Stoichiometry and Aqueous Reactions (Chapter 4)

Chemical Equations

1. Balancing Chemical Equations (from Chapter 3)

   Adjust coefficients to get equal numbers of each kind of element on both sides of arrow.

   Use smallest, whole number coefficients.

   e.g., start with unbalanced equation (for the *combustion* of butane):

$$C_4H_{10} \quad + \quad O_2 \longrightarrow CO_2 \quad + \quad H_2O$$

reactants ***products***

{ ***Hint*** -- first look for an element that appears only once on each side; e.g., C }

$$C_4H_{10} \quad + \quad 13/2\ O_2 \longrightarrow 4\ CO_2 \quad + \quad 5\ H_2O$$

multiply through by 2 to remove fractional coefficient:

$$\boxed{2\ C_4H_{10} \quad + \quad 13\ O_2 \longrightarrow 8\ CO_2 \quad + \quad 10\ H_2O}$$

2. Reaction Stoichiometry -- **Mole Method Calculations**

   Coefficients in balanced equation give the ratio by moles ! ! !

   e.g., in the above reaction:

   2 moles C_4H_{10} react with 13 moles O_2 to produce
   8 moles CO_2 and 10 moles H_2O

   Use these just like other conversion factors !

Problem:

How many moles of O_2 are required to react with 0.50 moles of C_4H_{10} according to the above equation?

$$0.50 \text{ mole } C_4H_{10} \quad \times \quad \frac{13 \text{ mole } O_2}{2 \text{ mole } C_4H_{10}} \quad = \quad 3.25 \text{ mole } O_2$$

Always convert given quantities (e.g., grams) to Moles ! ! !

grams A $\longrightarrow$ moles A $\longrightarrow$ moles B $\longrightarrow$ grams B

Problem:

What mass of CO_2 could be produced from the combustion of 100 grams of butane (C_4H_{10})?

will need formula masses to convert between grams and moles:

CO_2 = 44.01 g/mole $\qquad$ C_4H_{10} = 58.12 g/mole

Step 1: "grams A $\longrightarrow$ moles A"

$$100\text{ g } C_4H_{10} \times \frac{1\text{ mole } C_4H_{10}}{58.12\text{ g } C_4H_{10}} = 1.721\text{ mole } C_4H_{10}$$

Step 2: "moles A $\longrightarrow$ moles B"

$$1.721\text{ mole } C_4H_{10} \times \frac{8\text{ mole } CO_2}{2\text{ mole } C_4H_{10}} = 6.882\text{ mole } CO_2$$

Step 3: "moles B $\longrightarrow$ grams B"

$$6.882\text{ mole } CO_2 \times \frac{44.01\text{ g } CO_2}{1\text{ mole } CO_2} = 303\text{ g } CO_2$$

Alternatively, the 3 steps can be combined into one Factor-Label string:

$$100\text{ g } C_4H_{10} \times \frac{1\text{ mole } C_4H_{10}}{58.12\text{ g } C_4H_{10}} \times \frac{8\text{ mole } CO_2}{2\text{ mole } C_4H_{10}}$$

$$\times \frac{44.01\text{ g } CO_2}{1\text{ mole } CO_2} = 303\text{ g } CO_2$$

3. Limiting Reactant Calculations

In practice, reactants are often combined in a ratio that is different from that in the balanced chemical equation. One of the reactants will be completely consumed and some of the other will remain unreacted.

The *limiting reactant* is the one that is completely consumed. It determines the maximum amount (yield) of the products.

Whenever quantities of both reactants are given, the limiting reactant must be determined ! ! !

Problem:

In a commercial process, nitric oxide (NO) is produced as follows:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

What mass (in grams) of NO can be made from the reaction of 30.00 g NH_3 and 40.00 g O_2 ?

1st, find moles of reactants:

$$30.00\ g\ NH_3 \quad x \quad \frac{1\ mole\ NH_3}{17.03\ g\ NH_3} \quad = \quad 1.762\ mole\ NH_3$$

$$40.00\ g\ O_2 \quad x \quad \frac{1\ mole\ O_2}{32.00\ g\ O_2} \quad = \quad 1.250\ mole\ O_2$$

2nd, calculate amount of product based on each reactant, separately:

yield of NO based on NH_3:

$$1.762\ mole\ NH_3 \quad x \quad \frac{4\ mole\ NO}{4\ mole\ NH_3} \quad = \quad 1.762\ mole\ NO$$

yield of NO based on O_2:

$$1.250\ mole\ O_2 \quad x \quad \frac{4\ mole\ NO}{5\ mole\ O_2} \quad = \quad 1.000\ mole\ NO$$

Therefore, O_2 is the limiting reactant ! (excess of NH_3 exists)

3rd, calculate yield of product based on limiting reactant:

$$1.000\ mole\ NO \quad x \quad \frac{30.01\ g\ NO}{1\ mole\ NO} \quad = \quad \boxed{30.01\ g\ NO}$$

4. Theoretical and Percentage Yield

In actual experiments, the amount of a product that is *actually obtained* is always somewhat less than that *predicted* by the stoichiometry of the balanced chemical equations.

