Contents

Chapter 4

General Chemistry

4.1 Outline

- Aqueous solutions (electrolytes, concentrations)

- Precipitation reactions (soluble and insoluble compounds)

- Molecular, ionic, and net ionic equations

- Oxidation-Reduction reactions

4.2 Terminology

In solutions, we need to define the following terms:

- solvent – The medium (e.g., water, ethanol, benzene, etc.) in which a solute is dissolved to form a solution.

- solute – The substance (e.g. NaCl, glucose, etc.) dissolved in a solvent to form a solution.

4.3 Concentration of Solute

The amount of solute in a solution is given by its concentration.

$$\text{Molarity(M)} = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{4.1}$$

$$\begin{aligned}
[\text{NaCl}] &= 0.1M \\
&= \frac{0.1 \text{ moles of NaCl}}{1 \text{ L of solution}}
\end{aligned}$$

4.4   Preparing Solutions

- Weigh out a solid solute and dissolve in a given quantity of solvent.

- Dilute a concentrated solution to give one that is less concentrated.

4.5   Using Molarity

What mass of oxalic acid, $H_2C_2O_4$, is required to make 250.00 mL of a 0.0500 M solution?

$$\text{molar mass} = (2 * 1.008) + (2 * 12.011) + (4 * 15.999)$$
$$= 2.016 + 24.022 + 63.996$$
$$= 90.034 \text{ g mol}^{-1}$$

$$250.00 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} \times \frac{0.05 \text{ mol}}{1 \text{L}} \times \frac{90.034 \text{ g } H_2C_2O_4}{1 \text{ mol } H_2C_2O_4} = 1.125425 \text{ g } H_2C_2O_4$$

4.6   Preparing a Solution by Dilution

You have 50.0 mL of 3.0 M $NaOH$ and you want 0.50 M $NaOH$. What does one do?

$$M_1V_1 = M_2V_2$$
$$(3.0)(50.0) = (0.5)V_2$$
$$V_2 = \frac{(3.0)(50.0)}{0.5}$$
$$V_2 = (6.0)(50.0)$$
$$V_2 = 300.0 \text{ mL}$$
$$= 3.0 \times 10^2 \text{ mL}$$

In an acid-base titration, it takes 38.55 mL of 0.650 M perchloric acid ($HClO_4$) to completely neutralize 25.00 mol calcium hydroxide ($Ca(OH_2)$) solution.

$$Ca(OH_2)(aq) + 2\,HClO_4(aq) \longrightarrow Ca(ClO_4)_2\,(aq) + 2\,H_2O\,(l)$$
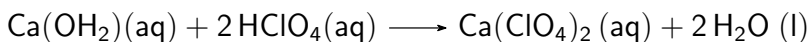
A) How many moles of $HClO_4$ are needed for the complete neutralization?

$$38.55\text{mL perchloric acid} \times \frac{1 \text{ L perchloric acid}}{1,000 \text{ mL perchloric acid}} \times \frac{0.650 \text{ mol}}{1 \text{ L}} = 0.0251 \text{ mol perchloric acid}$$

B) How many moles of $Ca(OH_2)_2$ got consumed during the neutralization?

$$0.0251 \text{ mol perchloric acid} \times \frac{1 \text{ mol } Ca(OH_2)_2}{2 \text{ mol perchloric acid}} = 0.01255 \text{ } Ca(OH_2)_2$$

C) What is the concentration of $Ca(OH_2)_2$ in the original solution before titration?

$$\frac{25.00 \text{ mol } Ca(OH_2)_2}{38.55\text{mL}} \times \frac{1,000 \text{ mL}}{1 \text{ mL}} =$$

4.7   Dissociation

- When an ionic compound dissolves in water, the solvent pulls the individual ions from the crystal and solvates them.

- This process is called dissociation.

$$NaCl(s) \longrightarrow Na^+ (aq) + Cl^-(aq)$$
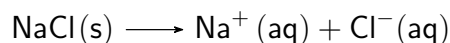
- An electrolyte is a substance that dissociates into ions when dissolved in water.

- Ionic compounds dissociate in water (e.g., $NaCl$, $BaCl_2$, etc.)

- Only a few molecular compounds are capable of dissociating in water.

- For example,
$$HCl(aq) \longrightarrow H^+(aq) + Cl^- (aq)$$
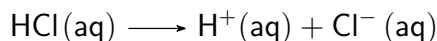
4.8   Electrolytes

- An electrolyte is a substance that dissociates into ions when dissolved in water.

- A nonelectrolyte may dissolve in water, but it does not dissociate into ions when it does so.

- There are many examples of molecular compounds (e.g., methanol (CH_3OH), table sugar (sucrose; $C_{12}H_{12}O_{11}$)) that serve as nonelectrolytes in water.

Table 4.1: Summary

	Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
Ionic	All	None	None
Molecular	Strong acids (see Table 4.2)	Weak acids	
		Weak bases	All other compounds

e.g., the molecular compound HCl is a strong acid that dissociates completely in water. As a result, HCl is a strong electrolyte.

$$HCl (aq) \longrightarrow H^+(aq) + Cl^-(aq)$$
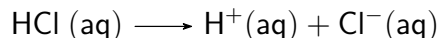
e.g., the molecular compound acetic acid, CH_3COOH, is a weak acid that is only partially dissociated. As a result, acetic acid is a weak electrolyte.

$$CH_3OOH (aq \cdot) \longleftrightarrow CH_3COO^- (aq \cdot) + H^+(aq \cdot)$$
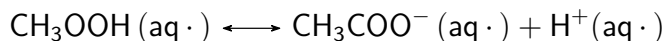
- Ion concentration can be measured using conductivity. Ions carry electrical charge from one electrode to the other, completing the electrical circuit.

No ions A nonelectrolyte solution does not contain ions, and the bulb does not light.

Few ions If the solution contains a small number of ions, the bulb will by only dimly lit.

Many ions If the solution contains a large number of ions, the bulb will be brightly lit.

4.9 Strong Electrolytes Are. . .

- Strong acids

  HCl Hydrochloric

  HBr Hydrobromic

  HI Hydroiodic

  HClO$_3$ Chloric

  HClO$_4$ Perchloric

  HNO$_3$ Nitric

  H$_2$SO$_4$ Sulfuric

- Strong bases

  - Group 1A metal hydroxides
    * LiOH
    * NaOH
    * KOH
    * RbOH
    * CsOH
  - Heavy group 2A metal hydroxides
    * Ca(OH)$_2$
    * Sr(OH)$_2$
    * Ba(OH)$_2$

- Also soluble ionic salts

Table 4.2: Solubility Guidelines for Common Ionic Compounds in Water

Soluble Ionic Compounds		Important Exceptions
Compounds containing	NO_3^-	None
	CH_3COO^-	None
	Cl^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	Br^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	I^-	Compounds of Ag^+, Hg_2^{2+}, and Pb^{2+}
	SO_4^{2-}	Compounds of Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
Insoluble Ionic Compounds		**Important Exceptions**
Compounds containing	S^{2-}	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+},
	CO_3^{2-}	Compounds of NH_4^+ and the alkali metal cations
	PO_4^{3-}	Compounds of NH_4^+ and the alkali metal cations
	OH^-	Compounds of NH_4^+, the alkali metal cations, Ca^{2+}, Sr^{2+},

- Note that all common ionic compounds of the alkali metal ions (group 1A of the periodic table) and the ammonium ion (NH_4^+) are soluble in water.

4.10   Precipitation Reactions

When ions that are insoluble (as could be predicted by the solubility guidelines in Table 4.2) are mixed and form compounds, a precipitate is formed.

The insoluble yellow solid formed on the right is lead iodide (PbI[2]).

$$2KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2KNO_3(aq)$$
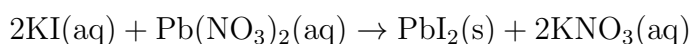
Figure 4.1: Lead Iodide

4.11   Metathesis (Exchange) Reactions

- Metathesis comes from a Greek word that means "to transpose."

- It appears that the ions in the reactants exchange, or transpose, ions.

- This is like switching dance partners!

$$\text{AgNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \leftrightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$$
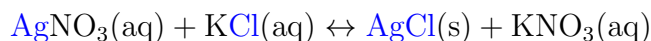
4.12   Molecular Equation

The molecular equation lists the reactants and products in their molecular forms.

$$\text{AgNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \leftrightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$$
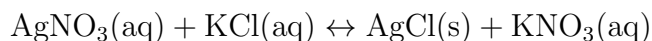
4.13   Ionic Equation

- In the ionic equation, all strong electrolytes (strong acids, strong bases, and soluble ionic salts) are dissociated into their ions.

