Chapter 1: Stoichiometry of Formulas and Equations

The Mole

Determining the Formula of an Unknown Compound

Writing and Balancing Chemical Equations

Calculating Quantities of Reactant and Product

Fundamentals of Solution Stoichiometry

The Role of Water as a Solvent

Writing Equations for Aqueous Ionic Reactions
The Mole

The mole (mol) is the amount of a substance that contains the same number of entities as there are atoms in exactly 12 g of carbon-12.

The term “entities” refers to atoms, ions, molecules, formula units, or electrons – in fact, any type of particle.

One mole (1 mol) contains $6.022 \times 10^{23}$ entities (to four significant figures).

This number is called Avogadro’s number and is abbreviated as $N$. 
For **molecular elements** and for **compounds**, the formula is needed to determine the molar mass.

The molar mass of O$_2$ = $2 \times M_{\text{of O}}$

= $2 \times 16.00$

= 32.00 g/mol

The molar mass of SO$_2$ = $1 \times M_{\text{of S}} + 2 \times M_{\text{of O}}$

= 32.07 + 2(16.00)

= 64.07 g/mol
Converting Between Amount, Mass, and Number of Chemical Entities

\[
\text{Mass (g)} = \text{amount (mol)} \times \text{molar mass (g/mol)}
\]

\[
\frac{\text{Amount (mol)}}{1 \text{ mol}} = \frac{\text{mass (g)}}{\text{Molar mass (g)}}
\]

\[
\text{No. of entities} = \frac{\text{Amount (mol)}}{1 \text{ mol}} \times \frac{6.022 \times 10^{23} \text{ entities}}{1 \text{ mol}}
\]

\[
\frac{\text{Amount (mol)}}{6.022 \times 10^{23} \text{ entities}} = \frac{\text{no. of entities}}{1 \text{ mol}}
\]
Mass-mole-number relationships for elements.
PROBLEM: Gallium (Ga) is a key element in solar panels, calculators and other light-sensitive electronic devices. How many Ga atoms are in $2.85 \times 10^{-3}$ mol of gallium?

PLAN: To convert mol of Ga to number of Ga atoms we need to use Avogadro’s number.

\[
\text{mol of Ga} \rightarrow \text{multiply by } 6.022 \times 10^{23} \text{ atoms/mol} \rightarrow \text{atoms of Ga}
\]
Sample Problem 3.2

SOLUTION:

\[ \frac{2.85 \times 10^{-3} \text{ mol Ga}}{} \times \frac{6.022 \times 10^{23} \text{ Ga atoms}}{1 \text{ mol Ga}} = 1.72 \times 10^{21} \text{ Ga atoms} \]
Calculating the Number of Entities in a Given Mass of an Element

PROBLEM: Iron (Fe) is the main component of steel and is therefore the most important metal in society; it is also essential in the body. How many Fe atoms are in 95.8 g of Fe?

PLAN: The number of atoms cannot be calculated directly from the mass. We must first determine the number of moles of Fe atoms in the sample and then use Avogadro’s number.

\[
\text{mass (g) of Fe} \div \text{M of Fe (55.85 g/mol)} \times 6.022 \times 10^{23} \, \text{atoms/mol} = \text{atoms of Fe}
\]
SOLUTION:

\[
95.8 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 1.72 \text{ mol Fe}
\]

\[
1.72 \text{ mol Fe} \times \frac{6.022 \times 10^{23} \text{ atoms Fe}}{1 \text{ mol Fe}} = 1.04 \times 10^{24} \text{ atoms Fe}
\]
Amount-mass-number relationships for compounds.
Calculating the Number of Chemical Entities in a Given Mass of a Compound I

**PROBLEM:** Nitrogen dioxide is a component of urban smog that forms from the gases in car exhausts. How many molecules are in 8.92 g of nitrogen dioxide?

**PLAN:** Write the formula for the compound and calculate its molar mass. Use the given mass to calculate first the number of moles and then the number of molecules.

\[
\text{mass (g) of NO}_2 \quad \text{divide by } M \quad \text{amount (mol) of NO}_2 \quad \text{multiply by } N_A \quad \text{number of NO}_2 \text{ molecules}
\]
SOLUTION: NO₂ is the formula for nitrogen dioxide.

\[ M = (1 \times M \text{ of N}) + (2 \times M \text{ of O}) \]
\[ = 14.01 \text{ g/mol} + 2(16.00 \text{ g/mol}) \]
\[ = 46.01 \text{ g/mol} \]

\[ \frac{8.92 \text{ g NO}_2}{46.01 \text{ g NO}_2} = 0.194 \text{ mol NO}_2 \]

\[ \frac{0.194 \text{ mol NO}_2}{1 \text{ mol NO}_2} \times 6.022 \times 10^{23} \text{ molecules NO}_2 = 1.17 \times 10^{23} \text{ molecules NO}_2 \]
Calculating the Number of Chemical Entities in a Given Mass of a Compound II

PROBLEM: Ammonium carbonate, a white solid that decomposes on warming, is a component of baking powder, fire extinguishers and smelling salts.

a) How many formula units are in 41.6 g of ammonium carbonate?

b) How many O atoms are in this sample?

PLAN:
Write the formula for the compound and calculate its molar mass. Use the given mass to calculate first the number of moles and then the number of formula units.

The number of O atoms can be determined using the formula and the number of formula units.
(NH₄)₂CO₃ is the formula for ammonium carbonate.

\[ M = (2 \times M_{\text{of N}}) + (8 \times M_{\text{of H}}) + (1 \times M_{\text{of C}}) + (3 \times M_{\text{of O}}) \]
\[ = (2 \times 14.01 \text{ g/mol}) + (8 \times 1.008 \text{ g/mol}) \]
\[ + (12.01 \text{ g/mol}) + (3 \times 16.00 \text{ g/mol}) \]
\[ = 96.09 \text{ g/mol} \]
41.6 g \(\text{(NH}_4\text{)}_2\text{CO}_3\) x \[\frac{1 \text{ mol (NH}_4\text{)}_2\text{CO}_3}{96.09 \text{ g (NH}_4\text{)}_2\text{CO}_3}\] = 0.433 mol \(\text{(NH}_4\text{)}_2\text{CO}_3\)

0.433 mol \(\text{(NH}_4\text{)}_2\text{CO}_3\) x \[\frac{6.022 \times 10^{23} \text{ formula units (NH}_4\text{)}_2\text{CO}_3}{1 \text{ mol (NH}_4\text{)}_2\text{CO}_3}\] = 2.61 \times 10^{23} \text{ formula units (NH}_4\text{)}_2\text{CO}_3

2.61 \times 10^{23} \text{ formula units (NH}_4\text{)}_2\text{CO}_3 x \[\frac{3 \text{ O atoms}}{1 \text{ formula unit of (NH}_4\text{)}_2\text{CO}_3}\] = 7.83 x 10^{23} \text{ O atoms}
Mass Percent from the Chemical Formula

Mass % of element X =

\[
\frac{\text{atoms of X in formula} \times \text{atomic mass of X (amu)}}{\text{molecular (or formula) mass of compound (amu)}} \times 100
\]

Mass % of element X =

\[
\frac{\text{moles of X in formula} \times \text{molar mass of X (g/mol)}}{\text{mass (g) of 1 mol of compound}} \times 100
\]
Calculating the Mass Percent of Each Element in a Compound from the Formula

**PROBLEM:** In mammals, lactose (milk sugar) is metabolized to glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), the key nutrient for generating chemical potential energy. What is the mass percent of each element in glucose?

**PLAN:** Find the molar mass of glucose, which is the mass of 1 mole of glucose. Find the mass of each element in 1 mole of glucose, using the molecular formula.