This is due to competing reactions and/or mechanical losses in isolation of the product.

actual yield -- amount of product obtained experimentally

theoretical yield -- amount of product predicted by balanced equation

percentage yield = (actual yield / theoretical yield) x 100%

Problem:

In the previous experiment for the production of NO from 30.00 g NH_3 and 40.00 g O_2, the chemist obtained 25.50 g NO. What is the percentage yield of this reaction?

theoretical yield = 30.01 g NO (based on limiting reactant as above)

actual yield = 25.50 g (given in problem)

% yield = (25.50 g NO / 30.01 g NO) x 100% = 85.0 %

{ **Note:** the % yield can never be more than 100 % }

Solution Concentrations and Solution Stoichiometry

1. Solution Terminology

solution - homogeneous (uniform) mixture, consisting of:
solvent - the bulk medium, e.g., H_2O
solute(s) - the dissolved substance(s), e.g., NaCl

concentration - measure of relative solute/solvent ratio

standard solution - accurately known concentration

saturated solution - contains maximum amount of solute

solubility - concentration of a saturated solution, e.g.:
solubility of NaCl is about 36 g NaCl / 100 g H_2O ("soluble")
solubility of CuS is about 10^{-5} g CuS / 100 g H_2O ("insoluble")

precipitate - an "insoluble" reaction product

e.g., a *precipitation reaction* where the precipitate is AgCl:

$$NaCl_{(aq)} + AgNO_{3\,(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3\,(aq)}$$

2. Molar Concentration

Molarity (M) = moles solute / liter of solution

units: moles/L or moles/1000 mL (**just a conversion factor!**)

e.g., a "0.10 M" NaCl solution contains 0.10 mole NaCl per liter of solution

Problem:

What mass of NaCl is required to prepare 300 mL of 0.10 M solution?

1st - **find moles** of NaCl required:

$$300 \text{ mL} \times \frac{0.100 \text{ moles NaCl}}{1000 \text{ mL}} = 0.0300 \text{ moles NaCl}$$

2nd - **convert to grams** of NaCl:

$$0.0300 \text{ moles NaCl} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mole NaCl}} = 1.75 \text{ g NaCl}$$

Prepare this solution by weighing 1.75 g NaCl, dissolving in some H_2O (about 250 mL), and then diluting to the 300 mL mark.

3. Dilution of Concentrated Solutions

concentrated solution + H_2O $\longrightarrow$ dilute solution

$$(\text{moles solute})_{conc} = (\text{moles solute})_{dil}$$

$$\mathbf{V_cM_c = V_dM_d}$$

Problem: A 5.00 M NaCl "stock" solution is available. How would prepare 300 mL of a 0.100 M NaCl "standard" solution?

$V_c \times (5.00\text{ M}) = (300\text{ mL}) \times (0.100\text{ M})$

$V_c = (300\text{ mL}) \times (0.100\text{ M}) / (5.00\text{ M}) = 6.00\text{ mL}$

Measure out 6.00 mL of the 5.00 M "stock" solution, then add H_2O to a total volume of 300 mL.

4. Stoichiometry Problems -- Reactions in Solution

Start with a <u>Balanced Equation</u> and Use the <u>Mole Method</u>

(Molarity is just a conversion factor!)

Problem: For the following reaction,

$$2\ AgNO_{3(aq)} + CaCl_{2(aq)} \longrightarrow 2\ AgCl_{(s)} + Ca(NO_3)_{2(aq)}$$

(a) What volume of 0.250 M $AgNO_3$ is required to react completely with 250 mL of 0.400 M $CaCl_2$?

(b) What mass of AgCl should be produced?

<u>Part (a)</u>: volume of $AgNO_3$?

