**Chapter 4 – Stoichiometry of Chemical Reactions**

This is the last of what I think of as the four core chapters to chemistry. You will see the material from these chapters in nearly every chapter in CHM 211 and 212 and in organic chemistry as well.

A term you should know is <u>stoichiometry</u>, which refers to the quantity relationship between reacting chemical species. The idea is fairly simple because it answers questions like: If I have a gallon of gasoline, how much carbon dioxide is produced when the gasoline burns? A real-life analogy would be if you were making 100 hamburgers, how many packages of buns would you need to purchase? More chemically, when hydrogen and oxygen gases react to form water, two hydrogen molecules react with one oxygen molecule to form two water molecules.

$$2 \ H_2 \quad + \quad O_2 \quad \rightarrow \quad 2 \ H_2O$$
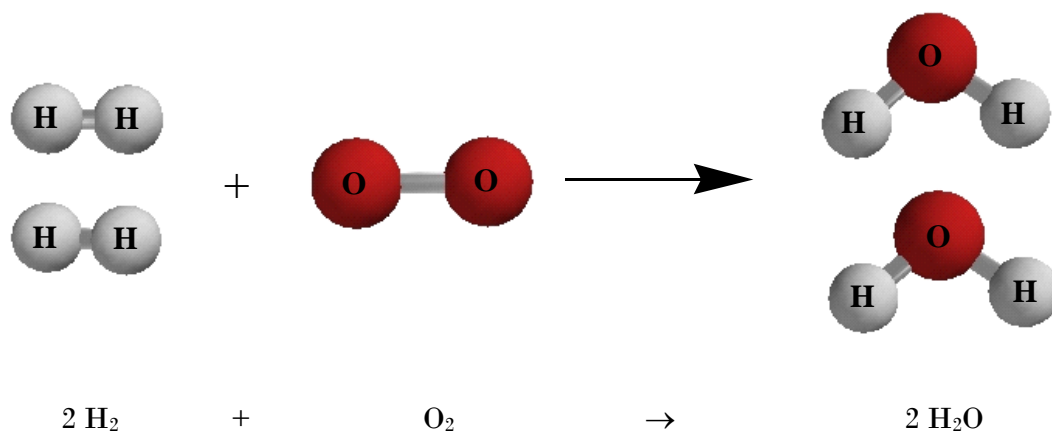
The 2 to 1 to 2 relationship is the stoichiometry of the reaction. Stoichiometry also allows the number of atoms or molecules involved in a reaction to be related to the measured quantities: mass and volume (for gases or liquids) of the substances. Thus, 1 gram of hydrogen reacts with 8 grams of oxygen to yield 9 grams of water.

4.1   <u>Writing and Balancing Chemical Equations</u>

By far and away, the most convenient way of describing chemical reactions is the chemical equation. The generic form is given as:

$$aA + bB \longrightarrow cC + dD$$
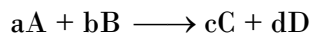
where a, b, c, and d are whole number, balancing coefficients ("1" is not used), A & B are reactants, and C & D are products. Sometimes the symbols Δ (heat) or hν (light) are placed above the arrow to indicate if outside sources of energy were used to facilitate the reaction. Also, sometimes the solvent is placed below the arrow if it isn't water. Usually the physical state of each species will be indicated by placing one of the following symbols after each reactant and product: (g) = gas, (ℓ) = liquid, (s) = solid, (aq) = aqueous (dissolved in water).

A chemical equation does **not** tell you:

1) Reaction rate (how fast the reaction goes)

2) Reaction pathway. (Most reactions go through several steps on the way to completion.)

You will learn about both of these topics in CHM 212.

How does one balance a chemical equation (determine the coefficients)? We begin by assuming that you know the reactants and products in the reaction mixture. The steps are:

1) Write out all reactants and products on the correct sides of the arrow.

2) Count out how many atoms of each element (or group) appear on either side of the arrow.

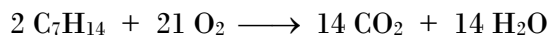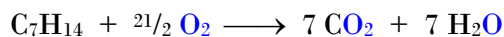3) Choose the element (or group) that appears in the fewest number of places <u>and</u> has different numbers on either side of the arrow. Balance using coefficients.

