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):

   \[ \text{C}_4\text{H}_{10} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

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

   \[ \text{C}_4\text{H}_{10} + \frac{13}{2} \text{O}_2 \rightarrow 4 \text{CO}_2 + 5 \text{H}_2\text{O} \]

   multiply through by 2 to remove fractional coefficient:

   \[
   \begin{align*}
   2 \text{C}_4\text{H}_{10} + 13 \text{O}_2 & \rightarrow 8 \text{CO}_2 + 10 \text{H}_2\text{O} \\
   \end{align*}
   \]

2. Reaction Stoichiometry -- Mole Method Calculations

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

   e.g., in the above reaction:

   2 moles \text{C}_4\text{H}_{10} react with 13 moles \text{O}_2 to produce
   8 moles \text{CO}_2 and 10 moles \text{H}_2\text{O}

   Use these just like other conversion factors !

   **Problem:**

   How many moles of \text{O}_2 are required to react with 0.50 moles of \text{C}_4\text{H}_{10} according to the above equation?

   \[
   0.50 \text{ mole C}_4\text{H}_{10} \times \frac{13 \text{ mole O}_2}{2 \text{ mole C}_4\text{H}_{10}} = 3.25 \text{ mole O}_2
   \]
Always convert given quantities (e.g., grams) to Moles !!!

grams A $\rightarrow$ moles A $\rightarrow$ moles B $\rightarrow$ grams B

Problem:
What mass of CO$_2$ could be produced from the combustion of 100 grams of butane (C$_4$H$_{10}$)?

will need formula masses to convert between grams and moles:

\[
\begin{align*}
CO_2 &= 44.01 \text{ g/mole} \\
C_4H_{10} &= 58.12 \text{ g/mole}
\end{align*}
\]

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

\[
100 \text{ g C}_4\text{H}_{10} \times \frac{1 \text{ mole C}_4\text{H}_{10}}{58.12 \text{ g C}_4\text{H}_{10}} = 1.721 \text{ mole C}_4\text{H}_{10}
\]

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

\[
1.721 \text{ mole C}_4\text{H}_{10} \times \frac{8 \text{ mole CO}_2}{2 \text{ mole C}_4\text{H}_{10}} = 6.882 \text{ mole CO}_2
\]

Step 3: "moles B $\rightarrow$ 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:

\[
100 \text{ g C}_4\text{H}_{10} \times \frac{1 \text{ mole C}_4\text{H}_{10}}{58.12 \text{ g C}_4\text{H}_{10}} \times \frac{8 \text{ mole CO}_2}{2 \text{ mole C}_4\text{H}_{10}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mole CO}_2} = 303 \text{ g CO}_2
\]
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:

\[
4 \text{ NH}_3 + 5 \text{ O}_2 \rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O}
\]

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:

\[
\frac{30.00 \text{ g NH}_3}{17.03 \text{ g NH}_3} \times 1 \text{ mole NH}_3 = 1.762 \text{ mole NH}_3
\]

\[
\frac{40.00 \text{ g O}_2}{32.00 \text{ g O}_2} \times 1 \text{ mole O}_2 = 1.250 \text{ mole O}_2
\]

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

yield of NO based on NH\(_3\):

\[
\frac{1.762 \text{ mole NH}_3}{4 \text{ mole NH}_3} \times 4 \text{ mole NO} = 1.762 \text{ mole NO}
\]

yield of NO based on O\(_2\):

\[
\frac{1.250 \text{ mole O}_2}{5 \text{ mole O}_2} \times 4 \text{ mole NO} = 1.000 \text{ mole NO}
\]

Therefore, O\(_2\) is the limiting reactant ! (excess of NH\(_3\) exists)

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

\[
\frac{1.000 \text{ mole NO}}{1 \text{ mole NO}} \times 30.01 \text{ g NO} = 30.01 \text{ g NO}
\]
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* = \((\text{actual yield} / \text{theoretical yield}) \times 100\%\)

**Problem:**

In the previous experiment for the production of NO from 30.00 g NH₃ and 40.00 g O₂, 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)

\[
\text{% yield} = \left(\frac{25.50 \text{ g NO}}{30.01 \text{ g NO}}\right) \times 100\% = 85.0\%
\]

{ **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., H₂O
  - **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 H₂O (“soluble”)
  - solubility of CuS is about 10⁻⁵ g CuS / 100 g H₂O (“insoluble”)

- **precipitate** - an "insoluble" reaction product
  - e.g., a **precipitation reaction** where the precipitate is AgCl:
    NaCl (aq) + AgNO₃ (aq) → AgCl (s) + NaNO₃ (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 H₂O (about 250 mL), and then diluting to the 300 mL mark.
3. Dilution of Concentrated Solutions

\[
\text{concentrated solution} + \text{H}_2\text{O} \rightarrow \text{dilute solution}
\]

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

\[
V_c M_c = V_d M_d
\]

**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\(_2\)O to a total volume of 300 mL.

4. Stoichiometry Problems -- Reactions in Solution

**Start with a Balanced Equation and Use the Mole Method**

(Molarity is just a conversion factor!)

**Problem:** For the following reaction,

\[
2 \text{AgNO}_3(\text{aq}) + \text{CaCl}_2(\text{aq}) \rightarrow 2 \text{AgCl(s)} + \text{Ca(NO}_3)_2(\text{aq})
\]

(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?

