FUNDAMENTAL LAWS OF CHEMISTRY

Lavoisier’s Fundamental Laws of Chemistry
- Father of Modern Chemistry
- Late 18th century French aristocrat
- Guillotined during the French Revolution.

1. **Law of Mass Conservation**
   - In any chemical processes, matter cannot be created or destroyed.

2. **Law of Definite Composition**
   - A chemical compound always has the same mass composition regardless of its source.

Dalton’s Atomic Theory
- Early 19th century British scientist

1. All matter is made of indivisible atoms.

2. **Elements** are made of one type of atom.
   - All atoms have the same chemical and physical properties (mostly).

3. Compounds are made of atoms in fixed proportions.
   - Can’t use $\frac{1}{2}$ of an atom to make a compound.
   - Also stated as **Law of Multiple Proportions**.

4. Atoms change arrangement in a chemical reaction, not identity.

*Law of Multiple Proportions*

When two elements combine to form two or more compounds, the ratio formed from each compound’s mass ratio always yields a fraction.

- In other words, elements cannot combine together with random compositions. The number of atoms of each element in a compound must be a whole number.
Example: Consider two compounds of sulfur and oxygen.

Compound A has a mass composition of
49.9% oxygen and 50.1% sulfur.

Compound B has a mass composition of
59.9% oxygen and 40.1% sulfur.

The oxygen to sulfur ratio for compound A is
\[ \frac{49.9}{50.1} = 0.9960 \]

The oxygen to sulfur ratio for compound B is
\[ \frac{59.9}{40.1} = 1.494 \]

The law of multiple proportions says that a ratio of these ratios must yield a simple fraction.

\[ \frac{0.9960}{1.494} = 0.6667 = \frac{2}{3} \]

Compound A has two-thirds the oxygen that compound B has. Modern analysis yields that compound A = SO₂ and compound B = SO₃.
ATOMIC STRUCTURE HISTORY

1897 – J.J. Thomson
- Discovered “cathode rays”
- Cathode rays were soon interpreted as beams of electrons.
- Thomson measured how the electrons were deflected by a magnetic field and calculated the charge to mass ratio (e/m).
- Thomson used his findings to construct the “plum pudding” model of the atom.
- Won Nobel Prize in 1906

1909 – Robert Milliken
- Milliken found that tiny drops of oil charged with static electricity had only discrete values of charge based on their deflection by an electric field.
- Milliken measured the fundamental unit of charge to be $1.6 \times 10^{-19}$ Coulombs. (Based on Thomson’s experiments, he also measured the mass of the electron to be $9 \times 10^{-31}$ kilograms.
- Won Nobel Prize in 1923

1910 – Ernest Rutherford
- Aimed a beam of alpha particles (⁴He nuclei) at a thin gold sheet.
- Most particles went right through the sheet.
  - a little surprising!
- Some particles deflected backwards
  - very surprising!!!
    - Rutherford said, "It was almost as incredible as if you fired a 15 inch shell at a piece of tissue paper and it came back and hit you!"
- Results were interpreted as the atom having a very small, yet very heavy nucleus.
- Won Nobel Prize in 1908
ATOMIC STRUCTURE

Two components of an atom

**Nucleus** (pl. nuclei)
- composite particle
- size $\approx 10^{-15}$ m $= 10^{-5}$ Å
- positively charged
  - SI units multiples of $1.609 \times 10^{-19}$ C
  - atomic units $+1, +2, +3, \ldots, +116$
- mass varies from $1.7 \times 10^{-27}$ to $5 \times 10^{-25}$ kg
  - 1 amu to 293 amu
- contains almost all the mass of an atom
- occupies very small volume in the atom

**Electrons** $-e^-$
- fundamental particle of nature
- size unknown $r < 10^{-18}$ m
- negatively charged
  - SI units $-1.609 \times 10^{-19}$ C
  - atomic units $-1$
- mass
  - SI units $9.109 \times 10^{-31}$ kg
  - atomic units $5.486 \times 10^{-4}$ amu
- movement of electron occupies the size of the atom $\approx 1$ Å $= 10^{-10}$ m

**NUCLEAR STRUCTURE**

Two components of nucleus

**Proton** – $p^+$
- size $\approx 10^{-15}$ m $= 10^{-5}$ Å
- charge $+1$ (atomic units)
- mass $1.673 \times 10^{-27}$ kg $= 1.0073$ amu
- number of $p^+$ defines element