4) Repeat with the remaining atoms/groups.

5) Make all coefficients whole numbers by multiplying through by the least common denominator of the existing coefficients.

Examples: (The blue atoms are being balanced.)

__ P + __ Cl$_2$ $\longrightarrow$ __ PCl$_3$ __ C$_7$H$_{14}$ + __ O$_2$ $\longrightarrow$ __ CO$_2$ + __ H$_2$O

P + 3 Cl$_2$ $\longrightarrow$ 2 PCl$_3$ C$_7$H$_{14}$ + O$_2$ $\longrightarrow$ 7 CO$_2$ + H$_2$O

2 P + 3 Cl$_2$ $\longrightarrow$ 2 PCl$_3$ C$_7$H$_{14}$ + O$_2$ $\longrightarrow$ 7 CO$_2$ + 7 H$_2$O

$$C_7H_{14} + {}^{21}/_2\ O_2 \longrightarrow 7\ CO_2 + 7\ H_2O$$

$$2\ C_7H_{14} + 21\ O_2 \longrightarrow 14\ CO_2 + 14\ H_2O$$

There are a couple of important points to add: (1) Never change subscripts in formulas. Doing so changes the identity of the substance. For example, H_2O is water, but H_2O_2 is hydrogen peroxide. CH_2O is formaldehyde, while $C_6H_{12}O_6$ is glucose. (2) Coefficients should not have a common divisor. That is, reaction between hydrogen and oxygen to form water is **not** properly balanced as: $4\ H_2 + 2\ O_2 \rightarrow 4\ H_2O$ because each coefficient is an even number. To balance it correctly, you must divide by 2 (point 5 above).

One common mistake when writing out consecutive reactions is to write the first reaction, then add a reactant to the product, draw an arrow, then the final reaction. For example, let's say that you burn phosphorus in oxygen to yield diphosphorus pentaoxide, then react it with water to produce phosphoric acid. It is **incorrect** to write:

$$4\ P_{(s)} + 5\ O_{2\ (g)} \longrightarrow 2\ P_2O_{5\ (s)} + 6\ H_2O_{(\ell)} \longrightarrow 4\ H_3PO_{4\ (aq)}$$
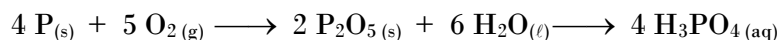
The reason for this is that it implies that the first reaction produces the water, which then further reacts with the P_2O_5. The correct way to write this pair of reactions is on two lines:

$$4\ P_{(s)} + 5\ O_{2\ (g)} \longrightarrow 2\ P_2O_{5\ (s)}$$

$$P_2O_{5\ (s)} + 3\ H_2O_{(\ell)} \longrightarrow 2\ H_3PO_{4\ (aq)}$$
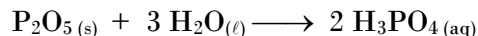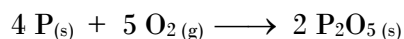
Ionic Reactions

Most reactions occur in liquid solutions and in nature that solvent is almost always water. A typical solution reaction might be written as follows:

$$NaCl_{(aq)} + AgNO_{3\ (aq)} \rightarrow NaNO_{3\ (aq)} + AgCl_{(s)}$$
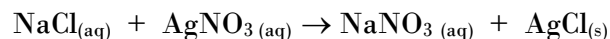
This style of depicting a reaction is called a <u>molecular equation</u>. It gets that name because all species are written out fully, as if they were all molecules. In reality, the sodium chloride, silver(I) nitrate, and sodium nitrate exist completely as ions in solution, so it would be more accurate to

write the equation like this:

$$Na^+_{(aq)} + Cl^-_{(aq)} + Ag^+_{(aq)} + NO_3^-_{(aq)} \rightarrow Na^+_{(aq)} + NO_3^-_{(aq)} + AgCl_{(s)}$$
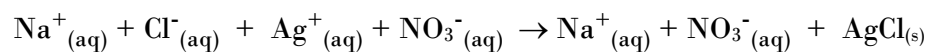
This <u>total ionic equation</u> shows how all of the species actually appear in solution. Here, only the silver(I) chloride is shown intact because it exists as an undissolved solid.