- This more accurately reflects the species that are found in the reaction mixture.

$$\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{K}^+(\text{aq}) + \text{Cl}^- \rightarrow$$
$$\text{AgCl}(\text{s}) + \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$$
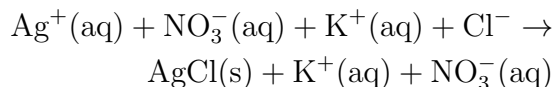
4.14   Net Ionic Equation

- To form the net ionic equation, cross out anything that does not change from the left side of the equation to the right.

$$\text{Ag}^+(\text{aq}) + \cancel{\text{NO}_3^-(\text{aq})} + \cancel{\text{K}^+(\text{aq})} + \text{Cl}^- \rightarrow$$
$$\text{AgCl}(\text{s}) + \cancel{\text{K}^+(\text{aq})} + \cancel{\text{NO}_3^-(\text{aq})}$$
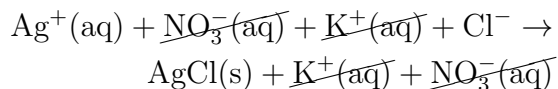
- The only things left in the equation are those things that change (i.e., react) during the course of the reaction.

$$\text{Ag}^+(\text{aq}) + \text{Cl}^- \qquad \text{AgCl}(\text{s})$$

4.15   Oxidation-Reduction Reactions

- An oxidation occurs when at atom or ion *loses* electrons.

- A reduction occurs when an atom or ion *gains* electrons.

- One cannot occur without the other.
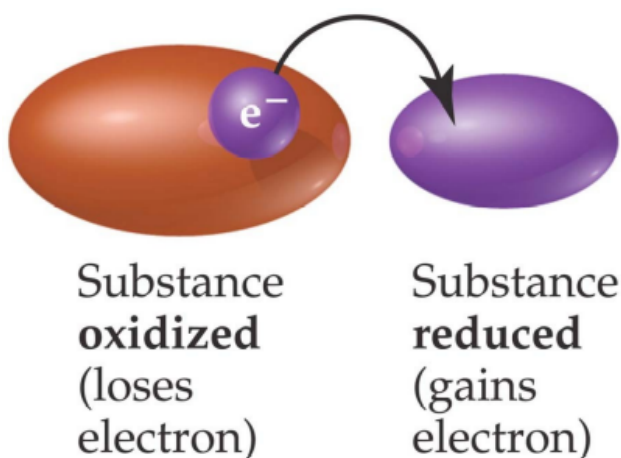
Figure 4.2: Oxidation-Reduction Reactions

4.16   Oxidation Numbers

- Elements in their elemental form have an oxidation number of 0.

- The oxidation number of a monatomic ion is the same as its charge.

- Nonmetals tend to have negative oxidation numbers, although some are positive in certain compounds or ions.

- Oxygen has an oxidation number of -2, except in the peroxide ion in which it has an oxidation number of -1.

- Hydrogen is -1 when bonded to a metal, $+1$ when bonded to a nonmetal.

- Fluorine always has an oxidation number of -1.

- The other halogens have an oxidation number of -1 when they are negative; they can have positive oxidation numbers; however, most notably in oxyanions (e.g., ClO_4^-).

- The sum of the oxidation numbers in a neutral compound is 0.

- The sum of the oxidation numbers in a polyatomic ion is the charge on the ion.

4.17   Acids and Bases

There are 3 definitions of acids and bases:

- Arrhenius

- Brønsted

- Lewis

The original one was Arrhenius. This describes the strong acids and bases, which was all they knew of at the time.

4.17.1   Arrhenius

Acids contain H^+, bases contain OH^-. This worked well until it was found that NH_3 was a base - but no OH^- in sight. So ... redefine bases.

4.17.2   Brønsted

Acids are H^+ donors, bases are H^+ acceptors. So acids have stayed essentially the same, but bases are now defined by the way they interact with acids. Acid base reactions are now seen as the transfer of an H^+ ion.

$$\begin{array}{lll} \text{HCl} & + \text{ NH}_3 & \rightarrow \text{NH}_4^+ + \text{Cl}^- \\ acid & base & \end{array}$$
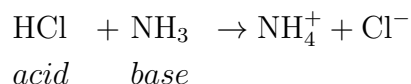
This also means that acids and bases come in pairs, called conjugate pairs.
Notice that the two conjugates differ by an H^+ ion.

$$NH_3 \text{ \& } NH_4^+ \quad HCl \text{ \& } Cl^-$$
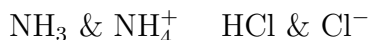
Some chemicals can act as both an acid & a base – we call them amphoteric. For example:
The Brønsted definition works for most acid-base reactions, so to predict the products of an acid-base reaction, you transfer an H^+ from one chemical (the acid) to another (the base). And then ... the found acids that do not contain H^+, like AlCl[3].

4.17.3   Lewis definition

It seemed reasonable that acid-base chemistry should be described by electrons, all other reactions are. So ...

Lewis acid e^- pair acceptor

Lewis base e^- pair donor

Notice that all the bases we have seen before have lone pairs of e$^-$. When you draw the Lewis structure

So things that are only Lewis acids are those with empty orbitals, metal cations (Fe^{2+}, Cu^+) and Group 13 elements (Al, B, etc.)

These three definitions are a hierarchy. All Arrhenius acids are also Brønsted acids and Lewis acids. But not all Lewis acids are Brønsted and/or Arrhenius acids; the same is true for bases.

Chapter 5

Gases

5.1 Characteristics of Gases

- Gas molecules are very far apart, so total volume of gases is mostly empty space.

- Gas molecules move at high velocities and high kinetic energies.

- Gas volume is dependent on pressure, temperature and moles of the gas.

5.2 Real Gases and Ideal Gases

- Real gases obey the laws of "ideal" gases at non-extreme conditions.

- Therefore, gas behavior (pressure, temperature, volume, and number of particles) is determined using gas laws.

5.3 Pressure

- Pressure is the force per unit area.

$$P = \frac{Force}{Area} \quad or \quad P = \frac{F}{A} \tag{5.1}$$

- So, the pressure will increase with a greater force exerted on an area or with a certain force exerted on a smaller area.

5.4 Measuring Pressure

- A barometer is one way to measure pressure.

- The height of the mercury column in the tube correlates to the atmospheric pressure.

5.5 Pressure Units

- There are several different units used to describe pressure. We will focus on four of them:

  atm atmospheres

  mmHg millimeters of Mercury

  torr

  psi pounds per square inch

- 1 atm = 760 mmHg, 1 atm = 760 torr, and 1 atm = 14.7 psi

- So 1 mmHg = 1 torr.

  - Note: atm, mmHg, and torr are all exact values; psi has been rounded to three sig figs.

5.6 Examples

1. A tire pressure gauge reads 33 psi. What is this pressure reading in torr?

$$33 \text{ psi} \times \frac{1 \text{ atm}}{14.7 \text{ psi}} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 1,\underline{7}06.12245 \text{ torr}$$

2. In a near-vacuum, the pressure is 0.100 mmHg. What is this pressure in atmospheres?

$$0.100 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 1.31579 \times 10^{-4} \text{ atm}$$

5.7 Temperature

- One factor involved in gas behavior is temperature (a measure of hot and cold).

- In the lab, temperature is measured in °C, but in gas law problems, the temperature needs to be in Kelvin (K)

$$K = C + 273.15 \tag{5.2}$$

- **Lecture Problem:** A gas is collected in the laboratory at 34°C. What is the temperature on the Kelvin scale? $34°C + 273.15 = 307.15°K$

5.8   The Gas Laws

- The Gas Laws focus on the relationship between pressure, temperature, volume, and the amount of a gas.

- We will discuss four gas laws in these sections: Boyle's Law, Charles' Law, Amonton's Law, and the Combined Gas Law.

- Note: Any references to standard temperature and pressure (STP) means 273 °K and 1 atm.

5.9   Boyle's Law

- If the temperature and amount of a gas are held constant, then the volume of a gas will be inversely proportional to its pressure.

$$\mathbf{P} \uparrow \mathbf{V} \downarrow \ \text{ and } \mathbf{P} \downarrow \mathbf{V} \uparrow \tag{5.3}$$

5.9.1   Boyle's Law Mathematically

Since volume and pressure are inversely proportional to each other, then the mathematical relationship would be:

$$V = \frac{k}{P} \text{ or } PV = k \text{ where } k \text{ is a constant.}$$

If PV is a constant then we can compare how P and V change.

$$P_1 V_1 = P_2 V_2 \tag{5.4}$$

5.10   Charles' Law

If the pressure and amount of a gas is held constant, then the volume of a gas will be directly proportional to its absolute temperature (temp. in Kelvin).

$$\mathbf{T} \downarrow \mathbf{V} \downarrow \ \text{ and } \mathbf{T} \uparrow \mathbf{V} \uparrow \tag{5.5}$$

5.10.1   Charles' Law Mathematically

Since temperature and volume are directly proportional to each other, then the mathematical relationship would be:

$$V = kT \text{ or } \frac{V}{T} = k \text{ where } k \text{ is a constant.}$$

If $\frac{V}{T}$ is a constant, then we can compare how T and V change.

$$\frac{P_1}{V_1} = \frac{P_2}{V_2} \tag{5.6}$$

5.11　Amonton's Law

If the volume and amount of a gas is held constant, then the pressure of a gas will be directly proportional to its absolute temperature (temp. in Kelvin).

$$\mathbf{T} \downarrow \mathbf{P} \downarrow \text{ and } \mathbf{T} \uparrow \mathbf{P} \uparrow \tag{5.7}$$

5.11.1　Amonton's Law Mathematically

Since temperature and pressue are directly proportional to each other, then the mathematical relationship would be:

$$P = kT \text{ or } \frac{P}{T} = k \text{ where } k \text{ is a constant.}$$

If $\frac{P}{T}$ is a constant, then we can compare how T and P change.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \tag{5.8}$$

5.12　The Combined Gas Law

The Combined Gas Law relates pressure, temperature, and volume of a gas given that the amount of the gas remains constant.