**Part (a):** 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, H\(_2\)C\(_2\)H\(_3\)O\(_2\), 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?

\[
\text{NaOH}_{(aq)} + \text{HAc}_{(aq)} \rightarrow \text{NaAc}_{(aq)} + \text{H}_2\text{O}
\]

\[
(15.4 \text{ mL NaOH}) \times \frac{0.504 \text{ mole NaOH}}{1,000 \text{ mL}} \times \frac{1 \text{ mole HAc}}{1 \text{ mole NaOH}} = 0.007762 \text{ mole HAc}
\]

\[
M = \frac{0.007762 \text{ mole HAc}}{(12.5 \text{ ml}) (1 \text{ L} / 1000 \text{ mL})} = 0.621 \text{ M}
\]
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., \( \text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) \)
\( (\text{NH}_4)_2\text{SO}_4(s) \rightarrow 2 \text{NH}_4^+(aq) + \text{SO}_4^{2-}(aq) \)

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 = \( \text{H}^+ \) supplier e.g., \( \text{HNO}_3, \text{HCl}, \text{H}_2\text{SO}_4, \) etc.

\( \text{HNO}_3(aq) \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq) \)
(see later section for "correct" reaction)

Base = \( \text{OH}^- \) supplier e.g., \( \text{NaOH}, \text{Mg(OH)}_2, \) etc.

\( \text{NaOH}(s) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq) \)

3. Acid-Base Neutralization Reactions

\( \text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water} \)
e.g., \( \text{HNO}_3(aq) + \text{NaOH}(aq) \rightarrow \text{NaNO}_3(aq) + \text{H}_2\text{O} \)
\( \text{H}_2\text{SO}_4(aq) + 2 \text{KOH}(aq) \rightarrow \text{K}_2\text{SO}_4(aq) + 2 \text{H}_2\text{O} \)
4. Anhydrides (oxides) -- **Not in the Textbook!**

**Acidic Anhydrides -- nonmetal oxides**
hydrolyze to yield oxo acids!

\[ \text{e.g., } \quad \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]
\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \]

**Basic Anhydrides -- metal oxides**
hydrolyze to yield metal hydroxides! (i.e., bases)

\[ \text{e.g., } \quad \text{MgO}_\text{(s)} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_\text{2(aq)} \]
\[ \text{K}_2\text{O}_\text{(s)} + \text{H}_2\text{O} \rightarrow 2 \text{KOH(aq)} \]

5. Ionization of Molecular Compounds

Some molecular compds produce ions in solution via reactions with \( \text{H}_2\text{O} \)

\[ \text{e.g., } \quad \text{HBr}_\text{(g)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Br}^-\text{(aq)} \]
\[ \text{HNO}_3\text{(aq)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \]

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]
HCl hydrochloric acid
HBr hydrobromic acid
HI hydroiodic acid
HNO$_3$ nitric acid
H$_2$SO$_4$ 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, HC₂H₃O₂, HNO₂, etc.

\[
\text{HNO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})
\]

Weak Bases: e.g., NH₃

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

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

\[
2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

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.:

\[
\text{Na}_2\text{CO}_3(\text{aq}) + \text{Ba(NO}_3)2(\text{aq}) \rightarrow \text{BaCO}_3(\text{s}) + 2\text{NaNO}_3(\text{aq})
\]

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.:

\[
2\text{Na}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) + \text{Ba}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq})
\rightarrow \text{BaCO}_3(\text{s}) + 2\text{Na}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq})
\]

Here, the Na⁺ and NO₃⁻ 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

\textit{net ionic equation}, e.g.:

\[
\text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{BaCO}_3(\text{s})
\]

The \textit{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

\textbf{Molecular Equation}
- shows all compounds with complete, neutral molecular formulas
- useful in planning experiments and stoichiometry calculations

\textbf{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

\textbf{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?

\textbf{!!! KNOW THE SOLUBILITY RULES --- Table 4.1 !!!}
**Oxidation-Reduction (Redox) Reactions**

1. General Redox Concepts

   **Redox reaction** -- electron transfer process
   
   e.g., \[ 2 \text{Na} + \text{Cl}_2 \rightarrow 2 \text{NaCl} \]
   
   Overall process involves **two Half Reactions**:
   
   - **oxidation** -- loss of electron(s)
   - **reduction** -- gain of electron(s)
   
   e.g., \[ \text{Na} \rightarrow \text{Na}^+ + e^- \] (oxidation)
   \[ \text{Cl}_2 + 2e^- \rightarrow 2 \text{Cl}^- \] (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).

   **Rules for assigning oxidation numbers** -- see page 177
   
   Learn the rules and practice many examples!

**Questions**

1. Assign all oxidation numbers in:
   
   \[ \text{Ag}_2\text{S} \quad \text{ClO}_3^- \quad \text{ClO}_4^- \quad \text{Cr(NO}_3)_3 \quad \text{H}_2\text{O} \quad \text{H}_2\text{O}_2 \]

2. Which of the following is a redox reaction? Determine what is being oxidized and reduced. Identify the oxidizing and reducing agents.
   
   \[ 4 \text{Al} + 3 \text{O}_2 \rightarrow 2 \text{Al}_2\text{O}_3 \]
   \[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \]