from both sides.)

(2) 3 H_2O appear on the left and 7 H_2O appear on the right. Net H_2O is 4 H_2O on the right. (Subtract 3 H_2O from both sides.)

The balanced net ionic redox reaction is

$$Cr_2O_7^{2-}\ (aq) + 3\,NO_2^-\ (aq) + 8\,H^+\ (aq) \rightarrow$$
$$2\,Cr^{3+}\ (aq) + 4\,H_2O + 3\,NO_3^-\ (aq)$$

b. Write a balanced net ionic equation for the following redox reaction

$$S_2O_3^{2-}\ (aq) + Cl_2\ (g) \rightarrow SO_4^{2-}\ (aq) + Cl^-\ (aq)$$

in both acidic and basic medium. **(E18)**

E. Stoichiometry

1. Stoichiometric calculations for redox reactions are carried out in much the same way as those for acid-base or precipitation reactions.

2. Exercises

a. When aluminum is added to a strong acid, the metal is oxidized to aluminum(III) ions by H^+ and hydrogen gas is produced. If 10.0 g of aluminum is added to 50.0 mL of 0.450 M HCl, what is the concentration of Al^{3+} in moles/liter after the reaction is complete? Assume no volume change. **(E19)** *b.* All the iron in an ore with mass 1.500 g is converted to Fe^{2+}. The Fe^{2+} ions are made to react with a $K_2Cr_2O_7$ solution. The reaction required 35.25 mL of a 0.05000 M solution of $K_2Cr_2O_7$. The reaction is

$$6\,Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14\,H^+(aq) \rightarrow 6\,Fe^{3+}(aq) + 2\,Cr^{3+}(aq) + 7\,H_2O$$

Calculate the percent of Fe in the ore. **(E20)**

SELF-TEST

A. Multiple choice:

1. Which of the following substances would precipitate from a mixture of barium, silver, chloride, sulfate, and nitrate ions in aqueous solution?

(1) $BaSO_4$ (2) $BaCl_2$ (3) $Ba(NO_3)_2$ (4) Ag_2SO_4 (5) $AgCl$

a. (2) **b.** (1),(5) **c.** (1),(2),(3)
d. (1),(2),(4) **e.** (1),(2),(5) **f.** (1),(2),(4),(5)

2. The acid-base reaction between aqueous solutions of HNO_2 and KOH

(1) will produce NO_2 (g) and NO (g).
(2) is a precipitation reaction.
(3) is a weak acid – strong base reaction.
(4) will produce only water.
(5) will produce NO_2^- (aq).

The correct statements are
a. (1),(2) **b.** (1),(3) **c.** (2),(5) **d.** (3),(5) **e.** (3),(4)

3. In which species does sulfur have the same oxidation number as chlorine in ClO_2^-?
a. H_2S **b.** S_8 **c.** SO_3^{2-} **d.** SO_4^{2-} **e.** none of these

4. In an acid-base reaction, the reacting species for $Ba(OH)_2$ is
a. H^+ **b.** OH^- **c.** $(OH)_2^-$ **d.** BaO **e.** Ba^{2+}

b. All the iron in an ore with mass 1.500 g is converted to Fe^{2+}. The Fe^{2+} ions are made to react with a $K_2Cr_2O_7$ solution. The reaction required 35.25 mL of a 0.05000 M solution of $K_2Cr_2O_7$. The reaction is

$$6\,Fe^{2+}\,(aq) + Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) \rightarrow 6\,Fe^{3+}\,(aq) + 2\,Cr^{3+}\,(aq) + 7\,H_2O$$

Calculate the percent of Fe in the ore. **(E20)**

SELF-TEST

A. Multiple choice:

1. Which of the following substances would precipitate from a mixture of barium, silver, chloride, sulfate, and nitrate ions in aqueous solution?

   (1) $BaSO_4$ (2) $BaCl_2$ (3) $Ba(NO_3)_2$ (4) Ag_2SO_4 (5) AgCl

   a. (2) **b.** (1),(5) **c.** (1),(2),(3)
   d. (1),(2),(4) **e.** (1),(2),(5) **f.** (1),(2),(4),(5)

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4. In an acid-base reaction, the reacting species for $Ba(OH)_2$ is
   a. H^+ **b.** OH^- **c.** $(OH)_2^-$ **d.** BaO **e.** Ba^{2+}

5. When NaOH was added to one liter of a solution containing 0.10 mol of each of two metal ions, a precipitate formed with one ion but the other stayed in solution. The solution could have contained
a. Mg^{2+} and Ba^{2+} **b.** K^+ and Ba^{2+} **c.** Mg^{2+} and Cr^{3+}
d. Cr^{3+} and Fe^{3+} **e.** none of these

