Chapter 4

Stoichiometry

Alkanes and Hydrocarbons

- Alkanes are hydrocarbons where the carbon atoms are linked together with single bonds.

$$C_nH_{2n+2}$$

- Hydrocarbons are compounds composed only of hydrogen and carbon.

$$C_nH_m$$

Fundamentals of Stoichiometry

- Stoichiometry is a term used to describe quantitative relationships in chemistry.
  - "How much?" of a product is produced or reactant is consumed.
  - A balanced chemical equation is needed.
  - Conversion between mass or volume to number of moles frequently needed.

Ratios from a Balanced Chemical Equation

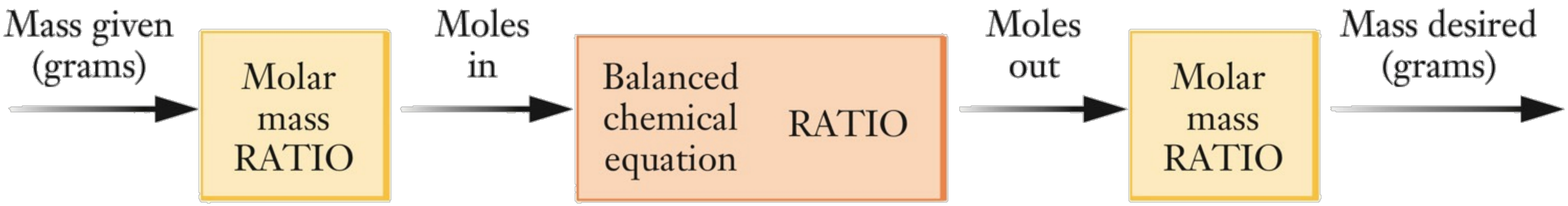
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$$

- Mole ratios are obtained from the coefficients in the balanced chemical reaction.
  - 1 CH_4 : 2 O_2 : 1 CO_2 : 2 H_2O
  - 1 mol CH_4 : 2 mol O_2 : 1 mol CO_2 : 2 mol H_2O
- These ratios can be used in solving problems:

$$\frac{1 \text{ mol } CH_4}{2 \text{ mol } O_2} \text{ or } \frac{2 \text{ mol } H_2O}{1 \text{ mol } CH_4}$$

Ratios from a Balanced Chemical Equation

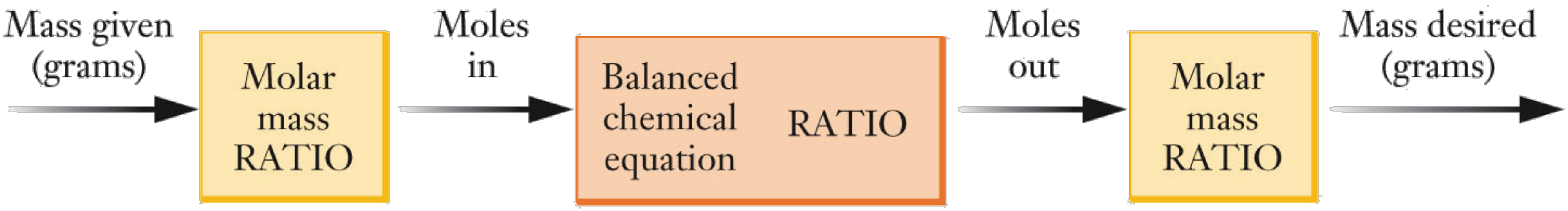
- This flow diagram illustrates the various steps involved in solving a typical reaction stoichiometry problem.
  - No different than unit conversion
  - Usually more than one conversion is necessary
  - Write all quantities with their complete units

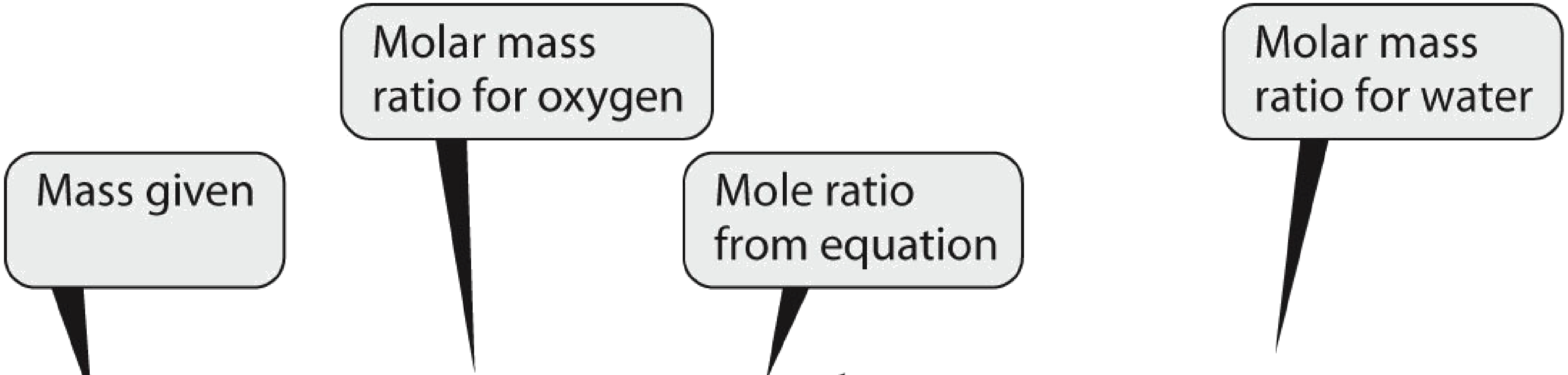


Example Question

- How many grams of water can be produced if sufficient hydrogen reacts with 26.0 g of oxygen?