**Neutron** – $n^0$
- size $\approx 10^{-15}$ m $= 10^{-5}$ Å (same as proton)
- charge $0$ (atomic units)
- mass $1.675 \times 10^{-27}$ kg $= 1.0087$ amu
- number of $n^0$ defines isotope of element

ATOMIC STRUCTURE HISTORY continued

1932 – James Chadwick
- Showed that atoms have a third particle different than the electron and proton.
- Aimed a beam of alpha particles ($^4$He nuclei) at a sheet of beryllium to produce uncharged particles.
- Interacting these uncharged particles with other nuclei showed that they must have approximately the same mass as a proton.
- Won Nobel Prize in 1935

Definition: **1 Angstrom (Å) = 10^{-10} m**
ATOMIC SYMBOLS - $^A_Z$Sy

**Atomic Number** - $Z$
- number of protons in an atom
- subscript before elemental symbol

**Mass Number** – $A$
- number of protons and neutrons in an atom
- superscript before elemental symbol
- mass number approximates how heavy the atom is in atomic mass units

Examples

Oxygen – 16 has 8 $p^+$ and 8 $n^o$ ⇒

<table>
<thead>
<tr>
<th>element</th>
<th># of $p^+$</th>
<th># of $n^o$</th>
<th>mass #</th>
<th>symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen</td>
<td>8</td>
<td>9</td>
<td>17</td>
<td>$^{17}_{8}$O</td>
</tr>
<tr>
<td>oxygen</td>
<td>8</td>
<td>10</td>
<td>18</td>
<td>$^{18}_{8}$O</td>
</tr>
<tr>
<td>carbon</td>
<td>6</td>
<td>6</td>
<td>12</td>
<td>$^{12}_{6}$C</td>
</tr>
<tr>
<td>carbon</td>
<td>6</td>
<td>8</td>
<td>14</td>
<td>$^{14}_{6}$C</td>
</tr>
<tr>
<td>lead</td>
<td>82</td>
<td>126</td>
<td>208</td>
<td>$^{208}_{82}$Pb</td>
</tr>
</tbody>
</table>

Definition: **isotope** – an atom with the same atomic number as another atom but a different mass number.
- i.e., isotopes have the same number of protons but a different number of neutrons.
- isotopes have the same chemical properties.

Notes:
- oxygen – 16 and oxygen – 18 are **isotopes** of oxygen
- carbon – 12 and carbon – 14 are isotopes of carbon
- nuclide refers to specific nucleus, often used interchangeably with isotope

**DEFINITION OF ATOMIC MASS UNIT**

Mass of $^{12}$C is 12.000000 amu **BY DEFINITION**
1 amu = 1.66 x 10^{-27} kg
amu also abbreviated as u ⇒ 1 amu = 1 u

For atomic masses, amu is much more convenient unit than kilograms.

\[ m(^{1}H) = 1.6737 \times 10^{-27} \text{ kg} = 1.0079 \text{ amu} \]
\[ m(^{14}N) = 2.3253 \times 10^{-26} \text{ kg} = 14.004 \text{ amu} \]
\[ m(^{56}Fe) = 9.2882 \times 10^{-26} \text{ kg} = 55.935 \text{ amu} \]
MASS SPECTROMETRY
- Modern method for measuring masses of atoms (or molecules)
- Sample of atoms (or molecules) is vaporized and ionized by hitting it with an electron beam
- Ionized atoms travel into a region with a magnetic field
- The magnetic field causes the path of the gaseous ion to curve
- The amount of curvature for the path depends on the charge and the mass
- Since the charge is fairly easy to guess (usually either +1 or +2), the curvature of the path yields the mass of the atom.

- Mass spectroscopy yields information about isotopic abundances as well as precise masses.

- Rubidium has two naturally occurring isotopes ($^{85}$Rb, 72% and $^{87}$Rb, 28%).

- Tin has ten(!) naturally occurring isotopes (from $^{112}$Sn to $^{124}$Sn).
ATOMIC AND MOLECULAR MASSES

Average Atomic Mass (also Atomic Weight)
- If element has more than one naturally occurring isotope, atomic mass is an average of the mass of the isotopes.
- Average is performed accounting for the relative natural abundance of each isotope.