6. The balanced equation for the reaction between NO_3^- and Br^- in acid is:

$$2\,NO_3^-\,(aq) + 4\,H^+\,(aq) + 2\,Br^-\,(aq) \rightarrow 2\,NO_2\,(g) + Br_2\,(\ell) + 2\,H_2O$$

When this equation is balanced in basic solution, the number of H_2O molecules is
a. 2 on the left **b.** 2 on the right
c. 4 on the left **d.** 4 on the right
e. zero on both sides of the equation

7. Consider the unbalanced equation for the following reaction in acid medium:

$$Se\,(s) + NO_3^-\,(aq) \rightarrow SeO_2\,(s) + NO\,(g)$$

In the balanced, net ionic equation, the smallest whole number coefficients for Se and NO_3^- respectively are
a. 3,4 **b.** 4,3 **c.** 2,4 **d.** 4,2 **e.** 2,3

8. How many of the following anions are derived from strong acids?

Cl^- $C_2H_3O_2^-$ PO_4^{3-} NO_3^- CO_3^{2-}

a. 1 **b.** 2 **c.** 3 **d.** 4 **e.** 5

9. For the reaction

$$Cu\,(s) + 4\,H^+\,(aq) + 2\,NO_3^-\,(aq) \rightarrow 2\,NO_2\,(g) + 2\,H_2O + Cu^{2+}\,(aq)$$

the oxidizing agent and the reducing agent are, in that order:
a. Cu, NO_3^- **b.** Cu, H^+ **c.** H^+
d. H^+, Cu **e.** NO_3^-, Cu

10. The equation for a redox reaction in basic solution
a. always has hydroxide ions as reactant.
b. may have hydroxide ions as either reactant or product.
c. may contain hydrogen ions.
d. always has water as a product.
e. None of the above is true.

B. Writing Equations:

Write balanced net ionic equations using smallest whole number coefficients for the following reactions between 0.1 M aqueous solutions of the following:

1. lead nitrate and sodium chloride

   ____

2. perchloric acid and barium hydroxide

   ____

3. hydriodic acid and ammonia

   ____

4. acetic acid and potassium hydroxide

   ____

5. sulfuric acid and barium chloride

   ____

6. nickel(II) nitrate and hydrochloric acid

   ____

C. Problems:

1. Consider mixing solutions of silver nitrate and calcium chloride.
   - **a.** Write a net ionic equation for the formation of the precipitate, if any.
   - **b.** If 200.0 mL of 0.300 M silver nitrate are mixed with 350.0 mL of 0.500 M calcium chloride, how many grams of precipitate are formed? How many moles of each ion are present after precipitation?

c. What volume of 0.250 M calcium chloride would be required to precipitate silver chloride if it is mixed with 600.0 mL of 0.650 M silver nitrate?

2. Consider two solutions. One solution is 0.1115 M $Ca(OH)_2$. The other is 0.1050 M $HClO_4$.

a. Write a balanced equation for the reaction between the two solutions.

b. How many mL of $Ca(OH)_2$ will be required to neutralize 25.00 mL of the $HClO_4$?

c. If a student starts to titrate 31.39 mL of the $Ca(OH)_2$ solution with $HClO_4$ and stops the titration after only 23.81 mL of $HClO_4$ have been added, then

(1) How many moles of H^+ have been added?

(2) How many moles of OH^- are left unreacted?

3. Balance the following equations:

a. $S_2O_3^{2-}$ (aq) + I_3^- (aq) → $S_4O_6^{2-}$ (aq) + I^- (aq)

b. Mn^{2+} (aq) + $HBiO_3$ (s) → MnO_4^- (aq) + BiO^+ (aq) (acid)

c. $Cr_2O_7^{2-}$ (aq) + H_3AsO_3 (aq) → H_3AsO_4 (aq) + Cr^{3+} (aq) (acid)

d. ClO^- (aq) + CrO_2^- (aq) → Cl^- (aq) + CrO_4^{2-} (aq) (basic)

e. OBr^- (aq) + HPO_3^{2-} (aq) → Br^- (aq) + PO_4^{3-} (aq) (basic)

4. The salt $NaBrO_3$ oxidizes Sn^{2+} to $SnCl_6^{2-}$ in the presence of hydrochloric acid according to the equation

$$3\,Sn^{2+}\,(aq) + 18\,Cl^{-}\,(aq) + BrO_3^{-}\,(aq) + 6\,H^{+}\,(aq) \rightarrow$$
$$3\,SnCl_6^{2-}\,(aq) + Br^{-}\,(aq) + 3\,H_2O$$

A sample weighing 2.000 g is dissolved in acid and all the tin present is converted to Sn^{2+}. For the reaction to go to completion, 32.50 mL of a 0.07500 M $KBrO_3$ solution are required. Find the percent of tin in the sample.