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$





$$26.0\ g\ O_2 \times \frac{1\ mol\ O_2}{32.0\ g\ O_2} \times \frac{2\ mol\ H_2O}{1\ mol\ O_2} \times \frac{18.0\ g\ H_2O}{1\ mol\ H_2O} = 29.3\ g\ H_2O$$

Limiting Reactants

- In many chemical reactions, one reactant is often exhausted before the other reactants. This reactant is the limiting reactant.

  - Limiting reactant is determined using stoichiometry.

  - The limiting reactant limits the quantity of product produced.

Q. If 43.0 kg NH_3 react with 35.4 kg of O_2, what mass of NO forms?

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

43.0 kg | 35.4 kg | ?? kg

$$43.0\times10^3\ g\ NH_3 \times \frac{1\ mol\ NH_3}{17.03\ g\ NH_3} \times \frac{4\ mol\ NO}{4\ mol\ NH_3} \times \frac{30.01\ g\ NO}{1\ mol\ NO}$$

in excess

75.77×10^3 g NO   75.8 kg NO

$$35.4\times10^3\ g\ O_2 \times \frac{1\ mol\ O_2}{32.00\ g\ O_2} \times \frac{4\ mol\ NO}{5\ mol\ O_2} \times \frac{30.01\ g\ NO}{1\ mol\ NO}$$

limiting

53.12×10^3 g NO   26.6 kg NO

smaller amt produced; O_2 is limiting reactant!!

Theoretical Yield

- The maximum mass of a product that can be obtained in a reaction is determined by the limiting reactant.
  - Determine which reactant is the limiting reactant.
  - Calculate the mass of product that can be made from the limiting reactant. This mass is the theoretical yield.
  - In stoichiometric mixtures, however, both reactants are consumed completely, so either could be considered the limiting reactant.

Theoretical and Percentage Yields

$$\text{Percentage Yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100\%$$

- Reaction efficiency is measured with percentage yield.
  - The mass of product obtained is the actual yield.
  - The ideal mass of product obtained from calculation is the theoretical yield.

Example Question

Q. If 10.0 g NO react with 14.0 g of NO_2 and 8.52 g of N_2O_3 are produced. What is the percentage yield?

$$NO + NO_2 \longrightarrow N_2O_3$$

$$\textit{Percent yield} = \frac{8.52\ \text{g}\ N_2O_3}{\text{Theoretical yield}} \times 100\ \% = ?$$

36.9 %

$$10.0\ \text{g NO} \times \frac{1\ mol\ NO}{30.01\ g\ NO} \times \frac{1\ mol\ N_2O_3}{1\ mol\ NO} \times \frac{76.02\ g\ N_2O_3}{1\ mol\ N_2O_3}$$

in excess

25.3 g N_2O_3

$$14.0\ \text{g}\ NO_2 \times \frac{1\ mol\ NO_2}{46.01\ g\ NO_2} \times \frac{1\ mol\ N_2O_3}{1\ mol\ NO_2} \times \frac{76.02\ g\ N_2O_3}{1\ mol\ N_2O_3}$$

limiting

23.1 g N_2O_3

Solution Stoichiometry

- For reactions occurring in solution, the concentration and volume of reactants and products are often used instead of mass to solve solution stoichiometry problems.

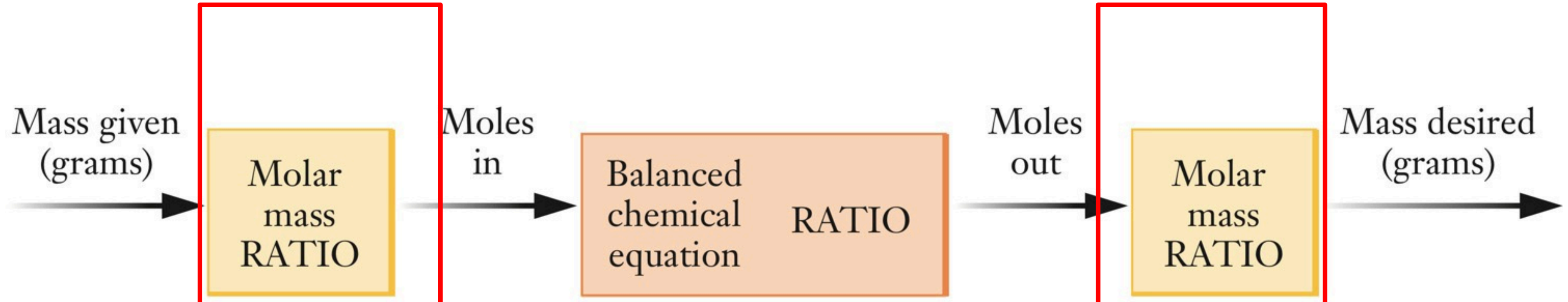
Moles can be solved from concentration (molarity) and volume (Liters)