5.12.1　The Combined Gas Law Mathematically

If we combine all the gas laws together, we get:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \tag{5.9}$$

5.13　Densities and Molar Masses of Gases

- The density of a gas is expressed in grams/liter.

- Since the volume of a gas is dependent on pressure and temperature, the pressure and temperature must be given for a specific density.

- At STP, 22.4 L of a gas contains one mole of the gas. This is known as the molar volume (22.4 L/mol).

5.14　Examples

- Calculate the density, in g/L, of chlorine gas at STP.

- What is the molar mass of a gas having a density of 2.99 g/L at STP?

- The molar mass of a gas at STP is 132.5 g/mol. What is the density at 56°C and 1250 torr?

5.15   The Ideal Gas Equation

- The Ideal Gas Law relates all four properties of a gas: pressure, temperature, volume, and amount (moles).

$$PV = k \quad \frac{V}{T} = k \quad \frac{P}{T} = k \quad \frac{V}{n} = k$$

- If all of the above relationships are combined we get:

$$k = \frac{PV}{nT} \tag{5.10}$$

- For the Ideal Gas Law, the constant is R (the universal gas constant, $0.0821 \frac{L \times atm}{mol \times K}$).

- So $\frac{PV}{nT} = R$ or $PV = nRT$

5.16   Examples

- 50.0 g of N_2O is placed in a 10.0 L container. The temperature is 10.0°C. What is the pressure, in torr, of the gas?

5.17   Mixture of gases and Partial Pressures

For a multicomponent gas mixture (consisting of gases a, b, c, etc).

$$\text{Partial Pressures: } P_a = \frac{n_a RT}{V}, P_b = \frac{n_b RT}{V}, P_c = \frac{n_c RT}{V}, \dots$$

Dalton's Law of Partial Pressures:

$$
\begin{aligned}
P_{total} &= P_a + P_b + P_c + \dots \\
&= \frac{n_a RT}{V} + \frac{n_b RT}{V} + \frac{n_c RT}{V} + \dots \\
&= \frac{RT}{V}(n_a + n_b + n_c + \dots) \\
&= \frac{RT}{V} n_{total} \\
\frac{P_a}{P_{total}} &= \frac{\frac{n_a RT}{V}}{n_{total} \times \frac{RT}{V}} \\
&= \frac{n_a}{n_{total}} \\
&= X_a \text{ (mole fraction)} \\
P_a &= X_a P_{total}
\end{aligned}
\tag{5.11}
$$

5.18   Gas Stoichiometry

How many grams of water form when 1.24 L of H_2 gas at STP completely reacts with O_2?

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g)$$
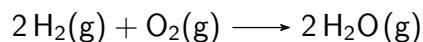
$$1.24 \text{ L } H_2 \times \frac{1 \text{ mol } H_2}{22.4 \text{ L } H_2}$$

5.19   Kinetic Molecular Theory: A Model for Gases

In this theory, a gas is modeled as a collection of particles (either molecules or atoms, depending on the gas) in constant motion. A single particle moves in a straight line until it collides with another particle (or with the container wall). Kinetic molecular theory has 3 basic postulates (assumptions)

1. The size of a particle is negligibly small: the particles themselves occupy no volume, even though they have mass

2. The average kinetic energy of a particle is proportional to the temperature in K: $KE \propto T$.

3. The collision of one particle with another (or with the walls) is completely elastic. This means that when two particles collide, they may exchange energy, but there is no overall loss of energy. Any kinetic energy lost by one particle is completely gained by the other.

   - The ideal gas law follows directly from the kinetic molecular theory, validating the latter, at least under conditions where the ideal gas law works.

   - The concept of pressure and each fo the gas laws follows conceptually from the kinetic molecular theory.

5.20   The Nature of Pressure

As each particle collides with a surface, it exerts a force upon that surface. The result of many particles in a gas sample exerting forces on the surfaces around them is a constant pressure.

5.20.1   Boyle's Law

Boyle's law states that, for a constant number of particles at constant temperature, the volume of a gas is inversely proportional to its pressue. If we decrease the volume of a gas, we force the gas particles to occupy a smaller space. It follows from the kinetic molecular theory that, as long as the temperature remains the same, the result is a greater number of collisions with the surrounding surfaces and therefore a greater pressure.

5.20.2   Charles' Law

Charles' Law states that, for a constant number of particles at constant pressure, the volume of a gas is proportional to its temperature (in K). According to the kinetic molecular theory, when we increase the temperature of a gas, the average speed, and thus the average kinetic energy of the particles increases. Since this greater kinetic energy results in more frequent collisions and more force per collision, the only way for the pressure to remain constant is for the volume to increase. The greater volume spreads the collision out over a greater area, so that the pressure $\frac{F}{A}$ in unchanged.

5.21   Avogadro's Law

Avogadro's Law states that, at constant temperature and pressure, the volume of a gas is proportional to the number of particles. According to the kinetic molecular theory, when we increase the number of particles in a gas sample, the number of collisions with the surrounding surfaces increases. Since the greater number of collisions would result in a greater overall force on surrounding surfaces, the only way for the pressure to remain constant is for the volume to increase so that the number of particles per unit volume (and thus the number of collisions) remains constant.

5.22   Temperature and Molecular Velocities

- The kinetic energy (KE) of a particle is $\frac{1}{2}mv^2$ where m is the mass of the particle and v is the velocity of the particle (KE is the integral of momentum mv).

- In a gas mixture at a given temperature, lighter particles travel faster (on average) than heavier ones.

- Root mean square velocity $u_{rms} = \sqrt{\vec{u^2}}$ where $\vec{u^2}$ is the average of the squares of the particle velocities.

- u_{rms} is conceptually similar to average velocity, but not identical

- Average KE of one mole of gas particles:

$$KE_{avg} = \frac{1}{2}N_A m \vec{u^2} \tag{5.12}$$

  where N_A is Avogadro's number and m is the mass of each particle.

- From postulate 2 of the Kinetic Molecular Theory, the average kinetic energy is proportional to the temperature in K. The proportionality constant is $\frac{3}{2}R$.

$$KE_{avg} = \frac{3}{2}RT \text{ (for 1 mole)} \tag{5.13}$$

where R is the gas constant in different units $R \Rightarrow 8.314\frac{J}{mol\times K}$