Unfortunately, total ionic equations are cumbersome and so are rarely used. One thing you may have noticed is that some of the species (e.g. Na^+) appear on both sides of the equation and, like a math equation, those things can be cancelled. That yields a simplified version, called the <u>net ionic equation</u>, which looks like this:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$
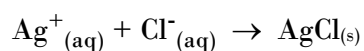
The ions that don't participate in reaction are called <u>spectator ions</u>. Only strong electrolytes are written as ions, weak electrolytes are written as molecules. Net ionic reactions can only be written if one of the products either precipitates from solution or forms a molecule.

Net ionic equations have the advantage of relating similar reactions that don't initially look alike as molecular equations. For example, for the following collection of acids and bases, any acid and base pairing gives exactly the same net ionic equation.

acids: HCl, HBr, HI, HNO_3, $HClO_4$

bases: $LiOH$, $NaOH$, KOH, $RbOH$, $CsOH$

molecular equation: $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(\ell)}$

net ionic equation: $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)}$

This yields 30 different possible combinations of reactants, but only one net ionic equation. It allows us to see similarities in reactions that would otherwise be difficult to find.

4.2   Classifying Chemical Reactions

In this section, we will consider three major classes of reactions.

<u>Precipitation Reactions and Solubility Rules</u>

<u>Precipitates</u> form when ions react in solution to produce a solid; with the reaction called a <u>precipitation reaction</u>. A reaction <u>must</u> occur for a precipitate to form. Simply having a solid form when some of the solvent evaporates (e.g. sodium chloride crystallizing when seawater evaporates) does not constitute precipitation. Although counterintuitive, "insoluble" means that only a very small amount of the compound dissolves, not that none (zero) of it dissolves. (For a true solubility of zero, not one single molecule/unit would dissolve). An example of a precipitation reaction is

$$AgNO_{3\ (aq)}\ +\ NaCl_{(aq)} \rightarrow\ NaNO_{3\ (aq)}\ +\ AgCl_{(s)}$$
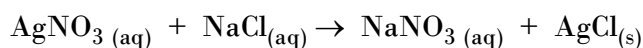
Some solubility rules are worth remembering because you'll use them repeatedly this year:

1) All ionic compounds containing alkali metal cations, NH_4^+, NO_3^-, and acetate are soluble.

2) Cl^-, Br^-, and I^- salts are soluble (except with Ag^+, Pb^{2+}, Hg_2^{2+}). [While many fluorides are soluble, there is much more variation with this anion.]

3) Most sulfate salts are soluble.

4) Except for (1) carbonate and phosphate salts are insoluble.

5) Except for (1) and Group IIA, sulfides and hydroxides are insoluble.

Table 4.1 (p. 183) gives more complete rules if you want to learn them (mine have a few simplifications). The rules in these notes will work for the rest of the year except for one lab next semester. Finally, most salts consisting of both a cation with a +2 or higher charge and an anion of -2 or more negative don't dissolve. Does this sound reasonable and can you explain this?

When a solid is added to solvent it begins to dissolve. The process of a solid entering the solution phase is called <u>dissolving</u>. The reverse process is called <u>crystallization</u>. Crystallization occurs when dissolved solute returns to the solid phase and can result from several conditions: *e.g.* solvent evaporation, cooling, addition of a miscible liquid in which the solute is insoluble.)

<u>Metathesis reactions</u> frequently produce a precipitate. Also called double displacement (or

exchange) reactions, they take the form:

$$AX + BY \rightarrow AY + BX$$
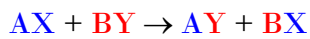
They usually involve the exchange of ions between ionic species, although such reactions can occur with weak electrolytes too. The acid/base reactions later in this section are metathesis reactions.