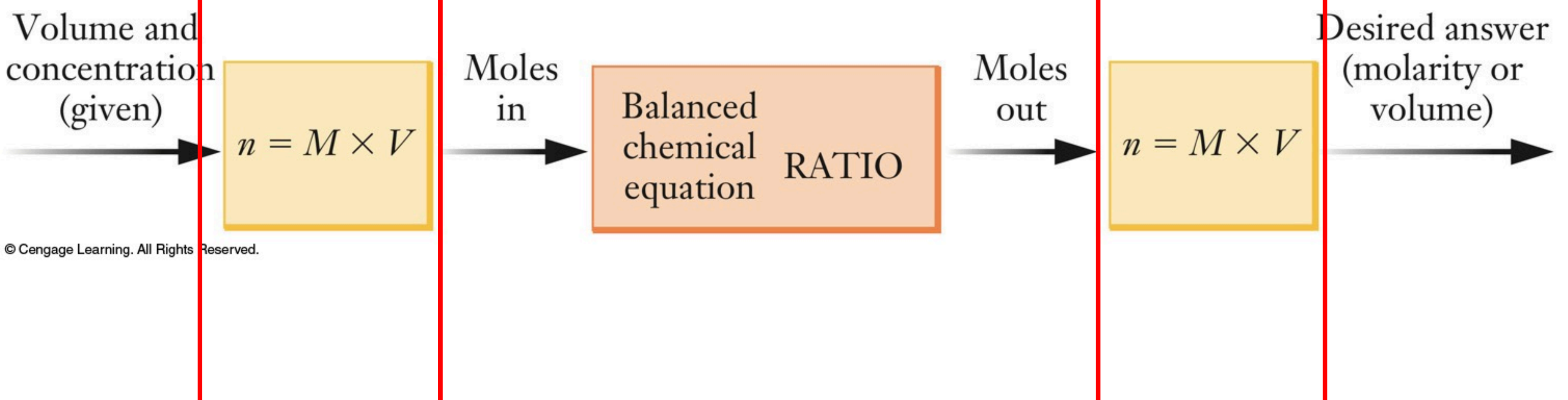
$$Molarity = \frac{moles}{volume\,(L)}$$

$$moles = Molarity \times volume\,(L)$$

previously: $$moles = \frac{mass}{molar\ mass}$$

Solution Stoichiometry





Example Question

What is the molarity of a solution of nitric acid if 0.216 g of barium hydroxide is required to neutralize a 20.00-mL sample of nitric acid?

acid **base** **salt**

$$2\ HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow Ba(NO_3)_2(aq) + 2\ H_2O(l)$$

$$0.216\ g\ Ba(OH)_2 \times \frac{1\ mol\ Ba(OH)_2}{171.34\ g\ Ba(OH)_2}$$ 1.26×10^{-3} mol $Ba(OH)_2$

$$1.26 \times 10^{-3}\ mol\ Ba(OH)_2 \times \frac{2\ mol\ HNO_3}{1\ mol\ Ba(OH)_2}$$ 2.52×10^{-3} mol HNO_3

Molarity = 2.52×10^{-3} mol $HNO_3 \times \frac{1}{0.0200\ L}$

0.126 M HNO_3

Solution Stoichiometry

- A titration is a common laboratory technique that uses solution stoichiometry.
  - A solution-phase reaction is carried out under controlled conditions so that the amount of one reactant can be determined with high precision.
  - An indicator is a dye added to a titration to indicate when the reaction is complete.

Chapter 5

Gases

Ideal Gas Law

- The ideal gas law is the quantitative relationship between pressure *(P)*, volume *(V)*, moles gas present *(n)*, and the absolute temperature *(T)*.

$$PV = nRT$$

- *R* is the universal gas constant.
  - *R* = 0.08206 L atm mol^{-1} K^{-1}: used in most gas equations (universal gas constant)

Pressure and Temperature

Units of Pressure

- 1 torr = 1 mm Hg
- 1 atm = 760 torr (exactly)
- 1 atm = 101,325 Pa (exactly)
- 760 torr = 101,325 Pa (exactly)

Units of Temperature

$$^{o}F = (1.8 \times {}^{o}C) + 32$$

$$^{o}C = ({}^{o}F - 32)/1.8$$

$$K = {}^{o}C + 273.15$$

$$^{o}C = K - 273.15$$

History and Application of the Gas Law

- Charles' s Law: $T \propto V$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- Boyle' s Law: $P \propto 1 / V$

$$P_1V_1 = P_2V_2$$

- Avogadro' s Law: $n \propto V$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

- The empirical gas laws led to the ideal gas law.

$$PV = nRT$$

Example Questions

Which of the following relationships are true for gases?

i) The number of moles of a gas is inversely proportional to its volume (at constant pressure and temperature). Wrong

ii) The pressure of a gas is directly proportional to its temperature in kelvins (at constant volume). True

iii) The volume of a gas is inversely proportional to its pressure (at constant temperature). True