The mass % for each element is calculated by dividing the mass of that element in 1 mole of glucose by the total mass of 1 mole of glucose, multiplied by 100.
PLAN:

- **amount (mol) of element X in 1 mol glucose**
  - multiply by $M$ (g/mol) of X
  - **mass (g) of X in 1 mol of glucose**
  - divide by mass (g) of 1 mol of glucose
  - **mass fraction of X in glucose**
  - multiply by 100
  - **mass % of X in glucose**
**SOLUTION:**

In 1 mole of glucose there are 6 moles of C, 12 moles H, and 6 moles O.

\[
\begin{align*}
6 \text{ mol C} \times \frac{12.01 \text{ g C}}{1 \text{ mol C}} &= 72.06 \text{ g C} \\
12 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} &= 12.096 \text{ g H}
\end{align*}
\]

\[
\begin{align*}
6 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} &= 96.00 \text{ g O} \\
M &= 180.16 \text{ g/mol}
\end{align*}
\]

Mass percent of C = \( \frac{72.06 \text{ g C}}{180.16 \text{ g glucose}} = 0.4000 \times 100 = 40.00 \text{ mass \% C} \)

Mass percent of H = \( \frac{12.096 \text{ g H}}{180.16 \text{ g glucose}} = 0.06714 \times 100 = 6.714 \text{ mass \% H} \)
Mass Percent and the Mass of an Element

Mass percent can also be used to calculate the mass of a particular element in any mass of a compound.

\[
\text{Mass of element} = \frac{\text{mass of element in 1 mol of compound}}{\text{mass of compound}} \times \frac{\text{mass of compound}}{\text{mass of 1 mol of compound}}
\]
Calculating the Mass of an Element in a Compound

**PROBLEM:** Use the information from Sample Problem before to determine the mass (g) of carbon in 16.55 g of glucose.

**PLAN:** The mass percent of carbon in glucose gives us the relative mass of carbon in 1 mole of glucose. We can use this information to find the mass of carbon in any sample of glucose.

\[
\text{mass of glucose sample} \quad \text{multiply by mass percent of C in glucose} \quad \text{mass of C in sample}
\]
SOLUTION:

Each mol of glucose contains 6 mol of C, or 72.06 g of C.

Mass (g) of C = mass (g) of glucose \times \frac{6 \text{ mol} \times M \text{ of } C \text{ (g/mol)}}{\text{mass (g) of 1 mol of glucose}}

= 16.55 \text{ g glucose} \times \frac{72.06 \text{ g C}}{180.16 \text{ g glucose}} = 6.620 \text{ g C}
Empirical and Molecular Formulas

The empirical formula is the simplest formula for a compound that agrees with the elemental analysis. It shows the lowest whole number of moles and gives the relative number of atoms of each element present.

The empirical formula for hydrogen peroxide is HO.

The molecular formula shows the actual number of atoms of each element in a molecule of the compound.

The molecular formula for hydrogen peroxide is $\text{H}_2\text{O}_2$. 
Determining an Empirical Formula from Amounts of Elements

PROBLEM: A sample of an unknown compound contains 0.21 mol of zinc, 0.14 mol of phosphorus, and 0.56 mol of oxygen. What is its empirical formula?

PLAN: Find the relative number of moles of each element. Divide by the lowest mol amount to find the relative mol ratios (empirical formula).

\[
\text{amount (mol) of each element} \rightarrow \text{use # of moles as subscripts} \rightarrow \text{preliminary formula} \rightarrow \text{change to integer subscripts} \rightarrow \text{empirical formula}
\]
SOLUTION: Using the numbers of moles of each element given, we write the preliminary formula $\text{Zn}_{0.21}\text{P}_{0.14}\text{O}_{0.56}$

Next we divide each fraction by the smallest one; in this case 0.14:

$$\frac{0.21}{0.14} = 1.5 \quad \frac{0.14}{0.14} = 1.0 \quad \frac{0.56}{0.14} = 4.0$$

This gives $\text{Zn}_{1.5}\text{P}_{1.0}\text{O}_{4.0}$

We convert to whole numbers by multiplying by the smallest integer that gives whole numbers; in this case 2:

$$1.5 \times 2 = 3 \quad 1.0 \times 2 = 2 \quad 4.0 \times 2 = 8$$

This gives us the empirical formula $\text{Zn}_3\text{P}_2\text{O}_8$
Determining an Empirical Formula from Masses of Elements

**PROBLEM:** Analysis of a sample of an ionic compound yields 2.82 g of Na, 4.35 g of Cl, and 7.83 g of O. What is the empirical formula and the name of the compound?

**PLAN:** Find the relative number of moles of each element. Divide by the lowest mol amount to find the relative mol ratios (empirical formula).

- **mass (g) of each element**
- divide by $M(g/mol)$
- **amount (mol) of each element**
- use # of moles as subscripts
- **preliminary formula**
- change to integer subscripts
- **empirical formula**
SOLUTION: 

\[
\begin{align*}
2.82 \text{ g Na} & \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 0.123 \text{ mol Na} \\
4.35 \text{ g Cl} & \times \frac{1 \text{ mol Cl}}{35.45 \text{ g Cl}} = 0.123 \text{ mol Cl} \\
7.83 \text{ g O} & \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.489 \text{ mol O}
\end{align*}
\]

Na and Cl = \( \frac{0.123}{0.123} = 1 \) and O = \( \frac{0.489}{0.123} = 3.98 \)

The empirical formula is \( \text{Na}_1\text{Cl}_1\text{O}_{3.98} \) or \( \text{NaClO}_4 \); this compound is named sodium perchlorate.
Determining the Molecular Formula

The molecular formula gives the *actual* numbers of moles of each element present in 1 mol of compound.

The molecular formula is a *whole-number multiple* of the empirical formula.

\[
\frac{\text{molar mass (g/mol)}}{\text{empirical formula mass (g/mol)}} = \text{whole-number multiple}
\]
Determining a Molecular Formula from Elemental Analysis and Molar Mass

**PROBLEM:** During excessive physical activity, lactic acid ($\mathcal{M} = 90.08$ g/mol) forms in muscle tissue and causes muscle soreness. Elemental analysis shows it contains 40.0 mass % C, 6.71 mass % H, and 53.3 mass % O. Determine the empirical formula and the molecular formula for lactic acid.

**PLAN:**

1. Assume 100 g lactic acid; then mass % = mass in grams
2. Divide each mass by $\mathcal{M}$
3. Amount (mol) of each element
4. Use # mols as subscripts; convert to integers
5. Empirical formula
6. Divide $\mathcal{M}$ by the molar mass for the empirical formula; multiply empirical formula by this number

**molecular formula**
**SOLUTION:** Assuming there are 100. g of lactic acid;

\[
\begin{align*}
40.0 \text{ g C} & \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 3.33 \text{ mol C} \\
6.71 \text{ g H} & \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 6.66 \text{ mol H} \\
53.3 \text{ g O} & \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.33 \text{ mol O}
\end{align*}
\]

\[
\begin{align*}
\frac{3.33}{3.33} & \quad \frac{6.66}{3.33} & \quad \frac{3.33}{3.33} \\
\text{C}_3\text{H}_6\text{O}_3 & \quad \text{empirical formula}
\end{align*}
\]

\[
\begin{align*}
\text{molar mass of lactate} & \quad 90.08 \text{ g/mol} \\
\text{mass of CH}_2\text{O} & \quad 30.03 \text{ g/mol}
\end{align*}
\]

\[
\frac{(\text{CH}_2\text{O}) \times 3}{3} = 3
\]

\[
\boxed{\text{C}_3\text{H}_6\text{O}_3 \text{ is the molecular formula}}
\]
Balancing a Chemical Equation

- **translate the statement**
magnesium and oxygen gas react to give magnesium oxide:
  \[ \text{Mg} + \text{O}_2 \rightarrow \text{MgO} \]

- **balance the atoms using coefficients; formulas cannot be changed**
  \[ 2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO} \]

- **adjust coefficients if necessary**

- **check that all atoms balance**

- **specify states of matter**
  \[ 2\text{Mg} \,(s) + \text{O}_2 \,(g) \rightarrow 2\text{MgO} \,(s) \]
Balancing Chemical Equations

PROBLEM: Within the cylinders of a car’s engine, the hydrocarbon octane (C₈H₁₈), one of many components of gasoline, mixes with oxygen from the air and burns to form carbon dioxide and water vapor. Write a balanced equation for this reaction.