You might ask: "Why should such a reaction occur?" and "Will any two salts undergo a metathesis reaction?" We'll use the answer to the 2nd question to help us answer the first. No, any two salts will not necessarily undergo a metathesis reaction. For example, the reaction

$$AgNO_{3\ (aq)} + NaCl_{(aq)} \rightarrow NaNO_{3\ (aq)} + AgCl_{(s)}$$
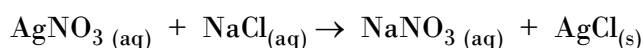
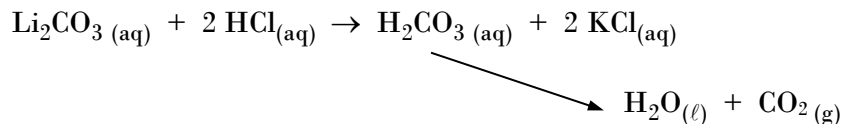goes to completion ($NaNO_3$ and $AgCl$ are the only materials left after mixing the $AgNO_3$ and $NaCl$). Now, consider what happens when you add iodized table salt to water:
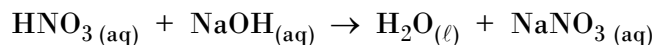
$$NaCl_{(aq)} + KI_{(aq)} \rightarrow NaI_{(aq)} + KCl_{(aq)}$$
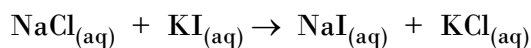
As you know, no precipitate forms. Do you see why no reaction occurs here? Since both materials dissolve in water, all four ions will be present in solution. When the water evaporates, a solid forms that regenerates the original mixture of salts since each of the cations binds roughly equally strongly to each of the anions. The first reaction is different because silver(I) chloride does not dissolve in water, so as silver(I) chloride forms it separates from solution. At the end of the reaction, the only ions left in solution are potassium and nitrate ions. Draining off the liquid and allowing it to evaporate yields potassium nitrate as the only compound in the solid, since only those ions remain in solution.

Metathesis reactions occur when one of the products holds together so strongly that it acts as a single unit. In the case of ionic precipitation reactions, the cations and anions attract each other so strongly that they do not strongly interact with water molecules and separate from solution. Metathesis reactions can also occur when molecules form since molecules tend to stay intact. The only condition on the molecule is that it not be a strong electrolyte, thus they can be liquids or

even weak electrolytes. The production of water in an acid/base reaction represents an example for this type of metathesis reaction. Examples of each case follow.

$$HNO_{3\,(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(\ell)} + NaNO_{3\,(aq)}$$

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

$$LiNH_{2\,(aq)} + HCl_{(aq)} \rightarrow NH_{3\,(aq)} + LiCl_{(aq)}$$

$$Li_2CO_{3\,(aq)} + 2\,HCl_{(aq)} \rightarrow H_2CO_{3\,(aq)} + 2\,KCl_{(aq)}$$
$$\searrow \quad H_2O_{(\ell)} + CO_{2\,(g)}$$
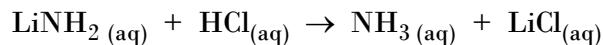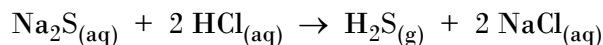
Acid-Base Reactions

We begin with definitions for acids and bases. As with much of chemistry, the reality is more complicated than what we begin with, but the following are good working definitions for acids and bases for the rest of CHM 211.

An <u>acid</u> is a substance that produces H^+ ions in aqueous solution, while a <u>base</u> produces OH^- ions in aqueous solution. As you will see in Chapter 15, this definition is incomplete and the reality is more subtle. If you've had AP chemistry, it's likely that you have already seen this.

Common acids that you encounter in everyday life include citric acid (citrus fruits) and phosphoric acid (soft drinks). Acids have a sour taste and dissolve many metals. Other examples include: HCl, $HClO_4$, and H_2SO_4. These 3 acids are strong electrolytes, while citric and phosphoric acids are weak electrolytes. For any acid containing more than one proton, at most one ionizes completely.

Examples of bases include NaOH, $Ba(OH)_2$, and NH_3. The first two are strong electrolytes; the last is a weak electrolyte. Almost all inorganic bases contain the OH^- group with ammonia being the most notable exception. Bases taste bitter and feel slippery.

