3.2 Determination of Chemical Formulas

• **Molecular formulas** – numbers of atoms of each element in a molecule

• **Empirical formulas** – relative numbers of atoms of each element using the smallest whole numbers

**Example:**
- acetic acid → C₂H₄O₂ (MF) → CH₂O (EF)
- formaldehyde → CH₂O (MF) → CH₂O (EF)
- glucose → C₆H₁₂O₆ (MF) → CH₂O (EF)

**Determining Empirical Formulas**

• **Elemental analysis** – gives the masses of the elements in a given mass of the compound or the Mass% composition

• EF from Mass% data
  1. Consider 100 g of the compound
  2. The masses of the elements equal their mass%
  3. Convert the masses of the elements to moles
  4. Determine the relative number of moles (mol ratio)
  5. Simplify the mole ratio to whole numbers

• EF from mass data
  – Omit steps 1 and 2 above

**Example:**
- Determine the EF of nicotine, if the mass% of C, H and N in it are 74.0, 8.7 and 17.3 %, respectively.
  1. Consider 100 g nicotine
  2. 74.0 g C, 8.7 g H, 17.3 g N
  3. Convert masses to moles:
     - 74.0 g C × (1 mol C/12.01 g C) = 6.16 mol C
     - 8.7 g H × (1 mol H/1.008 g H) = 8.6 mol H
     - 17.3 g N × (1 mol N/14.01 g N) = 1.23 mol N
  4. Mol ratio: 6.16 mol C : 8.6 mol H : 1.23 mol N
  5. Simplify the mole ratio:
     (divide by the smallest number, and if necessary, multiply by a factor to get whole numbers)
     - 6.16/1.23 = 5.01 ≈ 5
     - 8.6/1.23 = 7.0 ≈ 7
     - 1.23/1.23 = 1.00 ≈ 1
     → simplest whole-number ratio:
     - 5 mol C : 7 mol H : 1 mol N
     → EF: C₅H₇N
Determining Molecular Formulas

- The MF is a whole-number multiple of the EF
  \[ M = M_{EF} \times n \]
  - \( M \) \( \rightarrow \) molar mass
  - \( M_{EF} \) \( \rightarrow \) EF mass
  - \( n \) \( \rightarrow \) whole number (number of EFs per molecule)
  \[ \Rightarrow n = \frac{M}{M_{EF}} \]
  - Determining MFs from EFs and molar masses

Example:
- The empirical formula of nicotine is \( \text{C}_5\text{H}_7\text{N} \) and its molar mass is 162.23 g/mol. MF = ?
  \[ M_{EF} \rightarrow 5 \times 12.01 + 7 \times 1.008 + 1 \times 14.01 = 81.12 \text{ g/mol} \]
  \[ n = \frac{M}{M_{EF}} = \frac{162.23 \text{ g/mol}}{81.12 \text{ g/mol}} = 2.000 \approx 2 \]
  \[ \Rightarrow \text{MF} = 2 \times \text{EF} \]
  \[ \text{MF} \rightarrow \text{C}_{10}\text{H}_{14}\text{N}_2 \]

Combustion Analysis

- A method for elemental analysis of combustible organic compounds through their combustion in excess \( \text{O}_2 \)
  - The C in the sample is converted to \( \text{CO}_2 \) which is absorbed in a NaOH absorber and weighed
  - The H in the sample is converted to \( \text{H}_2\text{O} \) which is absorbed in a \( \text{P}_4\text{O}_{10} \) absorber and weighed
  - If a third element (O, N, …), it passes through the absorbers
  1 mol C from the sample \( \rightarrow \) 1 mol \( \text{CO}_2 \)
  2 mol H from the sample \( \rightarrow \) 1 mol \( \text{H}_2\text{O} \)

Example:
When 0.236 g aspirin is burned in excess \( \text{O}_2 \), 0.519 g \( \text{CO}_2 \) and 0.0945 g \( \text{H}_2\text{O} \) are formed.
Determine the mass % of C, H and O in aspirin.

\[ \text{Calculate the masses of C and H in the sample based on the masses of } \text{CO}_2 \text{ and } \text{H}_2\text{O}: \]
\[ \text{Calculate the mass of O by subtracting the masses of C and H from the total mass of the sample} \]
0.519 g CO₂ × \left( \frac{1 \text{ mol CO}_2}{44.01 \text{ g CO}_2} \right) × \left( \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right) × \left( \frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 0.142 \text{ g C} \\
0.0945 \text{ g H}_2\text{O} × \left( \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right) × \left( \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \right) × \left( \frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) = 0.0106 \text{ g H} \\
0.236 - 0.142 - 0.0106 = 0.084 \text{ g O} \\