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_1V_1 = P_2V_2$$

Example Questions

At constant temperature, 14.0 L of O_2 at 0.882 atm is compressed to 1.75 L. What is the final pressure of O_2?

$$P_1V_1 = P_2V_2$$

$$PV = nRT$$

$$P_2 = \frac{P_1V_1}{V_2}$$

$P_1 = 0.882$ atm

$V_1 = 14.0$ L

$V_2 = 1.75$ L

7.06 atm

Partial Pressure

- Dalton's law of partial pressures: The total pressure (*P*) of a mixture of gases is the sum of the partial pressures of the component gases (P_i).

$$P = \sum_i P_i \qquad P_i = \frac{n_i RT}{V} \qquad P = \sum_i P_i = \sum_i n_i \frac{RT}{V}$$

- Daltons Law can be expressed in terms of mole fraction.
  - Mole fraction (X_i) for a gas in a gas mixture is the moles of the gas (n_i) divided by the total moles of the gases present.
  - The partial pressure of each gas is related to its mole fraction.

$$X_i = \frac{n_i}{n_{\text{total}}} \qquad \Rightarrow \qquad P_i = X_i P$$

$$\frac{P_i}{P} = \frac{n_i(RT/V)}{n_{\text{total}}(RT/V)} = \frac{n_i}{n_{\text{total}}} = X_i$$

Example Questions

A mixture of He and O_2 is placed in a 4.00 L flask at 32 °C. The partial pressure of the He is 3.4 atm and the partial pressure of the O_2 is 2.6 atm. What is the mole fraction of O_2?

$$P = \sum_i P_i = P_{O2} + P_{He} = 3.4\ atm + 2.6\ atm = 6.0\ atm$$

$$\frac{P_i}{P} = \frac{n_i(RT/V)}{n_{\text{total}}(RT/V)} = \frac{n_i}{n_{\text{total}}} = X_i$$

$$X_{O2} = \frac{P_{O2}}{P} = \frac{2.6}{6.0} = 0.43$$

Stoichiometry of Reactions Involving Gases

- For reactions involving gases, the ideal gas law is used to determine moles of gas involved in the reaction.

  - Use mole ratios (stoichiometry)

  - Connect number of moles of a gas to its temperature, pressure, or volume with ideal gas law

$$PV = nRT$$

Example Questions

What volume of O_2, measured at 91.2 °C and 743 mm Hg, will be produced by the decomposition of 4.88 g $KClO_3$? (R = 0.08206 L·atm/mol·K)

$$2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$$

$$\frac{n_{KClO3}}{n_{O2}} = \frac{2}{3}$$

$$n_{O2} = \frac{3 \times n_{KClO3}}{2}$$

$$= \frac{3 \times n_{KClO3}}{2} = \frac{3 \times 4.88g \times \frac{1mole}{122.5495g}}{2} = 0.0597mol$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$T = 91.2 + 273.15 = 364.4\ K$$

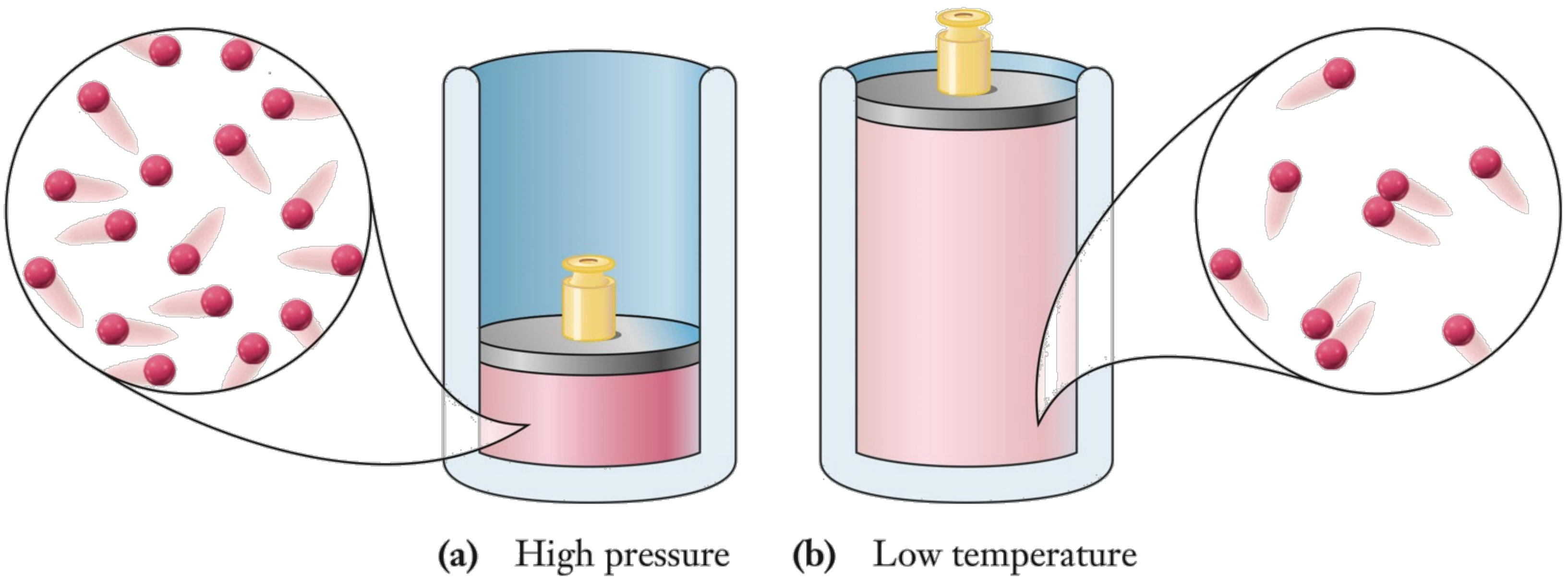
$$P = 743\ mm \times \frac{1\ atm}{760\ mm} = 0.978\ atm$$