PLAN:
- translate the statement
- balance the atoms
- adjust the coefficients
- check the atoms balance
- specify states of matter

SOLUTION:
\[
C_8H_{18} + O_2 \rightarrow CO_2 + H_2O
\]

\[
C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O
\]

\[
2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O
\]

\[
2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O
\]

\[
2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)
\]
Stoichiometric Calculations

• The coefficients in a balanced chemical equation
  – represent the relative number of reactant and product particles
  – and the relative number of moles of each.

• Since moles are related to mass
  – the equation can be used to calculate masses of reactants and/or products for a given reaction.

• The mole ratios from the balanced equation are used as conversion factors.
<table>
<thead>
<tr>
<th>Viewed in Terms of</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_3)H(_8)(g) + 5 O(_2)(g)</td>
<td>(3) CO(_2)(g) + 4 H(_2)O(g)</td>
<td></td>
</tr>
</tbody>
</table>

Molecules 1 molecule C\(_3\)H\(_8\) + 5 molecules O\(_2\) \(\rightarrow\) 3 molecules CO\(_2\) + 4 molecules H\(_2\)O

<table>
<thead>
<tr>
<th>Amount (mol)</th>
<th>1 mol C(_3)H(_8) + 5 mol O(_2)</th>
<th>3 mol CO(_2) + 4 mol H(_2)O</th>
</tr>
</thead>
</table>

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<th>Mass (amu)</th>
<th>44.09 amu C(_3)H(_8) + 160.00 amu O(_2)</th>
<th>132.03 amu CO(_2) + 72.06 amu H(_2)O</th>
</tr>
</thead>
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<th>Mass (g)</th>
<th>44.09 g C(_3)H(_8) + 160.00 g O(_2)</th>
<th>132.03 g CO(_2) + 72.06 g H(_2)O</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Total Mass (g)</th>
<th>204.09 g</th>
</tr>
</thead>
</table>

3-33
Summary of amount-mass-number relationships in a chemical equation.
Calculating Quantities of Reactants and Products: Amount (mol) to Amount (mol)

PROBLEM: In a lifetime, the average Canadian will use about 680 kg of copper in coins, plumbing and wiring. Copper is obtained from sulfide ores such as copper(I) sulfide (chalcopyrite) in a multistep process. It is “roasted” (heated strongly with oxygen gas) to form powdered copper(I) oxide and gaseous sulfur dioxide.

How many moles of oxygen are required to roast 10.0 mol of copper(I) sulfide?

PLAN: write and balance the equation

SOLUTION: \[2 \text{ Cu}_2\text{S} (s) + 3 \text{ O}_2 (g) \rightarrow 2 \text{ Cu}_2\text{O} (s) + 2 \text{ SO}_2 (g)\]

\[10.0 \text{ mol Cu}_2\text{S} \times \frac{3 \text{ mol O}_2}{2 \text{ mol Cu}_2\text{S}} = 15.0 \text{ mol O}_2\]
Calculating Quantities of Reactants and Products: Amount (mol) to Mass (g)

**PROBLEM:** During the process of roasting copper(I) sulfide, how many grams of sulfur dioxide form when 10.0 mol of copper(I) sulfide reacts?

**PLAN:** Using the balanced equation from the previous problem, we again use the mole ratio as a conversion factor.

\[
2 \text{Cu}_2\text{S} (s) + 3 \text{O}_2 (g) \rightarrow 2 \text{Cu}_2\text{O} (s) + 2 \text{SO}_2 (g)
\]

1. Use the mole ratio as a conversion factor:
   \[
   \frac{\text{mol of Cu}_2\text{S}}{\text{mol of SO}_2} = \frac{10.0 \text{ mol}}{2}
   \]

2. Multiply by the molar mass of sulfur dioxide:
   \[
   \text{mass of SO}_2 = 10.0 \text{ mol} \times 64.068 \text{ g/mol} = 640.68 \text{ g}
   \]
SOLUTION: \[ 2 \text{Cu}_2\text{S} (s) + 3 \text{O}_2 (g) \rightarrow 2 \text{Cu}_2\text{O} (s) + 2 \text{SO}_2 (g) \]

\[
\begin{align*}
10.0 \text{ mol Cu}_2\text{S} & \times \frac{2 \text{ mol SO}_2}{2 \text{ mol Cu}_2\text{S}} \times \frac{64.07 \text{ g SO}_2}{1 \text{ mol SO}_2} = 641 \text{ g SO}_2
\end{align*}
\]
Calculating Quantities of Reactants and Products: Mass to Mass

**PROBLEM:** During the roasting of copper(I) sulfide, how many kilograms of oxygen are required to form 2.86 kg of copper(I) oxide?

**PLAN:**

1. **Mass (kg) of Cu₂O**
   - 1 kg = 10³ g

2. **Mass (g) of Cu₂O**
   - Divide by \( \ell \) (g/mol).

3. **Amount (mol) of Cu₂O**
   - Molar ratio

4. **Amount (mol) of O₂**
   - Multiply by \( \ell \) (g/mol).

5. **Mass (g) of O₂**
   - 10³ g = 1 kg

6. **Mass (kg) of O₂**
**SOLUTION:** \[2 \text{Cu}_2\text{S (s) + 3 O}_2 (g) \rightarrow 2 \text{Cu}_2\text{O (s) + 2 SO}_2 (g)\]

\[
\begin{align*}
2.86 \text{ kg Cu}_2\text{O} & \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Cu}_2\text{O}}{143.10 \text{ g Cu}_2\text{O}} = 20.0 \text{ mol Cu}_2\text{O} \\
20.0 \text{ mol Cu}_2\text{O} & \times \frac{3 \text{ mol O}_2}{2 \text{ mol Cu}_2\text{O}} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 0.960 \text{ kg O}_2
\end{align*}
\]
Reactions in Sequence

- Reactions often occur in sequence.
- The product of one reaction becomes a reactant in the next.
- An overall reaction is written by combining the reactions;
  - any substance that forms in one reaction and reacts in the next can be eliminated.
Writing an Overall Equation for a Reaction Sequence

**PROBLEM:** Roasting is the first step in extracting copper from chalcocite, the ore used in the previous problem. In the next step, copper(I) oxide reacts with powdered carbon to yield copper metal and carbon monoxide gas. Write a balanced overall equation for the two-step process.

**PLAN:** Write individual balanced equations for each step.

Adjust the coefficients so that any common substances can be canceled.

Add the adjusted equations together to obtain the overall equation.
SOLUTION: Write individual balanced equations for each step:

\[ 2\text{Cu}_2\text{S} (s) + 3\text{O}_2 (g) \rightarrow 2\text{Cu}_2\text{O} (s) + 2\text{SO}_2 (g) \]
\[ \text{Cu}_2\text{O} (s) + \text{C} (s) \rightarrow 2\text{Cu} (s) + \text{CO} (g) \]

Adjust the coefficients so that the 2 moles of \( \text{Cu}_2\text{O} \) formed in reaction 1 are used up in reaction 2:

\[
\begin{align*}
2\text{Cu}_2\text{S} (s) + 3\text{O}_2 (g) & \rightarrow 2\text{Cu}_2\text{O} (s) + 2\text{SO}_2 (g) \quad \text{reaction 1} \\
2\text{Cu}_2\text{O} (s) + 2\text{C} (s) & \rightarrow 4\text{Cu} (s) + 2\text{CO} (g) \quad \text{reaction 2}
\end{align*}
\]

Add the equations together:

\[
2\text{Cu}_2\text{S} (s) + 3\text{O}_2 (g) + 2\text{C} (s) \rightarrow 2\text{SO}_2 (g) + 4\text{Cu} (s) + 2\text{CO} (g)
\]
Limiting Reactants

• So far we have assumed that reactants are present in the correct amounts to react completely.
• In reality, one reactant may limit the amount of product that can form.
• The limiting reactant will be completely used up in the reaction.
• The reactant that is not limiting is in excess – some of this reactant will be left over.
Using Molecular Depictions in a Limiting-Reactant Problem

**PROBLEM:** Nuclear engineers use chlorine trifluoride to prepare uranium fuel for power plants. The compound is formed as a gas by the reaction of elemental chlorine and fluorine. The circle in the margin shows a representative portion of the reaction mixture before the reaction starts. (Chlorine is green, and fluorine is yellow.)