$$\frac{1}{2}N_A m\vec{u} = \frac{3}{2}RT$$

$$\vec{u}^2 = \frac{3RT}{N_A m}$$

$$= \frac{3RT}{\mu}$$

$$\vec{u}^2 = u_{rms}$$

$$= \sqrt{\frac{3RT}{\mu}}$$

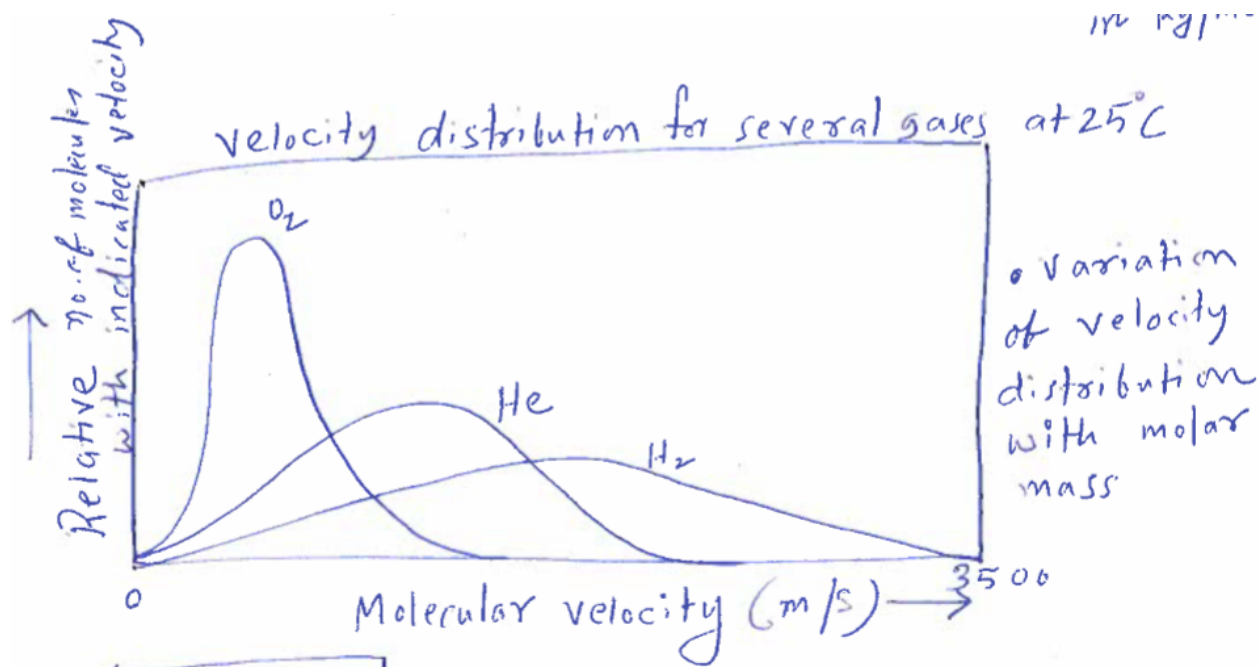where μ is the molar mass in kg/mol.

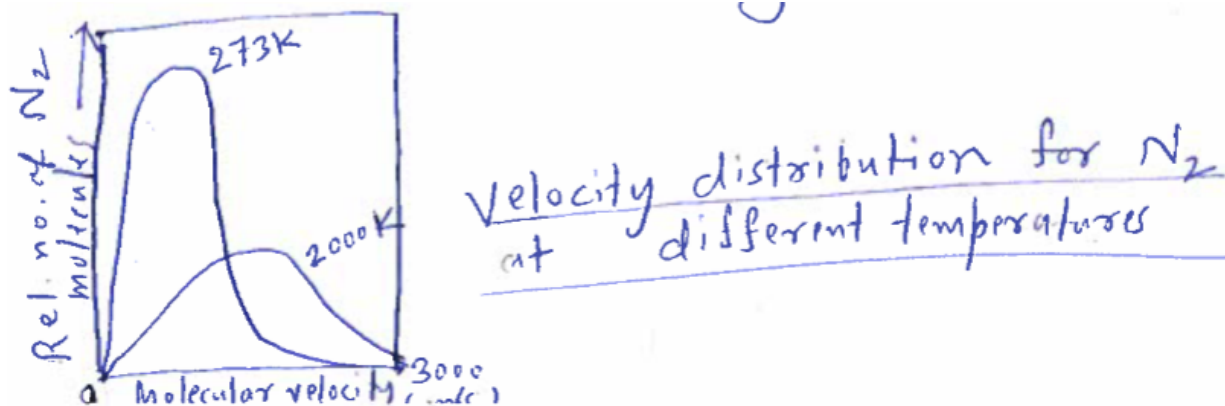Figure 5.1: Velocity distributions for several gases at 25°C

Figure 5.2: Velocity distributions for N_2 at different temperatures

5.23   Diffusion and Effusion

- The process by which gas molecules spread out in response to a concentration gradient is diffusion.

- Heavier molecules diffuse more slowly than lighter ones, so the first molecules you smell from a perfume mixture are the lighter ones.

- A process related to diffusion is effusion, the process by which a gas escapes from a container into a vacuum through a small hole.

- Heavier molecules effuse more slowly than lighter ones.

- Graham's law of effusion

$$\frac{\text{rate } A}{\text{rate } B} = \sqrt{\frac{\mu_B}{\mu_A}} \tag{5.14}$$

where rate A and rate B are effusion rates of gases A and B and μ_A and μ_B are their molar masses.

An unknown gas effuses at a rate that is 0.462 times that of N_2 gas (at the same temperature).

Calculate the molar mass of the unknown gas in g/mol.

$$\frac{\text{rate unknown}}{\text{rate } N_2} = \sqrt{\frac{\mu_{N_2}}{\mu_{\text{unknown}}}}$$

$$\frac{\text{rate unknown}^2}{\text{rate } N_2^2} = \frac{\mu_{N_2}}{\mu_{\text{unknown}}}$$

$$\frac{\text{rate unknown}^2 \times \mu_{\text{unknown}}}{\text{rate } N_2^2} = \mu_{N_2}$$

$$\mu_{\text{unknown}} = \frac{\mu_{N_2} \times \text{rate } N_2^2}{\text{rate unknown}^2} \div \frac{\text{rate } N_2^2}{\text{rate } N_2^2}$$

$$= \frac{\mu_{N_2}}{\left(\frac{\text{rate unknown}}{\text{rate } N_2}\right)^2}$$

$$= \frac{28.08 \text{ g/mol}}{(0.462)^2}$$

$$\approx 131 \text{ g/mol}$$

The unknown gas is most likely Xenon.

5.24 Real Gases: The Effects of Size and Intermolecular Forces

Ideal behavior:

$$V = \frac{nRT}{P} \tag{5.15}$$

Corrected for volume of gas particles:

$$V = \frac{nRT}{P} + nb$$
$$V - nb = \frac{nRT}{P} \tag{5.16}$$

where n is the number of particles and b is a constant depending on the gas.
Ideal behavior:

$$P = \frac{nRT}{V} \tag{5.17}$$

Corrected for intermolecular forces:

$$P = \frac{nRT}{V} - a\left(\frac{n}{V}\right)^2$$
$$P + a\left(\frac{n}{V}\right)^2 = \frac{nRT}{V} \tag{5.18}$$

VanderWaals Equation show the corrected equation with the correction for intermolecular forces and particle volumes:

$$\left[P + a\left(\frac{n}{V}\right)^2\right] \times [V - nb] = nRT \tag{5.19}$$

5.24.1   Conditions for Ideal Behaviors of Gases

1. Volume of gas particles is negligible compared to the space between them

2. Forces between the gas particles are not significant.

Chapter 6

Thermochemistry

Chapters 1-5 study matter, now we study energy.

Warming your hands with chemical hand warmers involves many of the principles of thermochemistry, the study of the relationships between chemistry and energy. When you open the package that contains the hand warmer, the contents are exposed to air, and a reaction that gives off heat to its surroundings occurs. Most handwarmers involve the oxidation of iron:

$$4\,Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)$$
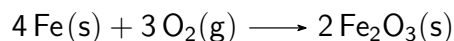
In this chapter, we look at how chemical reactions can exchange energy with their surroundings and how we can quantify the magnitude of those exchanges.

6.0.1 Applications

- Heating of homes
- Production of energy

6.1 Key Definitions

Energy Capacity to do work

Work Result of a force active through a distance

Examples of work

- Pushing a box across the floor
- a billiard ball rolling across a billiard table and colliding with a second, stationary ball

Potential energy Associated with position or composition. Example: Raising a billiard ball off the table increases its potential energy.

Chemical energy Associated with relative positions of electrons and nuclei in atoms and molecules

Law of conservation of energy energy can be neither created nor destroyed; it can assume different forms

System chemicals in a beaker (or handwarmers) for example

Surrounding water that the chemicals are dissolved in, the beaker, the lab bench, air in the room, etc.

- Surroundings gain the exact amount of energy lost by the system and vice versa.

6.2   Units of Energy

- $KE = \frac{1}{2}mv^2$, $[KE] = [m][v] = \text{kg} \times \frac{m}{s}$

- 1 Joule (J) $= 1 \frac{\text{kg m}^2}{\text{s}^2}$

- 1 calorie $= 4.184$ J

6.3   1st law of thermodynamics

- The total energy of the universe is constant $\rightarrow$ Energy is neither created, nor destroyed, universe does not exchange energy with anything else.

- According to the 1st law, a device that continually produces energy with no energy input cannot exist.

6.3.1   Internal Energy (IE)

- The internal energy of a system is the sum of the kinetic and potential energies of all the particles that compose the systems.

- It is a "state function".

- State of a chemical system is specified by parameters such as temperature, pressure, concentration, and phase (solid, liquid, or gas)

- Elevation of 10,000 ft, for example, is a state function no matter how you climbed it; the distance, however, is not a state function as you can take any route.

$$\Delta E = E_{final} - E_{initial}$$
$$\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$$
$$\Delta E = E_{product} - E_{reactant}$$
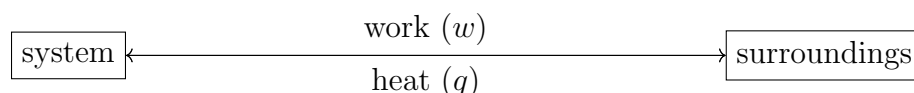
- System can exchange energy with its surrounding through heat and work.

- According to 1st law of thermodynamics

$$\Delta E = q + w \tag{6.1}$$

6.4   Quantifying Heat and Work

Experimentally, $q \propto \Delta t$ where q is heat absorbed by the system and Δt is the change of temperature.

$$q = c \times \Delta t \tag{6.2}$$

where c is the heat capacity (quantity of heat required to change temperature by 1°C).

$$q = m \times s \times \Delta t$$
$$[J] = [g] \times \left[\frac{J}{gC}\right] \times [C] \tag{6.3}$$

where m is the mass and s is the specific heat.

6.5   Work: Pressure Volume Work

$$\begin{aligned}
W &= -P\Delta V \\
&= -P(V_f - V_i) \\
&= P(V_i - V_f)
\end{aligned} \tag{6.4}$$

Combustion of gasoline causes gases within the cylinders of an automobile engine to expand, pushing the piston outward and moving the car wheels.

6.6   Enthalpy

Enthalpy – Heat evolved in a chemical reaction at constant pressure.
Firstly, at constant volume (chemical rxn [reaction] in a sealed container):

$$\begin{aligned}
W &= -P\Delta V \\
&= 0 \\
\Delta E_{rxn} &= q_v + w \\
&= q_v
\end{aligned}$$

When chemical reactions occur open to the atmosphere at constant pressure, both q and w are involved in ΔE_{rxn}.
We are often interested only in q, not w. For example, when we burn natural gas in the furnace to heat our homes.

Enthalpy H, a new thermodynamic quantity, is thus introduced.

$$H = E + PV$$
$$\Delta H = \Delta E + P\Delta V \quad \text{(at constant pressure)}$$
$$= (q_p + W) + P\Delta V \tag{6.5}$$
$$= q_p + W - W$$
$$= q_p$$

6.7 ΔE and ΔH

- Conceptually they are similar

- ΔE is a measure of all of the energy (q and w) exchanged with the surroundings

- ΔH is only a measure of heat exchanged (q) under conditions of constant pressure.

- For chemical rxns that do not exchange much work with the surroundings, i.e., $W = -P\Delta V$ is small as ΔV is small, $\Delta H \approx \Delta E$ (nearly identical)

- For chemical reactions that produce or consume large amounts of gas, hence have large ΔV (and hence large W), $\Delta H \neq \Delta E$ (significantly different)

6.8 Exothermic and Endothermic Reactions

- $\Delta H > 0$ is an endothermic reaction, chemical reaction absorbs heat from the surroundings.

  - Example: The reaction that occurs in the chemical cold packs used to ice athletic injuries $\rightarrow$ The surroundings, including the bruised wrist, get colder as the cold pack absorbs energy.

- $\Delta H < 0$ is an exothermic reaction, chemical reaction radiates heat to its surroundings.

  - Example: Chemical handwarmers.

6.9 Stoichiometry involving ΔH: Thermochemical Equations

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$$
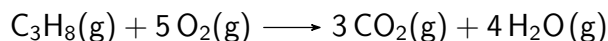
$$\Delta H_{rxn} = -2044 kJ$$
$$1 \text{ mol } C_3H_8 = -2044 kJ$$
$$5 \text{ mol } O_2 = -2044 kJ$$
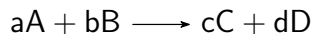$$1 \text{ mol } O_2 = \frac{-2044}{5} kJ$$
$$= -408.8 kJ$$

6.10   Hess' Law

6.11   Enthalpies of Reaction From Standard Heats of Formation

- Standard state

    - For a gas: pure gas at 1 atm

    - For a liquid or solid: pure substance in its most stable form at 1 atm (and other 25°C).

    - For a substance in solution: 1M concentration.

- Standard enthalpy change $(\Delta H°) \rightarrow \Delta H$ for a process when all reactants and products are in their standard states

- Standard Enthalpy of Formation $(\Delta H_f°)$

    - For a pure compound: ΔH when 1 mole of the compound forms from its constituent elements in their standard states

    - For a pure element: $(\Delta H_f°) = 0$

$$C(s, graphite) + 2\,H_2(g) \longrightarrow CH_4(g) \quad (\Delta H_f°) = -74.6 \text{ kJ/mol}$$
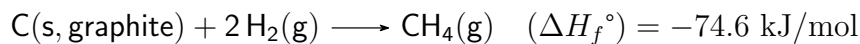
- Standard enthalpy change for a reaction (ΔH_{rxn})

$$aA + bB \longrightarrow cC + dD$$
$$\Delta H_{rxn} = [] - []$$

Chapter 7

Quantum Theory & the Electronic Structure of Atoms

7.1 Outline

- Examine the wavelike properties of light (wavelength, frequency, and speed)

- Describe particle behavior of light in terms of quantized energy and photons

- Line spectra and the Bohr model

- Wave behavior of matter and Heisenberg's Uncertainty Principle

- Quantum mechanics and atomic orbitals

- Representations of orbitals and electron configurations

7.2 Electromagnetic Radiation

- Electromagnetic Radiation – A form of energy that has wave characteristics and that propagates throguh a vacuum at the characteristic speed of light 3.00×10^8 m/s.

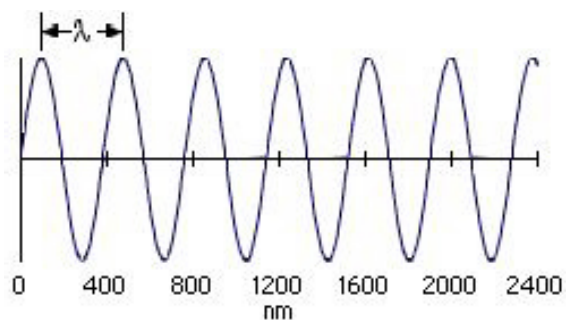- Most subatomic particles behave as PARTICLES and obey the physics of waves.

Figure 7.1: A picture of a wave in the ocean.

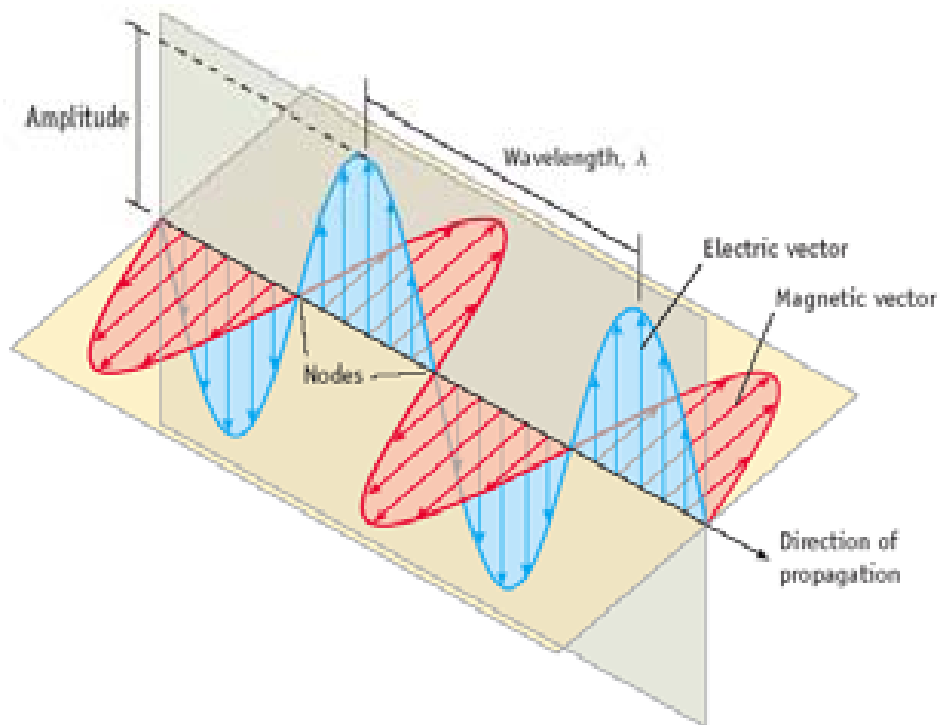Figure 7.2: A wave plotted on a 2-dimensional graph.

Figure 7.3: A combination of an electric component and magnetic component.

7.3   Wavelength and Frequency

- Wavelength – the distance between two adjacent peaks or between two adjacent troughs.