Example: Copper

<table>
<thead>
<tr>
<th>nuclide</th>
<th>abundance</th>
<th>mass(amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{63}\text{Cu}$</td>
<td>69.17%</td>
<td>62.940</td>
</tr>
<tr>
<td>$^{65}\text{Cu}$</td>
<td>30.83%</td>
<td>64.928</td>
</tr>
</tbody>
</table>

\[ m(\text{Cu}) = 0.6917 \times 62.940 \, \text{amu} + 0.3083 \times 64.928 \, \text{amu} = 63.55 \, \text{amu} \]

Example: Neon

<table>
<thead>
<tr>
<th>nuclide</th>
<th>abundance</th>
<th>mass(amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{20}\text{Ne}$</td>
<td>90.48%</td>
<td>19.992</td>
</tr>
<tr>
<td>$^{21}\text{Ne}$</td>
<td>0.27%</td>
<td>20.994</td>
</tr>
<tr>
<td>$^{22}\text{Ne}$</td>
<td>9.25%</td>
<td>21.991</td>
</tr>
</tbody>
</table>

\[ m(\text{Ne}) = 0.9048 \times 19.992 \, \text{amu} + 0.0027 \times 20.994 \, \text{amu} + 0.0925 \times 21.991 \, \text{amu} = 20.18 \, \text{amu} \]

PERIODIC TABLE OF GROUPS OF ELEMENTS
Two different classification schemes

Metal – Nonmetal Scheme (based on physical properties)

**Metals**
- characteristics of metals
  - **luster** (shine)
  - high electrical conductivity
  - high heat conductivity
- Ions are generally positively charged.
- Elements on left side of periodic table are metals.

**Nonmetals**
- characteristics of nonmetals
  - poor electrical conductivity (insulator)
  - poor heat conductivity (insulator)
- Ions are generally negatively charged.
- Elements in the upper right corner of table are nonmetals.

**Metalloids**
- in between metal and nonmetal
- B, Si, Ge, As, Sb, Te, At
Group Scheme (based on chemical properties)

**Alkali metals** – column 1A  (Ashes w/out air)
  Li, Na, K, Rb, Cs, Fr

**Alkaline earth metals** – column 2A
  Be, Mg, Ca, Sr, Ba, Ra

**Pnictogens** – column 5A  (Choke maker)
  N, P, As, Sb, Bi

**Chalcogens** – column 6A  (Ore maker)
  O, S, Se, Te, Po

**Halogens** – column 7A  (Salt maker)
  F, Cl, Br, I, At

**Noble gases** – column 8A
  He, Ne, Ar, Kr, Xe, Rn

**Transition metals** – four rows in middle of table
  Ex:  Sc to Zn,  Y to Cd,  La to Hg,  Ac to Mt(109)

**Rare earths** – bottom two rows beside table
  Ex:  Ce to Lu,  Th to Lr

Members of groups have similar chemical properties.

**CHEMICAL COMPOUNDS**

Chemical compounds consist of
  1.)  molecules
  2.)  ions

**Molecular Compounds**
  - tightly bound atoms in a single unit
  - atoms held together with **covalent** bonding
    - Electrons accumulate between nuclei and draw nuclei together.
  - **hydrocarbons** – compounds with only carbon and hydrogen.

**Molecular Elements**
  - gases:  H₂, N₂, O₂, F₂, Cl₂  (**diatomic**)
  - liquid:  Br₂
  - solids:  P₄, S₈, Se₈, I₂

**Molecular Formula**
  - indicates which elements are incorporated in molecule using elemental symbols
  - indicates number of atoms within a molecule using subscripts after elemental symbols
Examples:
- water
  \[ \text{H}_2\text{O} \]
- ammonia
  \[ \text{NH}_3 \]

EMPIRICAL FORMULA
- lowest integer ratios between atoms

Examples:
- hydrogen peroxide
  molecular formula: \( \text{H}_2\text{O}_2 \)
  empirical formula: \( \text{HO} \)
- octane
  molecular formula: \( \text{C}_8\text{H}_{18} \)
  empirical formula: \( \text{C}_4\text{H}_9 \)
- sodium nitrate
  molecular formula: \( \text{NaNO}_3 \)
  empirical formula: \( \text{NaNO}_3 \)
- glucose
  molecular formula: \( \text{C}_6\text{H}_{12}\text{O}_6 \)
  empirical formula: \( \text{CH}_2\text{O} \)

Ions and Ionic Compounds

Ions
- Neutral atoms have equal number of electrons and protons
- Anions gain \( e^- \) and become negatively charged
  \[ \text{Cl} + e^- \rightarrow \text{Cl}^- \]
- Cations lose \( e^- \) and become positively charged
  \[ \text{Na} - e^- \rightarrow \text{Na}^+ \]
  \[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \]
- Metals generally become cations and nonmetals may become anions