In aqueous solution, acids and bases produce hydronium (H_3O^+) and hydroxide ions (OH^-),

respectively. Most commonly, chemists will refer to "protons" as the active acid species in water, but protons cannot exist freely. The concentrated positive charge of a proton draws nearby water molecules close to it.   Thus, the terms proton, hydrogen ion, and hydronium ion are used interchangeably and mean the same thing: the active acid species in aqueous solution.   For simplicity, when writing out reactions we use H^+ instead of H_3O^+ for simplicity, even though it is less accurate.

Acids and bases that ionize completely are called <u>strong (i.e. strong electrolytes)</u>. Acids and bases that ionize less than 100% are called <u>weak</u> (i.e. weak electrolytes). Memorize the common strong acids (Table 4.2, p. 187). Generally, all other acids you will encounter this year are weak.

When acids and bases react, the products are almost always an ionic compound (frequently called a <u>salt</u>) and water. This kind of acid-base reaction is called a <u>neutralization</u> reaction. (For those of you familiar with the pH scale, neutralization reactions do not always yield a neutral solution.)   Table salt (sodium chloride) results from the reaction of hydrochloric acid with sodium hydroxide:

$$HCl_{(aq)} \; + \; NaOH_{(aq)} \rightarrow NaCl_{(aq)} \; + \; H_2O_{(\ell)}$$
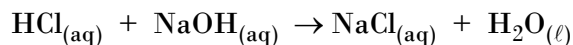
acid + base → salt + water

The reaction of sulfuric acid and potassium hydroxide yields potassium sulfate, K_2SO_4, as the salt. A salt contains the anion left over from the acid and the cation left over from the base and is <u>always</u> a strong electrolyte.

<u>Oxidation-Reduction Reactions</u>

Many reactions involve the transfer of electrons from one reactant to another. These reactions are called <u>oxidation-reduction</u> (<u>redox</u> for short) or <u>electron-transfer</u> reactions.   In nature, chlorophyll facilitates an electron transfer reaction that breaks up water into H^+ ions and oxygen

molecules. Corrosion (or rusting) represents a common type of redox reaction. Here, a metal (since in its elemental form it has a charge of zero) loses electrons and becomes part of an ionic compound (now with a positive charge). This is how acids dissolve metals. The "reduced iron" in breakfast cereal is nothing but finely powdered iron metal that reacts with your stomach acid to form the Fe(II) ions your body needs.

In Chapter 2, you learned about counting electrons on atoms and ions and assigning charges to atomic ions (e.g. Na^+ or Cl^-). We now discuss counting electrons in molecules and polyatomic ions. When hydrogen chloride dissolves in water, H^+ and Cl^- ions form. Not surprisingly, the electrons are already distributed in a favorable way for this to happen before the HCl enters the water. By this, we mean that although hydrogen chloride gas is a molecule, the electrons are distributed in a way that makes formation of the ions easier. Thus, the electrons holding the H-Cl together already spend more time near the chlorine atom than the hydrogen atom. Oxidation numbers or oxidation states provide a way to discuss this more simply. These are the charges that would be on atoms if all of the electron density in each bond were shifted on the atom that more strongly attracts electrons (i.e. more electronegative atom, see). For now, you can use the rule that an atom above or to the right of another atom has a greater tendency to pull electrons towards itself. Three rules allow you to assign oxidation numbers:

1) Atoms in elements possess oxidation numbers of zero. For example, the oxidation state on N in N_2 equals zero.

2) In binary compounds, shift charge as if the compound were ionic. For HCl, the oxidation number of H equals +1 and for Cl it is -1. For NH_3 the oxidation state of H is +1, so for nitrogen it is -3.

3) For compounds with 3 or more atoms, assign those with definite or highly probable values first, then do others as reasonable. On molecules, the sum of the oxidation numbers must
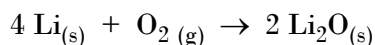
equal zero (since molecules carry no charge). On polyatomic ions, the sum of the oxidation numbers must equal the ionic charge.

e.g. HNO_3. H = +1 and O = -2. Calculate N: $0 = 1(+1) + x + 3(-2)$ x = +5 (the oxidation number on nitrogen).