1.83 L

Postulates of the Kinetic-Molecular Model

- Gases are made up of large collections of particles, which are in constant, random motion.
- Gas particles are infinitely small and occupy negligible volume.
- Gas particles move in straight lines except when they collide with other particles or with the container walls. These collisions are elastic, so kinetic energy of particles is conserved.
- Particles interact with each other only when collisions occur.
- The average kinetic energy of a gas is proportional to the absolute temperature of the gas but does not depend upon the identity of the gas

Breaking of the ideal gas law



- The ideal gas model breaks down at high pressures and low temperatures.
  - high pressure: volume of particles no longer negligible
  - low temperature: particles move slowly enough to interact

Chapter 6

The Periodic Table and Atomic Structure

The Wave-Particle Duality of Light

- The product of the frequency and wavelength is the speed of light.

$$c = \lambda \nu$$

  - $c = 2.99792458 \times 10^{8}$ m/s

- The energy of a photon *(E)* is proportional to its frequency (ν).
  - and is inversely proportional to the wavelength (λ).
  - h = Planck's constant = 6.626×10^{-34} J•s

$$E = h\nu \qquad c = \lambda \nu \qquad E = h\nu = \frac{hc}{\lambda}$$

Example Questions

When a hydrogen atom undergoes a transition from n = 2 to n = 1, it emits a photon with wavelength λ = 121.6 nm. What is the energy of a 1 mole of photons of this light?

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} J \cdot s \times 2.998 \times 10^{8} m/s}{121.6 \times 10^{-9} m} = 1.633 \times 10^{-18} J$$

$$E_{mol} = 1.633 \times 10^{-18} J \times 6.022 \times 10^{23} = 9.838 \times 10^{5} J$$

Quantum numbers

n Principle quantum number - *shell*

l Secondary quantum number - *subshell*

m_l Magnetic quantum number – *subshell direction*

m_s Spin quantum number – spin direction

$n = 1, 2, 3, \ldots.$

$l = 0, 1, 2, n\text{-}1$

$m_l = -l, \ldots 0, \ldots l$

$m_s = \pm\ 1/2$

1s

principal quantum number (n)

secondary quantum number (l)

indicates the principal shell of the orbital.

indicates the subshell of the orbital.

Example Questions

Which of the following represents invalid set of quantum numbers?

a) $n = 3, l = 2, m_l = -2$, b) $n = 2, l = 1, m_l = 0$, c) $n = 3, l = 3, m_l = 3$,
d) $n = 4, l = 3, m_l = 3$ e) $n = 5, l = 0, m_l = 0$