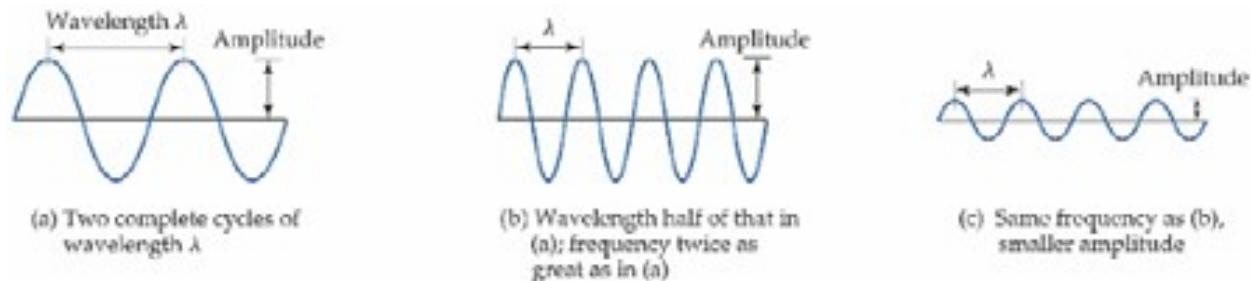- Frequency – the number of times per second that one complete wavelength passes a point.
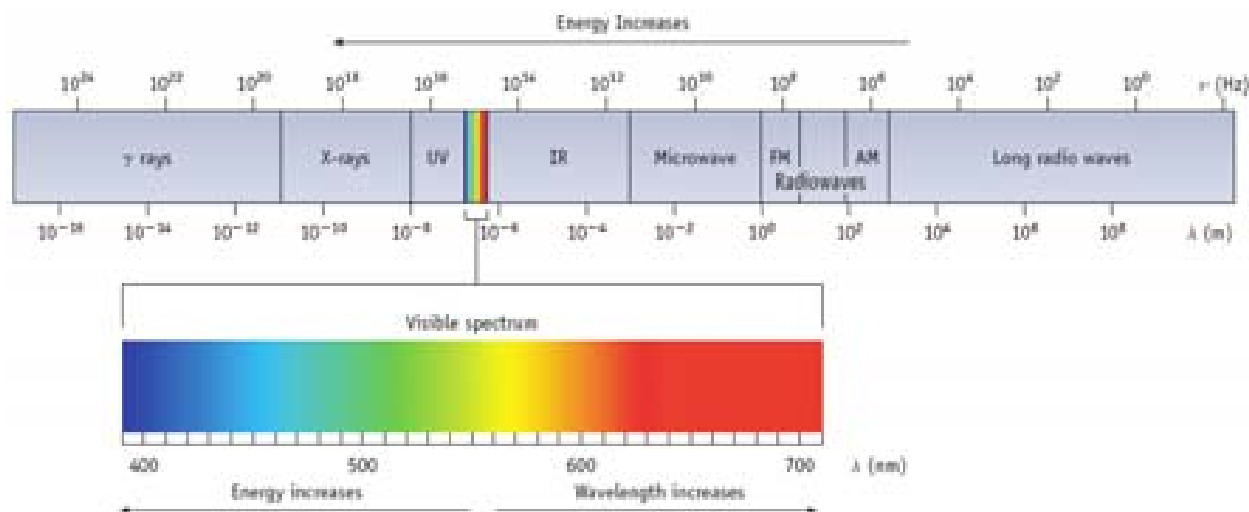
Figure 7.4: Wavelength and Frequency

Figure 7.5: Electromagnetic Spectrum

- long wavelength $\epsilon \to$ small frequency

- short wavelength $\epsilon \to$ high frequency

- Therefore, wavelength and frequency are inversely related.

7.4   Wavelength-Frequency Relationship

- All electromagnetic radiation moves at the same speed, specifically the speed of light. $c = 2.998 \times 10^8$ m/s.

- The inverse relationship between frequency and wavelength for electromagnetic radiation is

$$\nu = \frac{c}{\lambda} \tag{7.1}$$

where c is the speed of light, λ (lambda) is the wavelength, and ν (nu) is the frequency.

Table 7.1: Common Wavelength Units

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X-ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	TV, radio
Kilometer	km	1000	Radio

7.5   Common Frequency Unit

- Frequency is typically expressed in cycles per second, a unit also called a hertz (Hz). A hertz is equivalent to reciprocal second.

- A particular FM radio station at a frequency of 101.3 MHz, which could also be expressed as:
$$101.3 \times 10^6 \text{ or } 101.3 \times 10^6 \ s^{-1}$$

7.6   Hot Objects

- Solids emit radiation when heated (referred to as *Blackbody radiation*).

- For example, a stove burner glows bright red, while the filament in a tungsten light bulb glows white.

- Hotter objects glow more white.

- Wavelength distribution of radiation clearly depends on temperature.

7.7   Quantization of Energy

- An object can gain or lose enegry by absorbing or emitting radiant energy in discrete QUANTA.

- **Energy of radiation is proportional to frequency**

$$E = h \cdot \nu \tag{7.2}$$

where $h = 6.626 \times 10^{-34} J \times s$ is Planck's constant.

7.8   Photoelectric Effect

- Shining light on a clean metal surface causes electrons to be ejected.

- For example, cesium metal will emit electrons when irradiated by light with a frequency of 4.60×10^{14} Hz or greater. Electrons from cesium will not be ejected if lower frequencies are used.

- Einstein suggested that an incident stream of tiny energy packets (quanta) were responsible for causing electrons to be ejected from the metals surface.

- These discrete energy packets/particles are referred to as "photons".

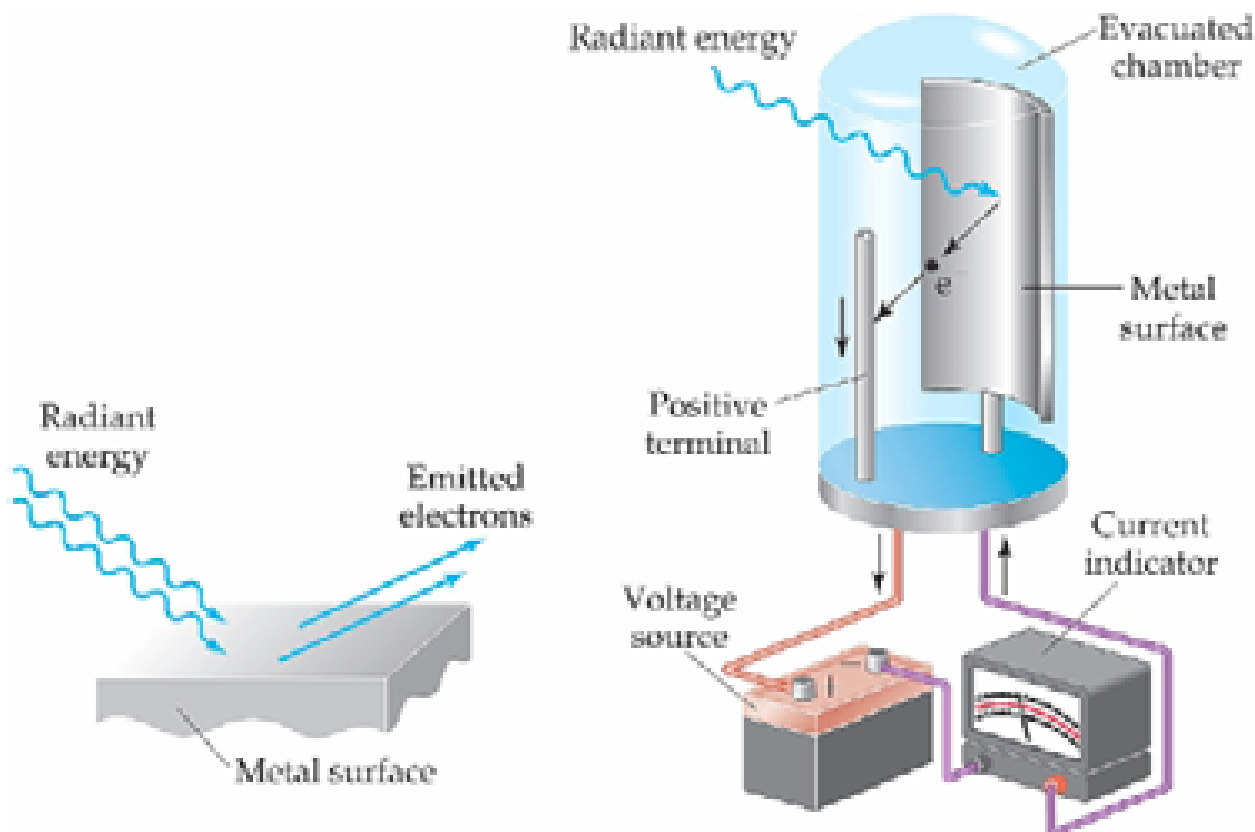- Once electrons were ejected, a current could be measured.

Figure 7.6: Photoelectric Effect

- Einstein was awarded the Nobel Prize in Physics in 1921 for his work on the photoelectric effect.

- **Energy of Photom** $= E = h\nu$, where the radiant energy is quanitzed.

- Radiant energy must be sufficient to overcome the attractive force between the electron and the metal itself.

- If an incident photon has more energy than required to remove an electron, the additional energy will be transferred to the electrons kinetic energy (i.e., energy associated with the electrons motion). See photoelectric worked example!

7.9 Continuous Spectrum of Wavelengths from White Light

- Continuous spectrum – a spectrum that contains radiation distributed over all wavelengths.