Molecules that gain or lose \( e^- \) are called polyatomic ions

\( \text{NO}_3^-, \text{CO}_3^{2-}, \text{NH}_4^+ \)

IMPORTANT: Polyatomic ions remain whole in ionic reactions, i.e. they do not break apart.
Predicting ionic charges
- charges of some ions can be predicted using periodic chart
- *most charges have to be memorized*

Alkali metals: Li, Na, K, Rb, Cs 1+
Alkaline earth metals: Be, Mg, Ca, Sr, Ba 2+
Chalcogens: O, S, Se, Te 2-
Halogens: F, Cl, Br, I 1-

- the tendency is for atoms to gain or lose e\(^{-}\) until the number of e\(^{-}\) is like a noble gas.

**Ionic Compounds**
Ions held together by ionic bonding.
- Opposite charges attract each other.

***All compounds are electrically neutral.***

Charges on an **ionic compound must balance** to be neutral.

Examples: KCl

\[
\text{K}^+ \quad \text{Cl}^- \quad \Rightarrow \quad \text{K}^+ \quad \text{Cl}^-
\]

Li\(_2\)S

\[
\text{Li}^+ \quad \text{Li}^- \quad \text{S}^{2-} \quad \Rightarrow \quad \text{Li}^+ \quad \text{S}^{2-} \quad \text{Li}^+
\]

MgBr\(_2\)

\[
\text{Mg}^{2+} \quad \text{Br}^- \quad \text{Br}^- \quad \Rightarrow \quad \text{Br}^- \quad \text{Mg}^{2+} \quad \text{Br}^-
\]

Fe\(_2\)O\(_3\)

\[
\text{Fe}^{3+} \quad \text{Fe}^{3+} \quad \text{O}^{2-} \quad \text{O}^{2-} \quad \text{O}^{2-} \quad \Rightarrow \quad \text{O}^{2-} \quad \text{Fe}^{3+} \quad \text{O}^{2-} \quad \text{Fe}^{3+} \quad \text{O}^{2-}
\]

Note: Ions do not form molecules, rather they form crystal lattices
NOMENCLATURE
Nomenclature of ions

Cations (positive)
- name of ion is same as metal
- with main group metals, Roman numerals are used to indicate the charge of the ion only if the metal can have more than one charge.
  Ex: $\text{Mg}^{2+}$ ⇒ magnesium
  $\text{Al}^{3+}$ ⇒ aluminum
  $\text{Sn}^{4+}$ ⇒ tin(IV)
  $\text{Tl}^+$ ⇒ thallium(I)
- with transition metals, the charge of cation is indicated with Roman numerals
  Ex: $\text{Fe}^{2+}$ ⇒ iron(II)
- many transition metals have only one common charge; thus, using the roman numeral is optional.
  - $\text{Sc}^{3+}$, $\text{Ni}^{2+}$, $\text{Zn}^{2+}$, $\text{Ag}^+$, $\text{Cd}^{2+}$, $\text{La}^{3+}$
- polyatomic cations are given –ium suffix
  Ex: $\text{NH}_4^+$ ⇒ ammonium

Anions (negative)
- monatomic anions have –ide suffix
  Ex: $\text{Cl}^-$ ⇒ chloride
  $\text{S}^{2-}$ ⇒ sulfide
  $\text{As}^{3-}$ ⇒ arsenide

*exceptions*
- $\text{OH}^-$ hydrogenide
- $\text{CN}^-$ cyanide
- $\text{O}_2^{2-}$ peroxide
Note: peroxides form usually with only alkali and alkaline earth metals.

- polyatomic ions with oxygen (oxyanions) have –ite or –ate suffix
  - ite is always one less oxygen than -ate
  Ex: $\text{SO}_4^{2-}$ sulfate
  $\text{SO}_3^{2-}$ sulfite
  Ex: $\text{ClO}_4^-$ perchlorate
  $\text{ClO}_3^-$ chlorate
  $\text{ClO}_2^-$ chlorite
  $\text{ClO}^-$ hypochlorite
NAMING IONIC COMPOUNDS

1. Write name of cation first (include Roman numeral, if necessary).
2. Write name of anion.

Binary Compounds

Example: NaI
Na$^+$ is metal ion and I$^-$ is nonmetal ion
NaI $\Rightarrow$ sodium iodide