1st, find moles of $CaCl_2$

$$(250\text{ mL}) \times \frac{0.400\text{ mole}}{1{,}000\text{ mL}} = 0.100\text{ mole } CaCl_2$$

2nd, find moles of $AgNO_3$

$$(0.100\text{ mole } CaCl_2) \times \frac{2\text{ mole } AgNO_3}{1\text{ mole } CaCl_2} = 0.200\text{ mole } AgNO_3$$

3rd, find volume of $AgNO_3$ solution

$$(0.200\text{ mole } AgNO_3) \times \frac{1{,}000\text{ mL } AgNO_3}{0.250\text{ mole } AgNO_3} = 800\text{ mL } AgNO_3$$

Part (b): mass of AgCl ?

$$(0.100 \text{ mole } CaCl_2) \times \frac{2 \text{ mole AgCl}}{1 \text{ mole } CaCl_2} = 0.200 \text{ mole AgCl}$$

$$(0.200 \text{ mole AgCl}) \times \frac{143 \text{ g AgCl}}{1 \text{ mole AgCl}} = 28.6 \text{ g}$$

WORK MORE PROBLEMS ! ! !

5. Titrations

Titration An unknown amount of one reactant is combined exactly with a precisely measured volume of a ***standard solution*** of the other.

End-point When exactly stoichiometric amounts of two reactants have been combined.

Indicator Substance added to aid in detection of the endpoint (usually via a color change)

Problem:

Vinegar is an aqueous solution of acetic acid, $HC_2H_3O_2$, which is often written as HAc for simplicity. A 12.5 mL sample of vinegar was titrated with a 0.504 M solution of NaOH. The titration required 15.40 mL of the base solution in order to reach the endpoint. What is the molar concentration of HAc in vinegar?

$$NaOH_{(aq)} + HAc_{(aq)} \longrightarrow NaAc_{(aq)} + H_2O$$

$$(15.4 \text{ mL NaOH}) \times \frac{0.504 \text{ mole NaOH}}{1{,}000 \text{ mL}} \times \frac{1 \text{ mole HAc}}{1 \text{ mole NaOH}}$$

$$= 0.007762 \text{ mole HAc}$$

$$M = \frac{0.007762 \text{ mole HAc}}{(12.5 \text{ ml})\ (1 \text{ L} / 1000 \text{ mL})} = 0.621 \text{ M}$$

Electrolytes

1. Dissociation Reactions of Salts (in aqueous solution)

Electrolytes are solutes that produce ions in solution via ***dissociation***
(these solutions can conduct electricity)

e.g., $NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

$(NH_4)_2SO_{4(s)} \longrightarrow 2\ NH_4^+{}_{(aq)} + SO_4^{2-}{}_{(aq)}$

these are "strong" electrolytes -- 100% ionized
some substances are "weak" electrolytes -- partially ionized (< 100%)
or, "non-electrolytes" -- not ionized at all

2. Acids and Bases as Electrolytes

Arrhenius acid-base concept

Acid = H^+ supplier e.g., HNO_3, HCl, H_2SO_4, etc.

$HNO_{3(aq)} \longrightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$

(see later section for "correct" reaction)

Base = OH^- supplier e.g., $NaOH$, $Mg(OH)_2$, etc.

$NaOH_{(s)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$

3. Acid-Base Neutralization Reactions

Acid + Base $\longrightarrow$ Salt + Water

e.g., $HNO_{3(aq)} + NaOH_{(aq)} \longrightarrow NaNO_{3(aq)} + H_2O$

$H_2SO_{4(aq)} + 2\ KOH_{(aq)} \longrightarrow K_2SO_{4(aq)} + 2\ H_2O$

4. Anhydrides (oxides) -- **Not in the Textbook!**

Acidic Anhydrides -- nonmetal oxides

hydrolyze to yield oxo acids!

e.g., $SO_3 + H_2O \longrightarrow H_2SO_4$

$N_2O_5 + H_2O \longrightarrow 2\ HNO_3$

Basic Anhydrides -- metal oxides

hydrolyze to yield metal hydroxides! (i.e., bases)

e.g., $MgO_{(s)} + H_2O \longrightarrow Mg(OH)_{2(aq)}$

$K_2O_{(s)} + H_2O \longrightarrow 2\ KOH_{(aq)}$

5. Ionization of Molecular Compounds

Some molecular compds produce ions in solution via reactions with H_2O

e.g., $HBr_{(g)} + H_2O \longrightarrow H_3O^+{}_{(aq)} + Br^-{}_{(aq)}$

$HNO_{3(aq)} + H_2O \longrightarrow H_3O^+{}_{(aq)} + NO_3^-{}_{(aq)}$

6. Strong and Weak Electrolytes

Strong Electrolytes (100% ionized)

Strong Bases: hydroxides of Group I or II metals
e.g., NaOH, $Ca(OH)_2$, etc.