(a) Find the limiting reactant.
(b) Write a reaction table for the process.
(c) Draw a representative portion of the mixture after the reaction is complete. (Hint: The ClF$_3$ molecule has 1 Cl atom bonded to 3 individual F atoms).
PLAN: Write a balanced chemical equation. To determine the limiting reactant, find the number of molecules of product that would form from the given numbers of molecules of each reactant. Use these numbers to write a reaction table and use the reaction table to draw the final reaction scene.

SOLUTION: The balanced equation is $\text{Cl}_2 (g) + 3\text{F}_2 (g) \rightarrow 2\text{ClF}_3 (g)$

There are 3 molecules of $\text{Cl}_2$ and 6 molecules of $\text{F}_2$ depicted:

$$3 \text{ molecules } \text{Cl}_2 \times \frac{2 \text{ molecules } \text{ClF}_3}{1 \text{ molecule } \text{Cl}_2} = 6 \text{ molecules } \text{ClF}_3$$

$$6 \text{ molecules } \text{F}_2 \times \frac{2 \text{ molecules } \text{ClF}_3}{3 \text{ molecule } \text{Cl}_2} = 4 \text{ molecules } \text{ClF}_3$$

Since the given amount of $\text{F}_2$ can form less product, it is the limiting reactant.
We use the amount of $F_2$ to determine the “change” in the reaction table, since $F_2$ is the limiting reactant:

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$Cl_2 (g)$</th>
<th>$3F_2 (g)$</th>
<th>$2ClF_3 (g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>3</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-2</td>
<td>-6</td>
<td>+4</td>
</tr>
<tr>
<td>Final</td>
<td>1</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>

The final reaction scene shows that all the $F_2$ has reacted and that there is $Cl_2$ left over. 4 molecules of $ClF_2$ have formed:
Calculating Quantities in a Limiting-Reactant Problem: Amount to Amount

**PROBLEM:** In another preparation of ClF₃, 0.750 mol of Cl₂ reacts with 3.00 mol of F₂.

(a) Find the limiting reactant.
(b) Write a reaction table.

**PLAN:** Find the limiting reactant by calculating the amount (mol) of ClF₃ that can be formed from each given amount of reactant. Use this information to construct a reaction table.

**SOLUTION:** The balanced equation is Cl₂ (g) + 3F₂ (g) → 2ClF₃ (g)

\[
0.750 \text{ mol Cl}_2 \times \frac{2 \text{ mol ClF}_3}{1 \text{ mol Cl}_2} = 1.50 \text{ mol ClF}_3
\]

\[
3.00 \text{ mol F}_2 \times \frac{2 \text{ mol ClF}_3}{3 \text{ mol F}_2} = 2.00 \text{ mol ClF}_3
\]

Cl₂ is limiting, because it yields less ClF₃.
All the Cl$_2$ reacts since this is the limiting reactant. For every 1 Cl$_2$ that reacts, 3 F$_2$ will react, so 3(0.750) or 2.25 moles of F$_2$ reacts.

<table>
<thead>
<tr>
<th>Moles</th>
<th>Cl$_2$ (g)</th>
<th>3F$_2$ (g)</th>
<th>2ClF$_3$ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.750</td>
<td>3.00</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-0.750</td>
<td>-2.25</td>
<td>+1.50</td>
</tr>
<tr>
<td>Final</td>
<td>0</td>
<td>0.75</td>
<td>1.50</td>
</tr>
</tbody>
</table>
Calculating Quantities in a Limiting-Reactant Problem: Mass to Mass

**PROBLEM:** A fuel mixture used in the early days of rocketry consisted of two liquids, hydrazine (N\(_2\)H\(_4\)) and dinitrogen tetraoxide (N\(_2\)O\(_4\)), which ignite on contact to form nitrogen gas and water vapor.

(a) How many grams of nitrogen gas form when 1.00 x 10\(^2\) g of N\(_2\)H\(_4\) and 2.00 x 10\(^2\) g of N\(_2\)O\(_4\) are mixed?

(b) Write a reaction table for this process.

**PLAN:** Find the limiting reactant by calculating the amount (mol) of N\(_2\) that can be formed from each given mass of reactant. Use this information to construct a reaction table.

\[2N_2H_4 (l) + N_2O_4 (l) \rightarrow 3N_2 (g) + 4H_2O (g)\]
mass (g) of \( \text{N}_2\text{H}_4 \)
\[
\text{divided by } M \text{ (g/mol)}
\]
\[
\text{mol of } \text{N}_2\text{H}_4
\]
\[
\text{mole ratio}
\]
\[
\text{mol of } \text{N}_2
\]

mass (g) of \( \text{N}_2\text{O}_4 \)
\[
\text{divided by } M \text{ (g/mol)}
\]
\[
\text{mol of } \text{N}_2\text{O}_4
\]
\[
\text{mole ratio}
\]
\[
\text{mol of } \text{N}_2
\]

Choose lower number of moles of \( \text{N}_2 \)
multiply by \( M \)

mass of \( \text{N}_2 \)
SOLUTION: \[ 2\text{N}_2\text{H}_4 (l) + \text{N}_2\text{O}_4 (l) \rightarrow 3\text{N}_2 (g) + 4\text{H}_2\text{O} (g) \]

For \text{N}_2\text{H}_4: \[ 1.00 \times 10^2 \text{ g N}_2\text{H}_4 \times \frac{1 \text{ mol N}_2\text{H}_4}{32.05 \text{ g N}_2\text{H}_4} = 3.12 \text{ mol N}_2\text{H}_4 \]

\[ 3.12 \text{ mol N}_2\text{H}_4 \times \frac{3 \text{ mol N}_2}{2 \text{ mol N}_2\text{H}_4} = 4.68 \text{ mol N}_2 \]

For \text{N}_2\text{O}_4: \[ 2.00 \times 10^2 \text{ g N}_2\text{O}_4 \times \frac{1 \text{ mol N}_2\text{O}_4}{92.02 \text{ g N}_2\text{O}_4} = 2.17 \text{ mol N}_2\text{O}_4 \]

\[ 2.17 \text{ mol N}_2\text{O}_4 \times \frac{3 \text{ mol N}_2}{1 \text{ mol N}_2\text{O}_4} = 6.51 \text{ mol N}_2 \]

\text{N}_2\text{H}_4 \text{ is limiting and only 4.68 mol of N}_2 \text{ can be produced:} \]

\[ 4.68 \text{ mol N}_2 \times \frac{28.02 \text{ g N}_2}{1 \text{ mol N}_2} = 131 \text{ g N}_2 \]
All the N$_2$H$_4$ reacts since it is the limiting reactant. For every 2 moles of N$_2$H$_4$ that react 1 mol of N$_2$O$_4$ reacts and 3 mol of N$_2$ form:

$$3.12 \text{ mol N}_2\text{H}_4 \times \frac{1 \text{ mol N}_2\text{O}_4}{2 \text{ mol N}_2\text{H}_4} = 1.56 \text{ mol N}_2\text{O}_4 \text{ reacts}$$

<table>
<thead>
<tr>
<th>Moles</th>
<th>2N$_2$H$_4$ (l)</th>
<th>N$_2$O$_4$ (l)</th>
<th>3N$_2$ (g)</th>
<th>4H$_2$O (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>3.12</td>
<td>2.17</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-3.12</td>
<td>-1.56</td>
<td>+4.68</td>
<td>+6.24</td>
</tr>
<tr>
<td>Final</td>
<td>0</td>
<td>0.61</td>
<td>4.68</td>
<td>6.24</td>
</tr>
</tbody>
</table>
The **theoretical yield** is the amount of product calculated using the molar ratios from the balanced equation.