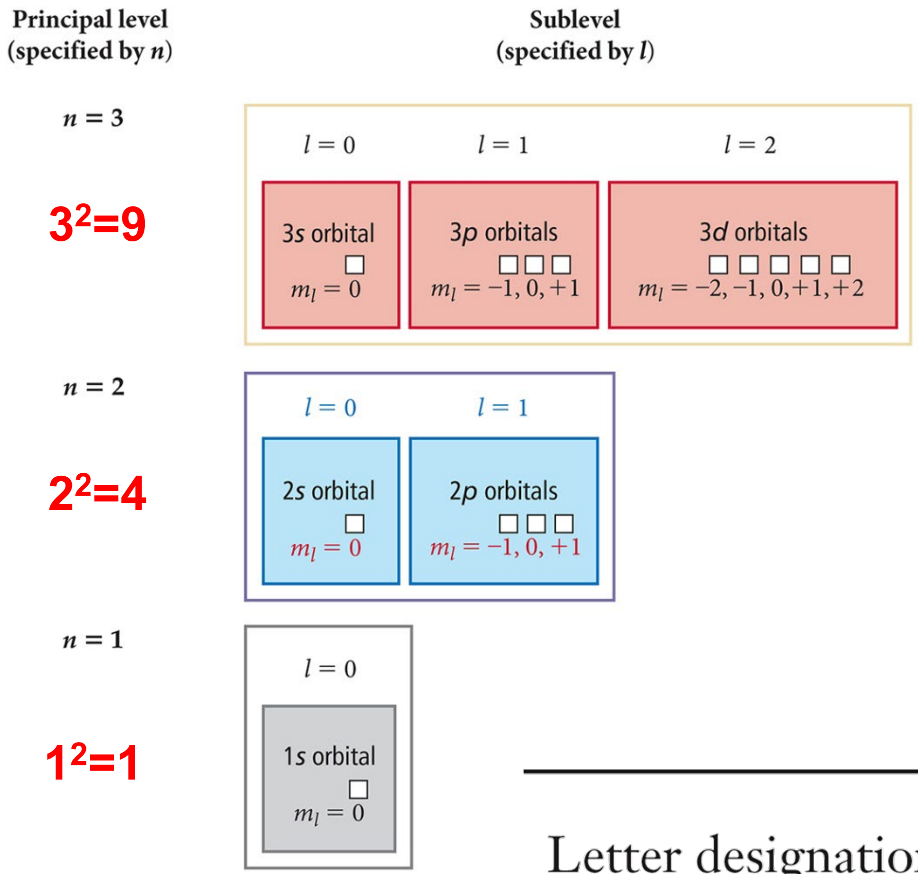
$$n = 1, 2, 3, ...$$

$$l = 0, 1, 2, n\text{-}1$$

$$m_l = -l, ...0, ... l$$

$$m_s = \pm 1/2$$

Quantum Numbers



- the number of sublevels within a level = *n.*
- the number of orbitals within a sublevel = 2*l* + 1.
- the number of orbitals in a level = n^2.

Letter designations for the secondary quantum number

ℓ-value	0	1	2	3	4
Letter Designation	*s*	*p*	*d*	*f*	*g*

Electron Configuration

Pauli Exclusion Principle: no more than two electrons can occupy any orbital

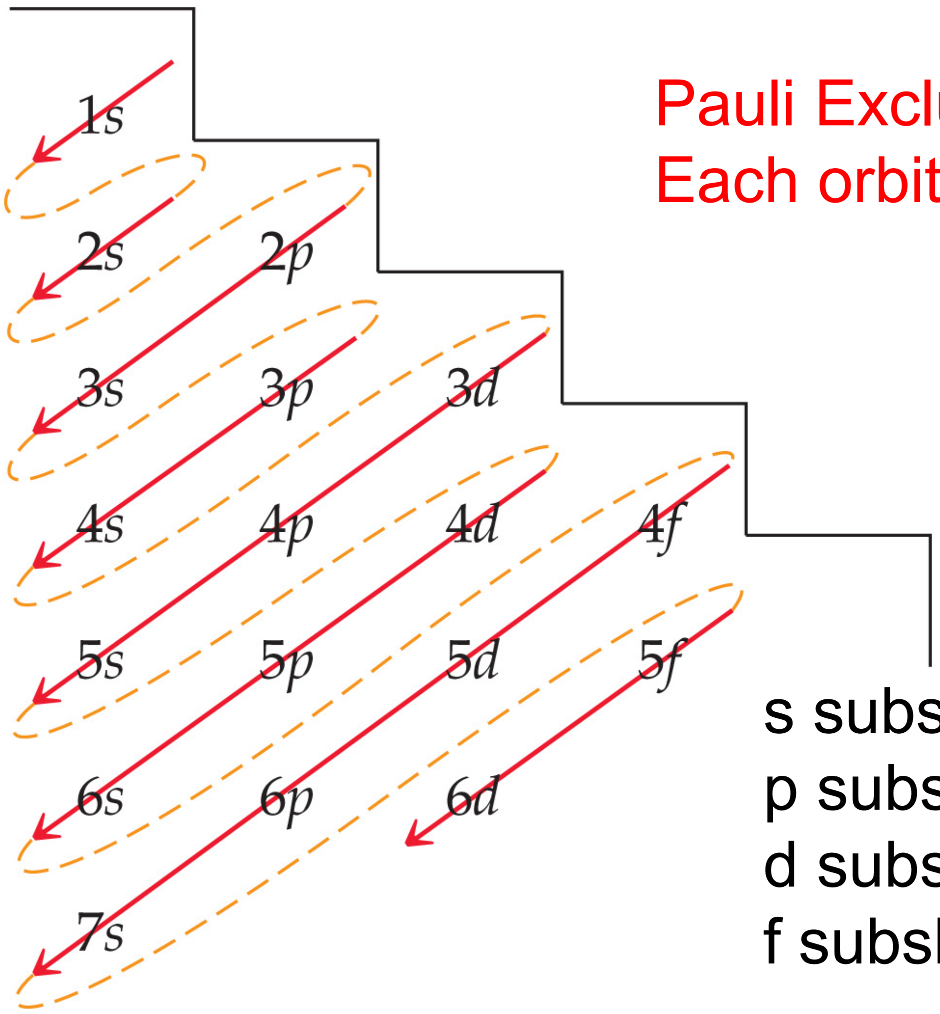
Aufbau Principle: Lower-energy orbitals fill before higher-energy orbitals.

Hund’s rule: Fill a set orbitals of same energy with electrons singly, with parallel spins, before pairing starts.