Example: SrBr$_2$
Sr$^{2+}$ is metal ion and Br$^-$ is nonmetal ion
SrBr$_2$ $\Rightarrow$ strontium bromide

Example: FeCl$_3$
Fe$^{3+}$ is metal ion and Cl$^-$ is nonmetal ion
FeCl$_3$ $\Rightarrow$ iron(III) chloride

BaH$_2$ $\Rightarrow$
magnesium chloride $\Rightarrow$
lithium oxide $\Rightarrow$

Cation-Polyatomic Anion Compounds

NaNO$_3$ $\Rightarrow$ Na$^+$ and NO$_3^-$ $\Rightarrow$ sodium nitrate
Fe(C$_2$H$_3$O$_2$)$_2$ – iron(II) acetate

aluminum cyanide –
barium sulfite –
ammonium oxalate –
KMnO$_4$ $\Rightarrow$
CoS$_2$O$_3$ $\Rightarrow$
NAMING MOLECULAR COMPOUNDS

1. Write the name of the element that is farthest from upper right-hand corner first.
2. Indicate number of atoms with numerical prefix.
   1 – mono **
   2 – di
   3 – tri
   4 – tetra
   5 – penta
   6 – hexa
   7 – hepta
   8 – octa
   9 – nono
   10 – deca

**use of the mono prefix is not preferred, except for carbon monoxide.
3. Add name of second element with –ide suffix.
4. Indicate number of atoms with numerical prefix.
5. Note: No numerical prefixes with hydrogen.
6. Important exceptions to rules
   a) H₂O – water
   b) NH₃ – ammonia
   c) CH₄ – methane
      - Hydrocarbons and their derivatives have their own nomenclature system.

Examples
   N₂O ⇒
   P₂S₃ ⇒
   boron trifluoride
   carbon tetrachloride ⇒

A BRIEF INTRODUCTION TO ACIDS

- By definition, acids dissolve in water and increase H⁺ concentration.

Example: HCl (aq) → H⁺ (aq) + Cl⁻ (aq)
- note ions separate from each other

- Cation of an acid is always hydrogen, H⁺.
- Acids generally dissolve metals.
- Concentrated acids dissolve skin and flesh.
  - Stomach acid is a concentrated acid (hydrochloric acid).
- Acids taste sour.
  - Vinegar is a weak acid (acetic acid).
- Technically, if a substance is not dissolved in water, it is not an acid. (This can be a source of confusion sometimes.)
NOMENCLATURE OF ACIDS

Binary acids H\text{\_}X
1. Write the prefix hydro-
2. Write the name of nonmetal anion with –ic suffix
3. Add the word acid

Examples

\begin{align*}
\text{HBr} & \Rightarrow \\
\text{HF} & \Rightarrow \\
\text{hydroiodic acid} & \Rightarrow \\
\text{hydrotelluric acid} & \Rightarrow \\
\end{align*}

Note: prefix hydro- implies a binary acid.
Exception: hydrocyanic acid \Rightarrow HCN

Oxyacids
1. Write the name of the anion
2. Change suffix
   a) change – ate to –ic
   b) change – ite to –ous
3. Add word acid

Examples:

\begin{align*}
\text{HClO}_2 & \Rightarrow \text{Chlorite anion} \Rightarrow \text{Chlorous acid} \\
\text{H}_2\text{C}_2\text{O}_4 & \Rightarrow \text{Oxalate anion} \Rightarrow \text{Oxalic acid} \\
\text{Sulfurous acid} & \Rightarrow \text{sulfite anion} \Rightarrow \text{H}_2\text{SO}_3 \\
& \quad \text{- note 2 H\textsuperscript{+} since SO}_3^2\textsuperscript{-} \text{ has 2- charge} \\
\text{Nitric acid} & \Rightarrow \text{nitrate anion} \Rightarrow \\
\text{Phosphoric acid} & \Rightarrow \text{phosphate anion} \Rightarrow \\
\text{HBrO}_3 & \Rightarrow \\
\text{HNO}_2 & \Rightarrow \\
\end{align*}

NOMENCLATURE OF HYDRATES
1. Name compound with previously stated rules.
2. At the end, add the word hydrate with the appropriate numerical prefix.

\begin{align*}
\text{FeCl}_3\bullet6\text{H}_2\text{O} & \Rightarrow \\
\text{calcium sulfate dihydrate} & \Rightarrow \\
\end{align*}