When a species loses electrons, it is said to be <u>oxidized</u>, with the process called <u>oxidation</u>. When a species gains electrons, it is said to be <u>reduced</u>. The process is called <u>reduction</u>. [The term oxidation refers to the fact that reactions originally recognized to engage in this type of behavior involved reaction with oxygen (which takes electrons away from metals). Once these reactions were understood at the atomic level, the name was applied to all processes in which species lose electrons.] You might recall these definitions by remembering that reduction leads to a reduction in charge (a positive number becomes smaller or a negative number becomes more negative). There is also a mnemonic that might help: OIL RIG = <u>o</u>xidation <u>i</u>s <u>l</u>oss and <u>r</u>eduction <u>i</u>s <u>g</u>ain (of electrons).

In chemical reactions, oxidations and reductions always occur simultaneously. So if one species oxidizes, somewhere there must be a species being reduced. This is true because the electrons coming off species "A" go onto species "B." For example, when lithium metal reacts with atmospheric oxygen, two separate, simultaneous processes can be envisaged:

$4 \, Li_{(s)} \; + \; O_{2 \, (g)} \; \rightarrow \; 2 \, Li_2O_{(s)}$

$Li \; \rightarrow \; Li^+ \; + \; e^-$ oxidation

$O \; + \; 2e^- \; \rightarrow \; O^{2-}$ reduction

We will not cover balancing redox reactions in this course beyond what you have already seen. For example, the two reactions we did on p. 2 of these notes were both oxidation-reduction reactions, but some electron transfer reactions are very difficult to balance using ordinary means and there is a separate method for them that you'll learn in CHM 212.

4.3   Reaction Stoichiometry

As was mentioned on the first page of these notes, and bears repeating, a term you should know is stoichiometry, which refers to the quantity relationship between reacting chemical species. For example, when hydrogen and oxygen gases react to form water, two hydrogen molecules react with one oxygen molecule to form two water molecules: $2 H_2 + O_2 \rightarrow 2 H_2O$. The 2 to 1 to 2 relationship is the stoichiometry of the reaction. Stoichiometry also allows the number of atoms or molecules involved in a reaction to be related to the measured quantities: mass and volume (for gases or liquids) of the substances. Thus, 1 gram of hydrogen reacts with 8 grams of oxygen to yield 9 grams of water.

In the real world, when we want to know how much of a substance we have, we usually measure its mass or volume. We never count the number of molecules present. On the other hand, when we discuss a chemical reaction, we consider the reaction of individual particles. How do we reconcile these viewpoints?   In a balanced equation, the coefficients tell us the relative numbers of atoms or molecules reacting. Because the mole is a number term, the coefficients also tell us the relative number of moles of atoms/molecules involved in a reaction.   Finally, molecular weights allow us to relate numbers of species to their masses. This allows the amount of all substances produced or consumed in a reaction to be calculated from only one reaction species. Two frequently asked questions in a chemistry lab are: (1) if I have x grams of reactant **A**, what mass of reactant **B** will I need to react with it? and (2) if I have x grams of reactant **A**, what mass of product **C** will be generated by the reaction?

The general solution to these problems is:

1) Write out the balanced equation.

2) Convert all quantities to moles.

3) Using the balanced equation, determine the molar ratio of desired to known species.

4) Convert the molar amount of desired species into the appropriate units.

5) Check for reasonability. This is very important.

Example: Consider the reaction: $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$. What mass of O_2 is required to react completely with 9.34 g carbon disulfide?

$$\text{mass}_{O2} = (9.34\ \text{g}_{CS2})\left(\frac{1\ \text{mol}_{CS2}}{76.13\ \text{g}_{CS2}}\right)\left(\frac{3\ \text{mol}_{O2}}{1\ \text{mol}_{CS2}}\right)\left(\frac{32.00\ \text{g}_{O2}}{1\ \text{mol}_{O2}}\right) = 11.8\ \text{g}_{O2}$$

In a similar way, the masses of CO_2 and SO_2 produced can be calculated. (5.40 g_{CO2} and 15.7 g_{SO2})

This pattern of starting with what you measure, convert to counting, convert to counting something else, then convert back to something you can measure is typical of stoichiometry problems.