% C = \left( \frac{0.142 \text{ g C}}{0.236 \text{ g sample}} \right) × 100\% = 60.0\% \\
% H = \left( \frac{0.0106 \text{ g H}}{0.236 \text{ g sample}} \right) × 100\% = 4.48\% \\
% O = \left( \frac{0.084 \text{ g O}}{0.236 \text{ g sample}} \right) × 100\% = 35.5\% \\
The empirical formula can be determined from the percentage composition in a subsequent step.

### 3.3 Chemical Equations

- Represent chemical reactions
  
  **Reactants → Products**

- Skeletal equations – show identities of reactants and products
  
  \( \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} \)

- Law of conservation of mass
  
  - Atoms are neither created nor destroyed (they only change bonding partners)
  
  - Same atoms are present in the reactants as in the products

- Balanced chemical equations
  
  - same number of atoms of each element appear on each side of the equation
  
  - stoichiometric coefficients – needed to balance the equations
  
  \( 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \)

  - Microscopic view
    
    \((2 \text{ molec. H}_2 + 1 \text{ molec. O}_2 \rightarrow 2 \text{ molec. H}_2\text{O})\)

  - Macroscopic view
    
    \((2 \text{ mol H}_2 + 1 \text{ mol O}_2 \rightarrow 2 \text{ mol H}_2\text{O})\)

    \((4.032 \text{ g H}_2 + 32.00 \text{ g O}_2 \rightarrow 36.032 \text{ g H}_2\text{O})\)
The stoichiometric coefficients can be treated as relative number of moles of reactants and products.

Physical state symbols:
- (s) solid; (l) liquid; (g) gas; (aq) aqueous solution

\[2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)\]

**Balancing Chemical Equations**

- Balancing by inspection (only simple cases)
  - Change stoichiometric coefficients only
  - Never change subscripts in formulas
  - Never add other substances to the equation

**Systematic method**

1. Write the skeletal equation
2. Balance one element at a time using coefficients
   - Start with the elements in the most complex substance and finish with those in the least complex one
   - Alternatively, start with the element present in the fewest number of formulas and finish with the element present in the greatest number of formulas
3. If necessary multiply the whole equation by a factor to clear the fractional coefficients
4. Verify that the equation is balanced and the coefficients are the smallest whole numbers
5. Specify physical states

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**Example:** Write the balanced equation for the combustion of ethane, \(C_2H_6\), to carbon dioxide and liquid water.

\[ \begin{align*}
C_2H_6 + O_2 & \rightarrow CO_2 + H_2O \\
\text{Skeletal} \\
C_2H_6 + O_2 & \rightarrow 2CO_2 + H_2O \\
\text{For C} \\
C_2H_6 + O_2 & \rightarrow 2CO_2 + 3H_2O \\
\text{For H} \\
C_2H_6 + (7/2)O_2 & \rightarrow 2CO_2 + 3H_2O \\
\text{For O} \\
\text{Multiply eq. by 2} \\
2C_2H_6 + 7O_2 & \rightarrow 4CO_2 + 6H_2O \\
2C_2H_6(g) + 7O_2(g) & \rightarrow 4CO_2(g) + 6H_2O(l)
\end{align*} \]

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Often polyatomic ions can be treated as single entities.

**Example:** Balance the following skeletal eq. in aqueous solution:

\[\text{Co(NO}_3)_3 + (\text{NH}_4)_2S \rightarrow \text{Co}_2\text{S}_3 + \text{NH}_4\text{NO}_3\]  
\[\text{Balance Co and S:} \]  
\[2\text{Co(NO}_3)_3 + 3(\text{NH}_4)_2S \rightarrow \text{Co}_2\text{S}_3 + \text{NH}_4\text{NO}_3\]  
\[\text{Balance NH}_4 \text{ and NO}_3:\]  
\[2\text{Co(NO}_3)_3 + 3(\text{NH}_4)_2S \rightarrow \text{Co}_2\text{S}_3 + 6\text{NH}_4\text{NO}_3\]  
\[\text{Add physical state symbols:} \]  
\[2\text{Co(NO}_3)_3(aq) + 3(\text{NH}_4)_2S(aq) \rightarrow \text{Co}_2\text{S}_3(s) + 6\text{NH}_4\text{NO}_3(aq)\]