Strong Acids: **[memorize]**

Strong Acids:	HCl	hydrochloric acid
[memorize]	HBr	hydrobromic acid
	HI	hydroiodic acid
	HNO_3	nitric acid
	H_2SO_4	sulfuric acid
	$HClO_4$	perchloric acid

Weak Electrolytes

- partially ionized via a "dynamic equilibrium"
- usually, the equilibrium state lies mainly on the reactant side

Weak Acids: e.g., HF, $HC_2H_3O_2$, HNO_2, etc.

$$HNO_{2(aq)} + H_2O \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Weak Bases: e.g., NH_3

$$NH_{3(aq)} + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Water itself is a weak electrolyte -- undergoes "autoionization"

$$2\ H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Ionic Reactions in Aqueous Solution

1. Equations for Ionic Reactions

Metathesis Reaction (also called "double displacement")

Ions from two different reactants simply trade partners, e.g.:

$$Na_2CO_{3(aq)} + Ba(NO_3)_{2(aq)} \longrightarrow BaCO_{3(s)} + 2\ NaNO_{3(aq)}$$

This was written as a ***molecular equation*** in which all reactants and products are shown as complete, neutral chemical formulas.

It could also have been written as a complete ***ionic equation*** in which all ***soluble*** ionic compounds are split up into their ions, e.g.:

$$2\ Na^+(aq) + CO_3^{2-}(aq) + Ba^{2+}(aq) + 2\ NO_3^-(aq)$$
$$\longrightarrow BaCO_{3(s)} + 2\ Na^+(aq) + 2\ NO_3^-(aq)$$

Here, the Na^+ and NO_3^- ions are called "***spectator ions***" because they appear unchanged on both sides of the equation.

The spectator ions do not participate in the chemically important part of the reaction -- the precipitation of $BaCO_3$

The essential chemical process can be written without the spectator ions in the

net ionic equation, e.g.:

$$Ba^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \longrightarrow BaCO_{3(s)}$$

The ***net ionic equation*** shows that, in general, a precipitate of $BaCO_3$ will form whenever the ions Ba^{2+} and CO_3^{2-} are combined in aqueous solution, regardless of their sources.

2. Summary of the three types of balanced chemical equations

Molecular Equation

- shows all compounds with complete, neutral molecular formulas
- useful in planning experiments and stoichiometry calculations

Ionic Equation (complete)

- all strong electrolytes are shown in their dissociated, ionic forms
- insoluble substances and weak electrolytes are shown in their molecular form
- "spectator ions" are included
- useful for showing all details of what is happening in the reaction

Net Ionic Equation

- "spectator ions" are omitted
- only the essential chemical process is shown, i.e., formation of a:
    - solid precipitate,
    - gaseous product, or
    - weak electrolyte (e.g., water)
- useful for generalizing the reaction -- same important product can often be formed from different sets of reactants

When will a precipitate form?

! ! ! KNOW THE SOLUBILITY RULES --- Table 4.1 ! ! !

Oxidation-Reduction (Redox) Reactions

1. General Redox Concepts

Redox reaction -- electron transfer process

e.g., $2\ Na + Cl_2 \longrightarrow 2\ NaCl$

Overall process involves ***two Half Reactions***:

oxidation -- loss of electron(s)

reduction -- gain of electron(s)

e.g., $Na \longrightarrow Na^+ + e^-$ (oxidation)

$Cl_2 + 2\ e^- \longrightarrow 2\ Cl^-$ (reduction)

related terms:

oxidizing agent = the substance that is reduced (Cl_2)

reducing agent = the substance that is oxidized (Na)

Oxidation and reduction always occur together so that there is no *net* loss or gain of electrons overall.

2. Oxidation Numbers (oxidation states)

Oxidation Number: a "charge" that is *assigned* to an atom
to aid in balancing redox reactions

Generally, oxidation number is the charge that would result if all of the bonding electrons around an atom were assigned to the more electronegative element(s).

<u>Rules</u> for assigning oxidation numbers **--** **see page 177**

Learn the rules and practice many examples !

Questions

(1) Assign all oxidation numbers in:

Ag_2S ClO_3^- ClO_4^- $Cr(NO_3)_3$ H_2O H_2O_2

(2) Which of the following is a redox reaction? Determine what is being oxidized and reduced. Identify the oxidizing and reducing agents.

$4\ Al + 3\ O_2 \longrightarrow 2\ Al_2O_3$

$CaO + CO_2 \longrightarrow CaCO_3$