4.4 Reaction Yields

In practice, reactions are rarely conducted with exact stoichiometric amounts of each reagent for three reasons. First, if one of the reactants is a gas, it may be difficult to measure out that reactant. Second, one reactant is nearly always more expensive than the others. In this case, one wants to use up all of that reagent. Adding small excesses of the others usually accomplishes this. Finally, some reactions can proceed through multiple paths and using excess amounts of some reagents can maximize the yield of a desired product.

When some reagents are used in excess, the completely consumed reagent is called the limiting reagent (or less commonly: limiting reactant). When doing a limiting reagent calculation, first convert the masses of all reactants to moles, which then must be converted to a common scale using stoichiometric coefficients.

Example: Reaction of tungsten with chlorine gas yields tungsten(VI) chloride. Find the mass of unreacted starting material when 12.6 g of tungsten is treated with 13.6 g of chlorine gas. How much tungsten(VI) chloride is formed?

We begin by generating a balanced chemical equation.

$$W_{(s)} + 3\ Cl_{2\ (g)} \rightarrow WCl_{6\ (s)}$$
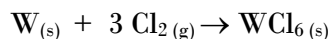
a) $mol_W = 12.6\ g_W \left(\dfrac{1\ mol_W}{183.9\ g_W} \right) = 0.0685\ mol_W$

$mol_{Cl2} = 13.6\ g_{Cl2} \left(\dfrac{1\ mol_{Cl2}}{70.90\ g_{Cl2}} \right) = 0.192\ mol_{Cl2}$

Now calculate how much chlorine is needed to completely react with tungsten

$(0.0685\ mol_W) \left(\dfrac{3\ mol_{Cl2}}{1\ mol_W} \right) = 0.206\ mol_{Cl2}$ but you only have 0.192 mol of chlorine, so it is the limiting reagent.

Calculate the mass of tungsten consumed:

$$mass_W = 13.6\ g_{Cl2} \left(\dfrac{1\ mol_{Cl2}}{70.90\ g_{Cl2}} \right) \left(\dfrac{1\ mol_W}{3\ mol_{Cl2}} \right) \left(\dfrac{183.9\ g_W}{mol_W} \right) = 11.8\ g_W$$

$$mass_{W(excess)} = 12.6\ g - 11.8\ g = 0.8\ g_W$$

b) $mass_{WCl6} = 13.6\ g_{Cl2} \left(\dfrac{1\ mol_{Cl2}}{70.90\ g_{Cl2}} \right) \left(\dfrac{1\ mol_{WCl6}}{3\ mol_{Cl2}} \right) \left(\dfrac{396.6\ g_{WCl6}}{mol_{WCl6}} \right) = 25.4\ g_{WCl6}$

Theoretical Yields

In real life, reactions rarely generate all of the product you would expect from the reaction stoichiometry because there are frequently side reactions that use some of the starting materials to make other products. Equilibria can also occur. Also, sometimes the products or reactants aren't extremely stable under the reaction conditions. The theoretical yield for a reaction is the amount of product expected based on stoichiometry. Part (b) of the previous example was a theoretical yield calculation.

The amount of product obtained is called the actual yield. The ratio of actual to theoretical yields is called the percent yield.

$$percent\ yield = \frac{actual\ yield}{theoretical\ yield} \times 100\%$$

Using the previous example, what would the percent yield be if 17.6 g of tungsten(VI) chloride actually formed?

$$\text{percent yield} = \left(\frac{17.6\ g}{25.4\ g}\right)(100\%) = 69.3\ \%$$

In this case, the side reactions might be production of WCl_2 or WCl_4 resulting from incomplete reaction of the starting materials.

4.5 Quantitative Chemical Analysis

Titrations are a primary method for determining the concentration of a solute in a solution by reacting the solute with a standard solution of known concentration. They are more easily understood by doing the experiment. You will cover titrations in CHM 217 and 218 and so we won't spend time on them here.

Read this section on your own.

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