The **actual yield** is the amount of product actually obtained.

The actual yield is usually less than the theoretical yield.

\[
\% \text{ yield} = \left( \frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100
\]
Calculating Percent Yield

PROBLEM: Silicon carbide (SiC) is made by reacting sand (silicon dioxide, SiO₂) with powdered carbon at high temperature. Carbon monoxide is also formed. What is the percent yield if 51.4 kg of SiC is recovered from processing 100.0 kg of sand?

PLAN:

1. Write balanced equation
2. Find mass of SiO₂
   - g to kg, then divide by \( M \) (g/mol)
3. Find mol SiO₂
4. Find molar ratio
5. Find mol SiC
   - Multiply by \( M(\text{g/mol}) \), Convert g to kg
6. Find kg of SiC
   - percent yield
SOLUTION: \[ \text{SiO}_2(s) + 3\text{C}(s) \rightarrow \text{SiC}(s) + 2\text{CO}(g) \]

\[
100.0 \text{ kg SiO}_2 \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol SiO}_2}{60.09 \text{ g SiO}_2} = 1664 \text{ mol SiO}_2
\]

\[
\text{mol SiO}_2 = \text{mol SiC} = 1664 \text{ mol SiC}
\]

\[
1664 \text{ mol SiC} \times \frac{40.10 \text{ g SiC}}{1 \text{ mol SiC}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} = 66.73 \text{ kg}
\]

\[
\frac{51.4 \text{ kg}}{66.73 \text{ kg}} \times 100 = 77.0\%
\]
Solution Stoichiometry

• Many reactions occur in solution.
• A solution consists of one or more solutes dissolved in a solvent.
• The concentration of a solution is given by the quantity of solute present in a given quantity of solution.
• Molarity (M) is often used to express concentration.

\[
C \text{ or } M = \frac{\text{Moles solute (mol)}}{\text{volume of solution (L)}}
\]
Calculating the Molarity of a Solution

**PROBLEM:** Glycine has the simplest structure of the 20 amino acids that make up proteins. What is the concentration of an aqueous solution that contains 0.715 mol of glycine (\(\text{H}_2\text{NCH}_2\text{COOH}\)) in 495 mL?

**PLAN:**
Molarity is the number of moles of solute per liter of solution.

**SOLUTION:**

\[
\text{molarity of glycine} = \frac{0.715 \text{ mol glycine}}{495 \text{ mL soln}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.44 \text{ M glycine}
\]
Calculating Mass of Solute in a Given Volume of Solution

**PROBLEM:** Biochemists often study reactions in solutions that contain phosphate ions. These solutions are commonly found in cells. What mass of solute is in 1.75 L of 0.460 M sodium monohydrogen phosphate buffer solution?

**PLAN:** Calculate the moles of solute using the given concentration and volume. Convert moles to mass using the molar mass of the solute.

**SOLUTION:**

\[
1.75 \text{ L} \times \frac{0.460 \text{ moles}}{1 \text{ L}} = 0.805 \text{ mol Na}_2\text{HPO}_4
\]

\[
0.805 \text{ mol Na}_2\text{HPO}_4 \times \frac{141.96 \text{ g Na}_2\text{HPO}_4}{1 \text{ mol Na}_2\text{HPO}_4} = 114 \text{ g Na}_2\text{HPO}_4
\]
Preparing a Dilute Solution from a Concentrated Solution

**PROBLEM:** Isotonic saline is 0.15 \( M \) aqueous NaCl. It stimulates the total concentration of ions in many cellular fluids and its uses range from cleaning contact lenses to washing red blood cells. How would you prepare 0.80 L of isotonic saline from a 6.0 \( M \) stock solution?

**PLAN:** To dilute a concentrated solution, we add only solvent, so the moles of solute are the same in both solutions. The volume and concentration of the dilute solution gives us the moles of solute. Then we calculate the volume of concentrated solution that contains the same number of moles.

\[
\text{volume of dilute solution} \times \text{M of dilute solution} = \text{amount(mol) of NaCl in dilute solution} = \frac{\text{amount(mol) NaCl in concentrated solution}}{\text{M of concentrated solution}}
\]

**Volume(L) of concentrated solution**
\[ M_{\text{dil}} \times V_{\text{dil}} = \text{# mol solute} = M_{\text{conc}} \times V_{\text{conc}} \]

**SOLUTION:**

Using the volume and concentration for the dilute solution:

\[
0.80 \text{ L soln} \times \frac{0.15 \text{ mol NaCl}}{1 \text{ L soln}} = 0.12 \text{ mol NaCl}
\]

Using the amount of solute and concentration for the concentrated solution:

\[
\frac{0.12 \text{ mol NaCl}}{6.0 \text{ mol NaCl}} \times \frac{1 \text{ L soln}}{6.0 \text{ mol NaCl}} = 0.020 \text{ L soln}
\]

A 0.020 L portion of the concentrated solution must be diluted to a final volume of 0.80 L.
Calculating Quantities of Reactants and Products for a Reaction in Solution

**PROBLEM:** You use 0.10 mol/L HCl solution to simulate the acid concentration of the stomach. How many liters of “stomach acid” react with a tablet containing 0.10 g of magnesium hydroxide?

**PLAN:** Write a balanced equation and convert the mass of Mg(OH)$_2$ to moles. Use the mole ratio to determine the moles of HCl, then convert to volume using concentration.
SOLUTION:

\[
\text{Mg(OH)}_2 (s) + 2\text{HCl} (aq) \rightarrow \text{MgCl}_2 (aq) + 2\text{H}_2\text{O} (l)
\]

\[
0.10 \text{ g Mg(OH)}_2 \times \frac{1 \text{ mol Mg(OH)}_2}{58.33 \text{ g Mg(OH)}_2} = 1.7 \times 10^{-3} \text{ mol Mg(OH)}_2
\]

\[
= 1.7 \times 10^{-3} \text{ mol Mg(OH)}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Mg(OH)}_2} = 3.4 \times 10^{-3} \text{ mol HCl}
\]

\[
3.4 \times 10^{-3} \text{ mol HCl} \times \frac{1 \text{ L HCl soln}}{0.10 \text{ mol HCl}} = 3.4 \times 10^{-2} \text{ L HCl}
\]
Solving Limiting-Reactant Problems for Reactions in Solution

PROBLEM: Mercury and its compounds have many uses, from fillings for teeth (as a mixture containing silver, copper and tin) in the past to the current production of chlorine. Because of their toxicity, however, soluble mercury compounds, such as mercury(II) nitrate must be removed from industrial wastewater. One removal method reacts the wastewater with a sodium sulfide solution to produce solid mercury(II) sulfide and sodium nitrate solution. In a laboratory simulation, 0.050 L of 0.010 mol/L mercury(II) nitrate reacts with 0.020 L of 0.10 mol/L sodium sulfide.