Electron Configurations

Aufbau Principle: order of electron filling

1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d* 4*p* 5*s* 4*d* 5*p* 6*s* *4f* *5d* *6p* *7s* *5f* *6d* *7p*



Pauli Exclusion Principle:
Each orbital can hold 2 electrons

s subshell: 1 orbital, 2 electrons
p subshell: 3 orbitals, 6 electrons
d subshell: 5 orbitals, 10 electrons
f subshell: 7 orbitals, 14 electrons

Example Questions

Write the ground state electron configuration for iron.

a) [Ar] $4s^2 4p^6$ b) [Ar] $4s^2 3d^6$ c) [Ar] $3d^8$
d) [Ar] $4s^2 3d^5 4p^1$ e) [Kr] $4s^2 3d^6$

$_{26}Fe$

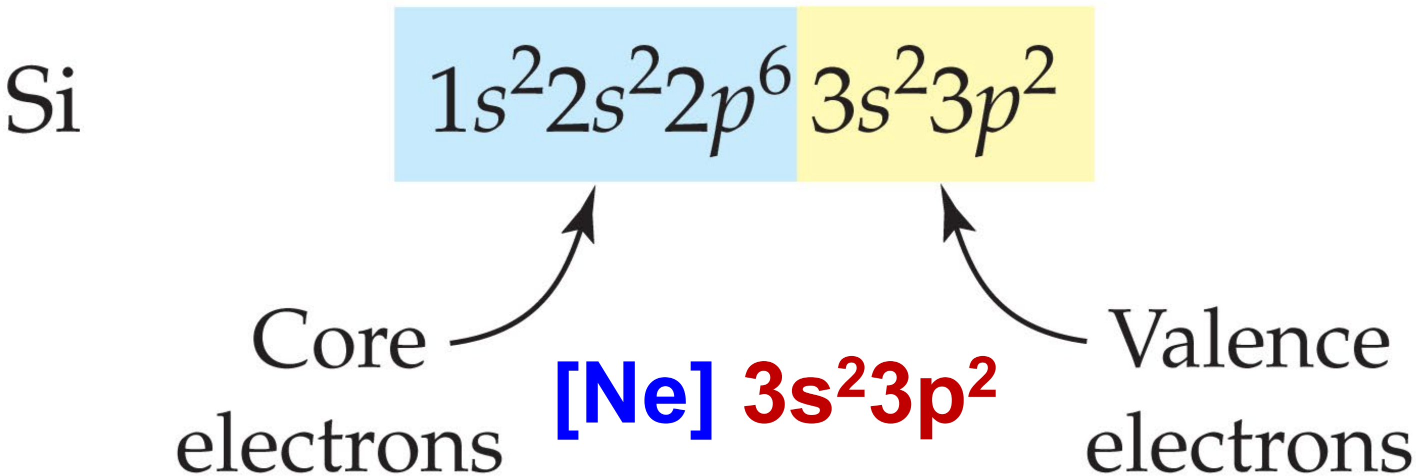
Orbitals Fill in the Following Order:
1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d* 4*p* 5*s* 4*d* 5*p* 6*s* 4*f* 5*d* 6*p* 7*s* 5*f* 6*d* 7*p*

$_{26}Fe$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

[Ar] $4s^2 3d^6$

Valence Electrons and Core Electrons

Si has 4 valence electrons (those in the n = 3 principal shell) and 10 core electrons.



[Ne] $3s^2 3p^2$

Valence electrons: electrons in the outermost shell [the shell with the highest principal quantum number(s), n].

Example Questions

How many valence electrons are in selenium?

a) 1 b) 2 c) 4 d) 6 e) 8

$_{34}Se$

Orbitals Fill in the Following Order:

1*s* 2*s* 2*p* 3*s* 3*p* 4*s* 3*d* 4*p* 5*s* 4*d* 5*p* 6*s* 4*f* 5*d* 6*p* 7*s* 5*f* 6*d* 7*p*

$_{34}Se$: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

[Ar] $4s^2 3d^{10} 4p^4$

Example Questions

Which element has the electron configuration [Ar] $4s^1 3d^{10}$?