(a) What mass of mercury(II) sulfide forms?

\[ \text{Hg(NO}_3\text{)}_2 (aq) + \text{Na}_2\text{S (aq)} \rightarrow \text{HgS (s)} + 2\text{NaNO}_3 (aq) \]
**PLAN:** Write a balanced chemical reaction. Determine limiting reactant. Calculate the grams of mercury(II) sulfide product.
SOLUTION: \[ \text{Hg(NO}_3\text{)}_2 (aq) + \text{Na}_2\text{S (aq) → HgS (s) + 2NaNO}_3 \text{ (aq)} \]

\[
0.050 \text{ L Hg(NO}_3\text{)}_2 \times \frac{0.010 \text{ mol Hg(NO}_3\text{)}_2}{1 \text{ L Hg(NO}_3\text{)}_2} \times \frac{1 \text{ mol HgS}}{1 \text{ mol Hg(NO}_3\text{)}_2} = 5.0 \times 10^{-4} \text{ mol HgS}
\]

\[
0.020 \text{ L Na}_2\text{S} \times \frac{0.10 \text{ mol Na}_2\text{S}}{1 \text{ L Na}_2\text{S}} \times \frac{1 \text{ mol HgS}}{1 \text{ mol Na}_2\text{S}} = 2.0 \times 10^{-3} \text{ mol HgS}
\]

Hg(NO₃)₂ is the limiting reactant because it yields less HgS.

\[
5.0 \times 10^{-4} \text{ mol HgS} \times \frac{232.7 \text{ g HgS}}{1 \text{ mol HgS}} = 0.12 \text{ g HgS}
\]
Water as a Solvent

• Water is a polar molecule
  – since it has uneven electron distribution
  – and a bent molecular shape.

• Water readily dissolves a variety of substances.

• Water interacts strongly with its solutes and often plays an active role in aqueous reactions.
Electron distribution in molecules of $\text{H}_2$ and $\text{H}_2\text{O}$.

A. Electron charge distribution in $\text{H}_2$ is symmetrical.

B. Electron charge distribution in $\text{H}_2\text{O}$ is asymmetrical.

C. Each bond in $\text{H}_2\text{O}$ is polar.

D. The whole $\text{H}_2\text{O}$ molecule is polar.
An ionic compound dissolving in water.
Determining Amount (mol) of Ions in Solution

PROBLEM: What amount (mol) of each ion is in each solution?

(a) 5.0 mol of ammonium sulfate dissolved in water
(b) 78.5 g of cesium bromide dissolved in water
(c) $7.42 \times 10^{22}$ formula units of copper(II) nitrate dissolved in water
(d) 35 mL of 0.84 mol/L zinc chloride

PLAN: Write an equation for the dissociation of 1 mol of each compound. Use this information to calculate the actual number of moles represented by the given quantity of substance in each case.
SOLUTION:

(a) The formula is \((\text{NH}_4)_2\text{SO}_4\) so the equation for dissociation is:

\[(\text{NH}_4)_2\text{SO}_4 (s) \rightarrow 2\text{NH}_4^+ (aq) + \text{SO}_4^{2-} (aq)\]

\[
\frac{5.0 \text{ mol } (\text{NH}_4)_2\text{SO}_4 \times 2 \text{ mol } \text{NH}_4^+}{1 \text{ mol } (\text{NH}_4)_2\text{SO}_4} = 10. \text{ mol } \text{NH}_4^+
\]

\[
\frac{5.0 \text{ mol } (\text{NH}_4)_2\text{SO}_4 \times 1 \text{ mol } \text{SO}_4^{2-}}{1 \text{ mol } (\text{NH}_4)_2\text{SO}_4} = 5.0 \text{ mol } \text{SO}_4^{2-}
\]
SOLUTION:

(b) The formula is CsBr so the equation for dissociation is:

\[
\text{CsBr (s)} \rightarrow \text{Cs}^+ (aq) + \text{Br}^- (aq)
\]

\[
\frac{78.5 \text{ g CsBr}}{212.8 \text{ g CsBr}} \times \frac{1 \text{ mol CsBr}}{1 \text{ mol CsBr}} = 0.369 \text{ mol Cs}^+
\]

There is one Cs\(^+\) ion for every Br\(^-\) ion, so the number of moles of Br\(^-\) is also equal to 0.369 mol.
SOLUTION:

(c) The formula is Cu(NO$_3$)$_2$ so the formula for dissociation is:

Cu(NO$_3$)$_2$ (s) $\rightarrow$ Cu$^{2+}$ (aq) + 2NO$_3^-$ (aq)

7.42x10$^{22}$ formula units Cu(NO$_3$)$_2$ x $\frac{1 \text{ mol}}{6.022x10^{23} \text{ formula units}}$

= 0.123 mol Cu(NO$_3$)$_2$

0.123 mol Cu(NO$_3$)$_2$ x $\frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu(NO}_3)_2}$

= 0.123 mol Cu$^{2+}$ ions

There are 2 NO$_3^-$ ions for every 1 Cu$^{2+}$ ion, so there are 0.246 mol NO$_3^-$ ions.
SOLUTION:

(d) The formula is ZnCl$_2$ so the formula for dissociation is:

\[ \text{ZnCl}_2 (s) \rightarrow \text{Zn}^{2+} (aq) + 2\text{Cl}^- (aq) \]

\[
\begin{align*}
35 \text{ mL soln} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.84 \text{ mol ZnCl}_2}{1 \text{ L soln}} &= 2.9 \times 10^{-2} \text{ mol ZnCl}_2 \\
2.9 \times 10^{-2} \text{ mol ZnCl}_2 \times \frac{2 \text{ mol Cl}^-}{1 \text{ mol ZnCl}_2} &= 5.8 \times 10^{-2} \text{ mol Cl}^- \\
\end{align*}
\]

There is 1 mol of Zn$^{2+}$ ions for every 1 mol of ZnCl$_2$, so there are \(2.9 \times 10^{-2}\) mol Zn$^{2+}$ ions.
Redox reactions involve movement of electrons from one reactant to another (from the reactant which has less attraction for electrons to the one with more attraction for electrons).

**Ionic Compounds**: involves transfer of electrons, 

\[ 2\text{Mg}(s) + \text{O}_2 (g) \rightarrow 2 \text{MgO}(s) \]

Figure 19.1 A
Covalent Compounds: involves shift of electrons

$$H_2(g) + Cl_2(g) \rightarrow 2 \text{HCl}(g)$$

Figure 19.1B
Overview of Redox Reactions (ch 17)

*Oxidation* is the *loss* of electrons and *reduction* is the *gain* of electrons. These processes occur *simultaneously*. In the formation of MgO, Mg loses electrons and O gains electrons. Mg got oxidized and O got reduced.

\[
\text{Oxidation} \quad \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \quad (\text{Mg is oxidized})
\]

\[
\text{Reduction} \quad \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{O}^{2-} \quad (\text{O}_2 \text{ is reduced})
\]

The *oxidizing agent* (O\(_2\), here) takes electrons from the substance being oxidized. The oxidizing agent is therefore reduced.

The *reducing agent* (Mg, here) adds electrons to the substance being reduced. The reducing agent is therefore oxidized.
Using Oxidation Numbers

Oxidation Number or Oxidation State is the charge that the atom would have if the electrons were transferred completely, not shared.

A set of rules is used to assign Oxidation Numbers to an atom.

An Oxidation Number has a sign before the number (eg +2,-1 etc) where as ionic charge has a sign after the number (eg. 2+,1+ etc)
General Rules

1. For an atom in its elemental form (such as Na, O₂, and Cl₂): Oxidation number = 0
2. For a monatomic ion: Oxidation number = ion charge (with the sign before the numeral)
3. The sum of the oxidation number values for the atoms in a molecule or formula unit of a compound equals zero. The sum of the oxidation number values for the atoms in a polyatomic ion equals the charge of the ion.

Rules for Specific Atoms or Periodic Table Groups

1. For Group 1: Oxidation number = +1 in all compounds
2. For Group 2: Oxidation number = +2 in all compounds
3. For hydrogen: Oxidation number = +1 in combination with nonmetals
   Oxidation number = −1 in combination with metals and boron
4. For fluorine: Oxidation number = −1 in all compounds
5. For oxygen: Oxidation number = −2 in most cases, unless coupled to a more electronegative centre (such as F) or a Group 1 or Group 2 metal (in which case, it might be +2 or −1)
6. For Group 17: Oxidation number = −1 in combination with metals, nonmetals (except O), and other halogens lower in the group
Determine the Oxidation Number of each element in a) zinc chloride, b) Sulfur trioxide, c) nitric acid and d) dichromate ion.

**Plan:** From the rules from table 19.1, we can use an equation,
Net Charge on species = Σ (Ox:Number of atom X)(number of X atoms in the species)

**Solution:**

a) \( \text{ZnCl}_2 \)  
We know that Cl has Ox:Number -1. Let Ox:Number of Zn be \( y \). Net charge on \( \text{ZnCl}_2 \) is zero.

\[
0 = (y)(1) + (-1)(2),
\]

therefore \( y = 2 \) ie, **Ox:Number of Zn is +2**

b) \( \text{SO}_3 \)  
Knowing the Ox:Number of O to be -2,

\[
0 = (y)(1) + (-2)(3),
\]

\( y = 6 \), **Ox:Number of S is +6**

c) \( \text{HNO}_3 \)  
Knowing the Ox:Number of O to be -2, and H to be +1,

\[
0 = (+1)(1) + (y)(1) + (-2)(3),
\]

\( y = 5 \), **Ox:Number of N is +5**
d) \( \text{Cr}_2\text{O}_7^{2-} \) Knowing the Ox: Number of O to be -2 and the net charge on the species is 2-,

\[-2 = (y)(2) + (-2)(7) ,\]

Therefore \( y=6 \) , Ox: **Number of Cr is +6**
Use oxidation numbers to decide whether each of the following equations represents a redox reaction:

(a) $\text{CaO} \ (s) + \ \text{CO}_2 \ (g) \rightarrow \text{CaCO}_3(s)$

(b) $4\text{KNO}_3(s) \rightarrow 2\text{K}_2\text{O} \ (s) + 2\text{N}_2(g) + 5\text{O}_2(g)$

(c) $\text{H}_2\text{SO}_4(aq) + 2\text{NaOH} \ (aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + 2\text{H}_2\text{O} \ (l)$

**Solution:**

(a) 

\[
\begin{align*}
\text{CaO} & : +2 \quad \text{CO}_2 : +4 \\
\text{CaO}(s) + \text{CO}_2(g) & \rightarrow \text{CaCO}_3(s)
\end{align*}
\]

Since oxidation numbers are not changing here, this is **NOT** a redox reaction.
This IS a redox reaction

\[
\begin{align*}
4\text{KNO}_3(s) & \rightarrow 2\text{K}_2\text{O}(s) + 2\text{N}_2(g) + 5\text{O}_2(g) \\
\end{align*}
\]

Since oxidation numbers are not changing here, this is NOT a redox reaction
Identify the oxidizing agent and the reducing agent in each of the following reactions:
(a) $2\text{Al}_\text{(s)} + 3\text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{Al}_2(\text{SO}_4)_3\text{(aq)} + 3\text{H}_2\text{(g)}$
(b) $\text{PbO}_\text{(s)} + \text{CO}_\text{(g)} \rightarrow \text{Pb}_\text{(s)} + \text{CO}_2\text{(g)}$
(c) $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O}_\text{(g)}$

Solution:

(a) $\begin{align*}
\text{oxidation} & \\
\text{Al}^{0} + 1 \text{H}_2\text{SO}_4^{0} & \rightarrow \text{Al}^{3+} \text{SO}_4^{2-} + 3\text{H}_2^{+} \\
\text{reduction} & \\
\end{align*}$

Al is losing electrons (oxidized) and $\text{H}^+$ is gaining electrons (reduced) So Al is the Reducing agent and $\text{H}^+$ is the Oxidizing agent.
(b) PbO(s) + CO(g) → Pb(s) + CO₂(g)

C is losing electrons (oxidized) and Pb is gaining electrons (reduced) so CO is the reducing agent and PbO is the oxidizing agent.

(c) 2H₂(g) + O₂(g) → 2H₂O(g)

H is losing electrons (oxidized) and O is gaining electrons (reduced) so H₂ is the reducing agent and O₂ is the oxidizing agent.
A Summary of terminology for redox reactions

- X loses electron(s).
- X is oxidized.
- X is the reducing agent.
- X increases its oxidation number.

- Y gains electron(s).
- Y is reduced.
- Y is the oxidizing agent.
- Y decreases its oxidation number.
Balancing Redox Equations

Oxidation Number Method

Step 1: assign oxidation numbers to all atoms

Step 2: Identify the oxidized and reduced species

Step 3: Draw tie-lines between the reactant and product species and write the # of electrons lost (oxidation) and electrons gained (reduction) on the line.

Step 4: Multiply the # of electrons by factors so that the # of electrons lost = the # of electrons gained and use the factor as balancing coefficients

Step 5: Complete the balancing by inspection and add states of matter
Problem: Use the oxidation number method to balance the following equations:

(a) \( \text{Cu} \ (s) + HNO_3 \ (aq) \rightarrow \text{Cu(NO}_3)_2 \ (aq) + NO_2(g) + H_2O(l) \)

(b) \( \text{PbS} \ (s) + O_2(g) \rightarrow \text{PbO} \ (s) + \text{SO}_2(g) \)

Copper in nitric acid

Solution:

(a) \( \text{Step:1} \)

Assign Oxidation Numbers

\[
\begin{array}{c|c|c}
\text{Cu} & +1 & -2 \\
HNO_3 & +5 & \\
\hline
\text{Cu(NO}_3)_2 & +2 & -2 \\
NO_2 & +4 & \\
H_2O & +1 & -2 \\
\end{array}
\]

\( \text{Cu} + \text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O} \)

\( \text{Step:2} \)

Identify the oxidized and reduced species.

Cu is oxidized and HNO\(_3\) is reduced here.
Step: 3

Compute electrons lost and gained and draw tie-lines

\[
\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}
\]

- \text{Cu} \text{ loses } 2e^- \\
- \text{HNO}_3 \text{ gains } 1e^- \\

Step: 4

Make electrons lost and gained to same number

\[
\text{Cu} + 2\text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + 2\text{NO}_2 + \text{H}_2\text{O}
\]

Step: 5

Complete balancing by inspection

\[
\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu(NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}
\]

and add states,

\[
\text{Cu}(s) + 4\text{HNO}_3(aq) \rightarrow \text{Cu(NO}_3)_2(aq) + 2\text{NO}_2(g) + 2\text{H}_2\text{O(l)}
\]
Solution: (b)

\[
\begin{align*}
\text{PbS} + \text{O}_2 & \rightarrow \text{PbO} + \text{SO}_2 \\
\text{PbS} + \text{O}_2 & \rightarrow \text{PbO} + \text{SO}_2 \\
\text{PbS} + \frac{3}{2}\text{O}_2 & \rightarrow \text{PbO} + \text{SO}_2 \\
2\text{PbS}(s) + 3\text{O}_2(g) & \rightarrow 2\text{PbO}(s) + 2\text{SO}_2(g)
\end{align*}
\]
Balancing Redox Reactions in Acidic Solution

\[ \text{Cr}_2\text{O}_7^{2-}(aq) + I^{-}(aq) \rightarrow \text{Cr}^{3+}(aq) + I_2(s) \]

**Step 1:** Divide the reaction into half-reactions.

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]
\[ I^{-} \rightarrow I_2 \]

**Step 2:** Balance the atoms and charges in each half-reaction.

For the \(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}\) half-reaction:

Balance atoms other than O and H:

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]

Balance O atoms by adding \(\text{H}_2\text{O}\) molecules:

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
Balance H atoms by adding H⁺ ions:

\[ 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \]

Balance charges by adding electrons:

\[ 6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \]

This is the **reduction** half-reaction. Cr\(_2\)O\(_7\)\(^{2-}\) is reduced, and is the oxidizing agent. The O.N. of Cr decreases from +6 to +3.