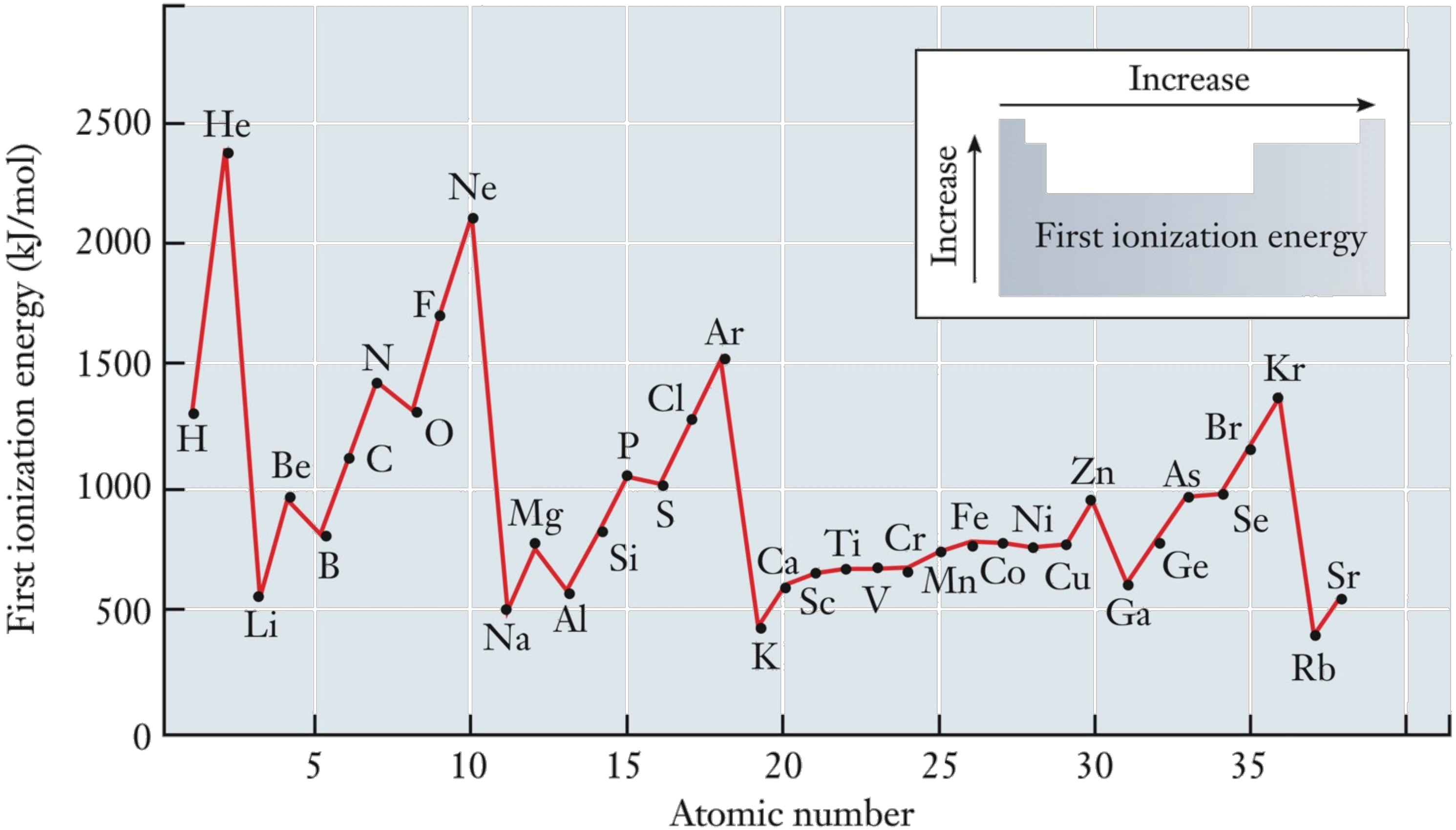
a) Co b) Zn c) Ga d) Ag e) Cu

$$[Ar]\ 4s^1 3d^{10}$$

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$$

$${}_{29}Cu$$

Ionization Energy



- Graph of the first ionization energy (in kJ/mol) vs. atomic number for the first 38 elements.

Example Problem

Q. Arrange these elements based on their increasing first ionization energies.

Se, Ge, K, S

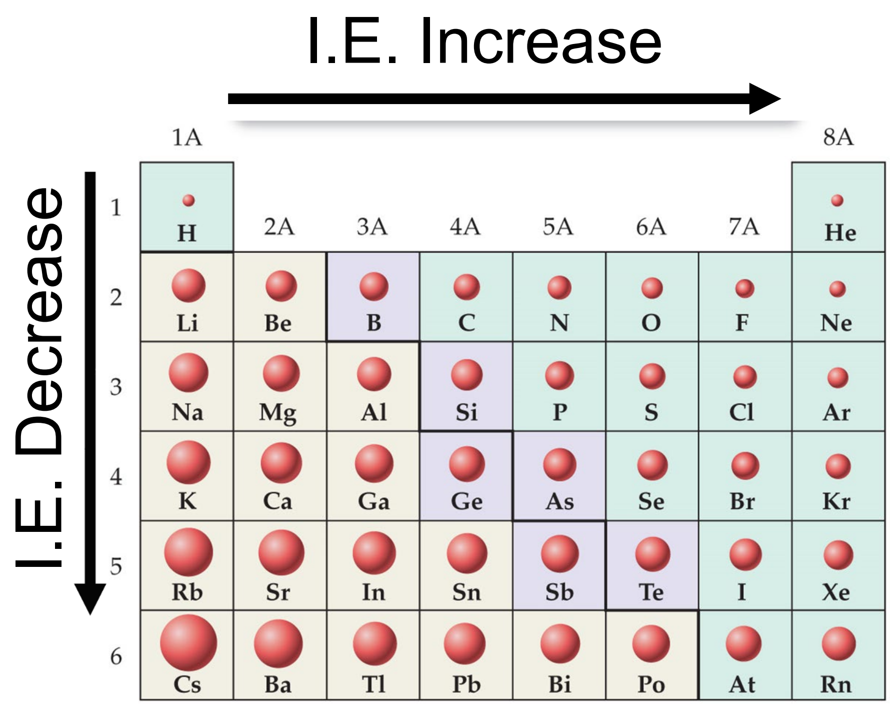
Se, S, *Group 6A (same group)*

Se < S

Se, Ge, K, Row 4 (same period)

K < Ge < Se

K < Ge < Se < S



Down a group, I.E. ***decreases.***

Across a row (L to R), I.E. ***increases.***