For the I\(^{-}\)/I\(_2\) half-reaction:

Balance atoms other than O and H:

\[ 2I^- \rightarrow I_2 \]

There are no O or H atoms, so we balance charges by adding electrons:

\[ 2I^- \rightarrow I_2 + 2e^- \]

This is the **oxidation** half-reaction. I\(^{-}\) is oxidized, and is the reducing agent. The O.N. of I increases from -1 to 0.
Step 3: Multiply each half-reaction, if necessary, by an integer so that the number of e\(^{-}\) lost in the oxidation equals the number of e\(^{-}\) gained in the reduction.

The reduction half-reaction shows that 6e\(^{-}\) are gained; the oxidation half-reaction shows only 2e\(^{-}\) being lost and must be multiplied by 3:

\[
\begin{align*}
3(2I^- & \rightarrow I_2 + 2e^-) \\
6I^- & \rightarrow 3I_2 + 6e^- \\
\end{align*}
\]

Step 4: Add the half-reactions, canceling substances that appear on both sides, and include states of matter. Electrons must always cancel.

\[
\begin{align*}
6e^- + 14H^+ + Cr_2O_7^{2-} & \rightarrow 2Cr^{3+} + 7H_2O \\
6I^- & \rightarrow 3I_2 + 6e^- \\
\hline
6I^-(aq) + 14H^+(aq) + Cr_2O_7^{2-}(aq) & \rightarrow 3I_2(s) + 7H_2O(l) + 2Cr^{3+}(aq)
\end{align*}
\]
Balancing Redox Reactions in Basic Solution

An acidic solution contains $\text{H}^+$ ions and $\text{H}_2\text{O}$. We use $\text{H}^+$ ions to balance H atoms.

A basic solution contains $\text{OH}^-$ ions and $\text{H}_2\text{O}$. To balance H atoms, we proceed as if in acidic solution, and then add one $\text{OH}^-$ ion to both sides of the equation.

For every $\text{OH}^-$ ion and $\text{H}^+$ ion that appear on the same side of the equation we form an $\text{H}_2\text{O}$ molecule.

Excess $\text{H}_2\text{O}$ molecules are canceled in the final step, when we cancel electrons and other common species.
Balancing a Redox Reaction in Basic Solution

**PROBLEM:** Permanganate ion reacts in basic solution with oxalate ion to form carbonate ion and solid manganese dioxide. Balance the skeleton ionic equation for the reaction between NaMnO$_4$ and Na$_2$C$_2$O$_4$ in basic solution:

\[ \text{MnO}_4^- (aq) + \text{C}_2\text{O}_4^{2-} (aq) \rightarrow \text{MnO}_2 (s) + \text{CO}_3^{2-} (aq) \] [basic solution]

**PLAN:** We follow the numbered steps as described in the text, and proceed through step 4 as if this reaction occurs in acidic solution. Then we add the appropriate number of OH$^-$ ions and cancel excess H$_2$O molecules.

**SOLUTION:**

**Step 1:** *Divide the reaction into half-reactions.*

\[ \text{MnO}_4^- \rightarrow \text{MnO}_2 \] \[ \text{C}_2\text{O}_4^{2-} \rightarrow \text{CO}_3^{2-} \]
**Step 2:** Balance the atoms and charges in each half-reaction.

Balance atoms other than O and H:

\[
\text{MnO}_4^- \rightarrow \text{MnO}_2 \quad \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_3^{2-}
\]

Balance O atoms by adding H\(_2\)O molecules:

\[
\text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \quad 2\text{H}_2\text{O} + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_3^{2-}
\]

Balance H atoms by adding H\(^+\) ions:

\[
4\text{H}^+ + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \quad 2\text{H}_2\text{O} + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_3^{2-} + 4\text{H}^+
\]

Balance charges by adding electrons:

\[
3\text{e}^- + 4\text{H}^+ + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \quad 2\text{H}_2\text{O} + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_3^{2-} + 4\text{H}^+ + 2\text{e}^-
\]

[reduction] [oxidation]
**Step 3:** Multiply each half-reaction, if necessary, by an integer so that the number of e\(^-\) lost in the oxidation equals the number of e\(^-\) gained in the reduction.

\[
x 2 \quad 6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O
\]
\[
x 3 \quad 6H_2O + 3C_2O_4^{2-} \rightarrow 6CO_3^{2-} + 12H^+ + 6e^-
\]

**Step 4:** Add the half-reactions, canceling substances that appear on both sides.

\[
\begin{array}{l}
6e^- + 8H^+ + 2MnO_4^- \rightarrow 2MnO_2 + 4H_2O \\
2(6H_2O + 3C_2O_4^{2-} \rightarrow 6CO_3^{2-} + 12H^+ + 6e^-)
\end{array}
\]
\[
2MnO_4^- + 2H_2O + 3C_2O_4^{2-} \rightarrow 2MnO_2 + 6CO_3^{2-} + 4H^+
\]
**Basic.** Add OH\(^-\) to both sides of the equation to neutralize H\(^+\), and cancel H\(_2\)O.

\[
2\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{C}_2\text{O}_4^{2-} + 4\text{OH}^- \rightarrow 2\text{MnO}_2 + 6\text{CO}_3^{2-} + [4\text{H}^+ + 4\text{OH}^-]
\]

Including states of matter gives the final balanced equation:

\[
2\text{MnO}_4^- (aq) + 3\text{C}_2\text{O}_4^{2-} (aq) + 4\text{OH}^- (aq) \rightarrow 2\text{MnO}_2 (s) + 6\text{CO}_3^{2-} (aq) + 2\text{H}_2\text{O} (l)
\]
Quantifying Redox Reactions by Titration

In a Redox titration, known concentration of an oxidizing agent is used to find an unknown concentration of a reducing agent.

Figure 19.3 The redox titration of $C_2O_4^{2-}$ with $MnO_4^-$

Net ionic equation

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$
Calcium ion (Ca$^{2+}$) is necessary for blood clotting and many other physiological processes. To measure the Ca$^{2+}$ concentration in 1.00 mL of human blood, Na$_2$C$_2$O$_4$ solution is added, causing Ca$^{2+}$ to precipitate as solid CaC$_2$O$_4$. This solid is dissolved in dilute H$_2$SO$_4$ to release C$_2$O$_4^{2-}$ and 2.05 mL of 4.88 $\times$ 10^{-4} mol/L KMnO$_4$ is required to reach the end point. The balanced equation is given below:

$$2\text{KMnO}_4(\text{aq}) + 5\text{CaC}_2\text{O}_4(\text{s}) + 8\text{H}_2\text{SO}_4(\text{aq}) \rightarrow$$

$$2\text{MnSO}_4(\text{aq}) + \text{K}_2\text{SO}_4(\text{aq}) + 5\text{CaSO}_4(\text{s}) + 10\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$$

Calculate the amount (mol) of Ca$^{2+}$ in 1.00 mL of blood.

**Solution:**

\[
\text{Mol of KMnO}_4 = \frac{2.05 \text{ mL}}{1000 \text{ mL}} \times \frac{1 \text{ L}}{10^{-6} \text{ mol}} = 1.00 \times 10^{-6} \text{ mol}
\]
Using molar ratio, converting this to mols of CaC$_2$O$_4$, 

\[
\text{mol of CaC}_2\text{O}_4 = 1.00 \times 10^{-6} \text{ mol KMnO}_4 \times \frac{5 \text{ mol of CaC}_2\text{O}_4}{2 \text{ mol KMnO}_4}
\]

\[
= 2.50 \times 10^{-6} \text{ mol of CaC}_2\text{O}_4
\]

\[
\text{mol of Ca}^{2+} = 2.50 \times 10^{-6} \text{ mol of CaC}_2\text{O}_4 \times \frac{1 \text{ mol of Ca}^{2+}}{1 \text{ mol of CaC}_2\text{O}_4}
\]

\[
= 2.50 \times 10^{-6} \text{ mol of Ca}^{2+}
\]