- In the schematic above, a white light source is used that is separated into its component colors by use of a prism.
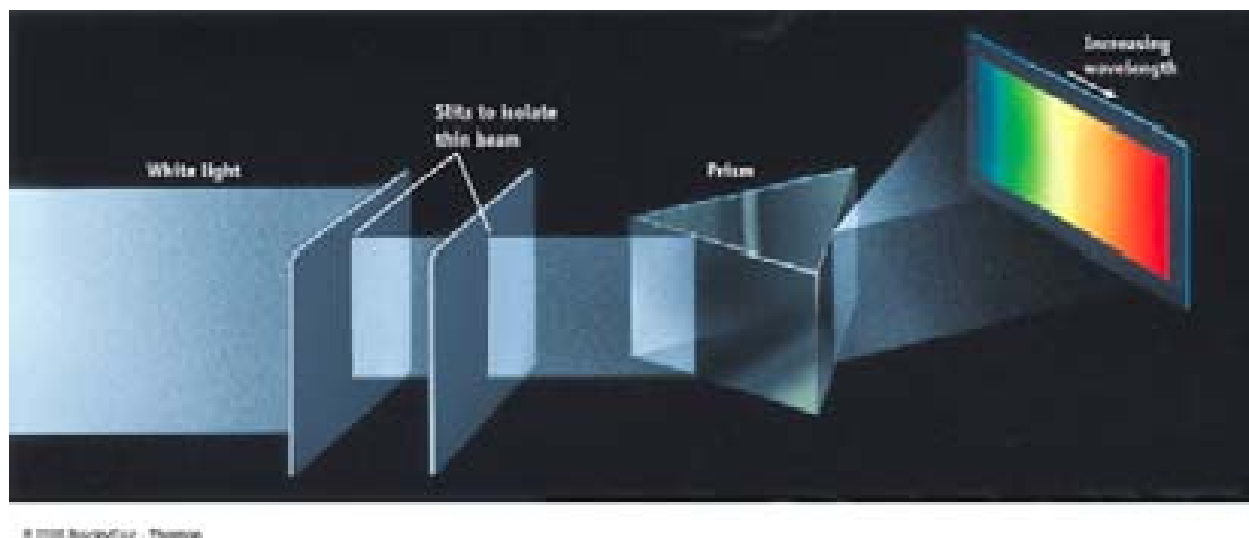

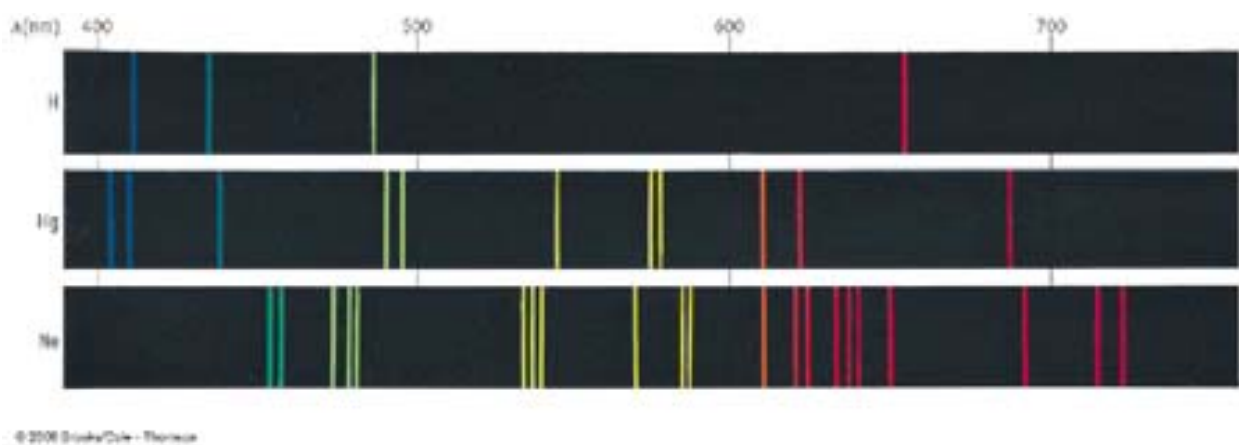Figure 7.7: Continuous Spectrum of Wavelengths from White Light

7.10 Line Emission Spectrum of Hydrogen

- Line spectrum – a spectrum that contains radiation at only specific wavelengths.

- In the schematic above, a potential is applied to a sealed tube of hydrogen at reduced pressure. Passing this light through a prism results in a 4 line pattern, each with its own specific wavelength. The wavelengths in the hydrogen spectrum are: 410 nm (violet), 434 nm (blue), 486 nm (blue-green), and 656 nm (red).
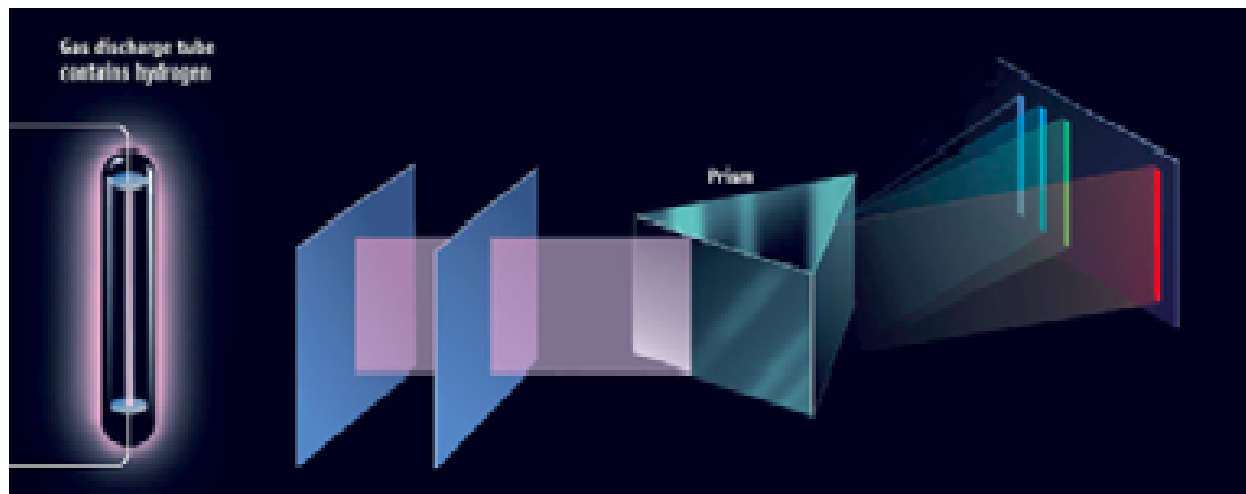
Figure 7.8: Line Emission Spectrum of Hydrogen

Figure 7.9: Line Emission Spectra of Hydrogen, Mercury, and Neon

7.11   Niels Bohr's Model of the Hydrogen Atom

Model based on the following three postulates:

- Only orbits of certain radii, corresponding to certain definite energies, are permitted for the electron in the hydrogen atom.

- An electron in a permitted orbit has a specific energy and is in an "allowed" energy state. An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.

- Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. (This energy is emitted or absorbed as a photon (7.2))
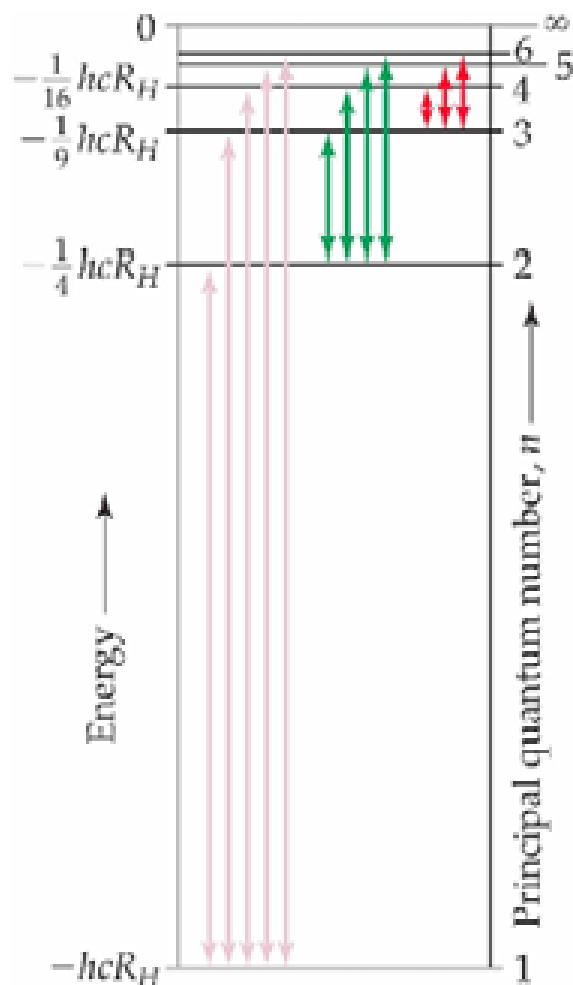
7.12   The Energy States of the Hydrogen Atom
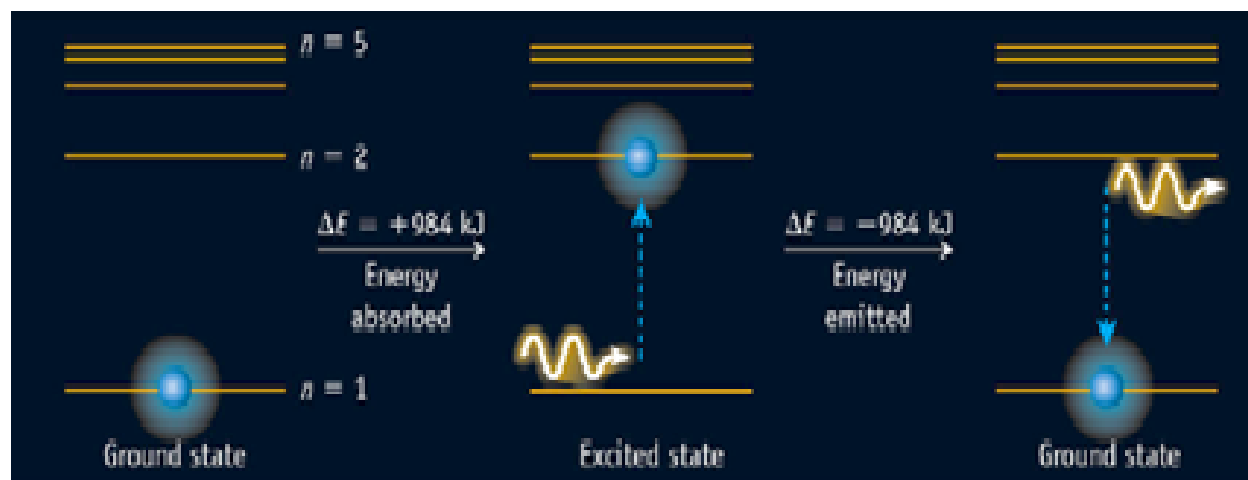

Figure 7.10: The Energy States of the Hydrogen Atom

$$E_n = -hcR_H \left(\frac{1}{n^2} \right)$$

$$= -2.18 \times 10^{-18} J \left(\frac{1}{n^2} \right) \quad (7.3)$$

- h, c and R_H are Planck's constant, the speed of light, and Rydberg's constant, respectively.

- n is called the principal quantum number, and takes on whole integer values in $[1, \infty)$.

- The lowest energy state ($n = 1$) is called the ground state.

- When an electron occupies the $n = 2$ orbit or higher, the atom is said to be in an excited state.

7.13   Electronic Transitions in the Hydrogen Atom

- An electron can move to a higher energy state if energy is absorbed.

- Conversely, radiant energy is emitted when the electron falls to a lower energy state.

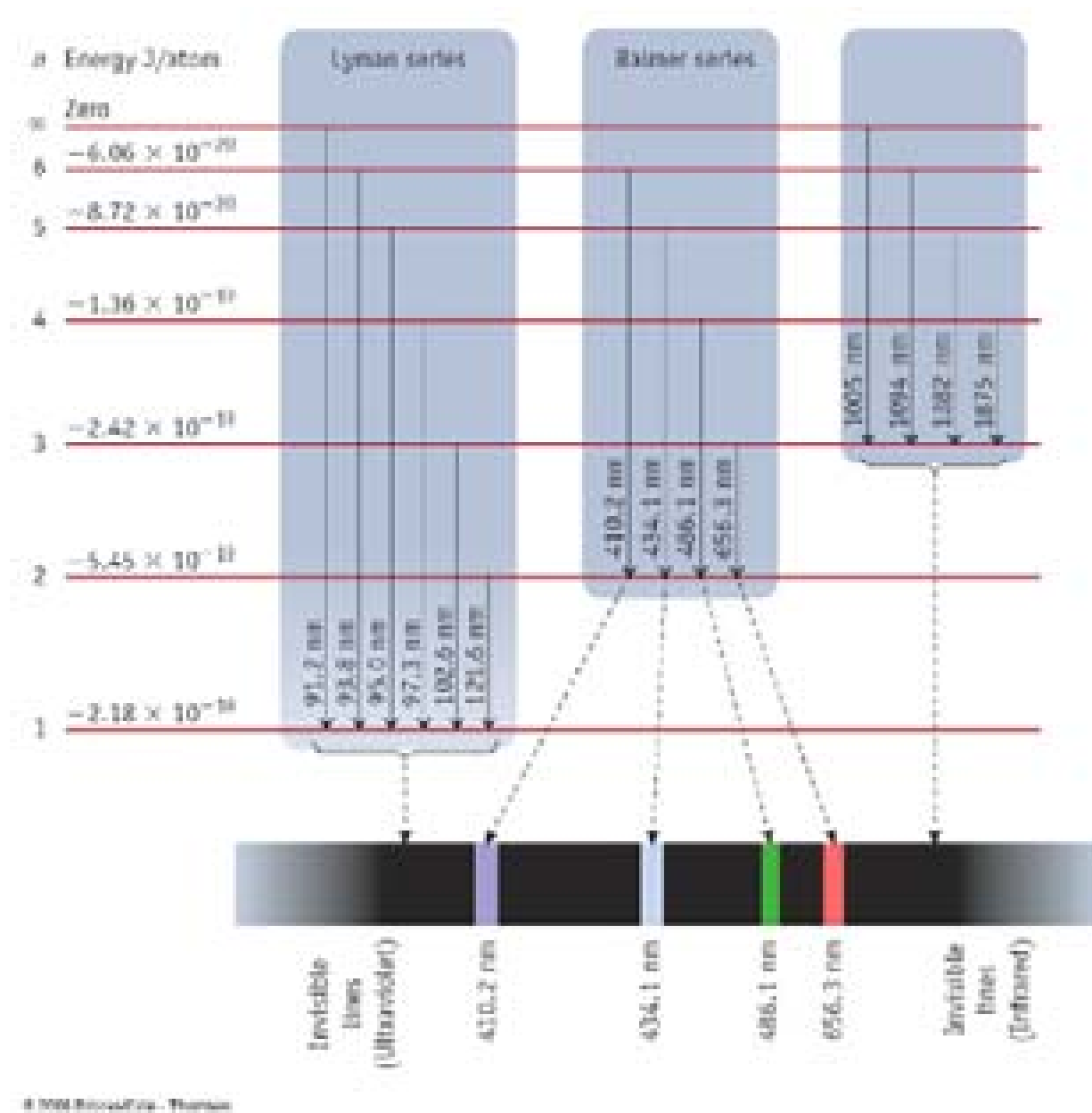Figure 7.11: Electron Transitions in the Hydrogen Atom

Figure 7.12: Paschen Series

- Notice that the energy is lowest (most negative) for $n = 1$.

- The energy difference between the *final* and *initial* states is given by the following equation:

$$\Delta E = E_{final} - E_{initial}$$
$$= E_{photon} \tag{7.4}$$
$$= h\nu$$

- Substituting (7.3) into the above equation, while taking into account that (7.1), the

following results:

$$\Delta E = h\nu$$

$$= \frac{hc}{\lambda}$$

$$= -2.18 \times 10^{-18} J \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \tag{7.5}$$

$$= 2.18 \times 10^{-18} J \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

- Another useful equation for directly calculating wavelength is as follows:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \tag{7.6}$$

7.14   The Wave Behavior of Matter

- Louis de Broglie (1892-1987) suggested that a stream of particles should also exhibit properties of a wave.

- He proposed that the characteristic wavelength of a particle (e.g., an electron) depends on its mass (m) and velocity (v). The quantity mv is the momentum and h is simply Planck's constant.

$$\lambda = \frac{h}{mv} \tag{7.7}$$

- The equation provides sufficient wavelengths for particles of small mass (e.g., an electron) but not for ones for large mass. Due to the inverse relationship, as the mass gets very large, the corresponding wavelength becomes small and thus difficult to observe experimentally.

7.15   Heisenberg's Uncertainty Principle

- Werner Heisenberg (1901-1976). The Heisenberg uncertainty principle states that there is an inherent uncertainty in the precision with which we can simultaneously specify the position and momentum of extremely small particles, such as an electron.

- Mathematically:

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi} \tag{7.8}$$

- where Δx is the uncertainty in the particle's position and $\Delta(mv)$ is the uncertainty in its momentum.

7.16   Quantum Mechanics and Atomic Orbitals

- Erwin Schrödinger (1887-1961), an Austrian physicist, developed an equation to describe both the wave- and particle-like behavior of the electron.

- Requires the use of complex calculus.

- Solving the Schrödinger equation provides a series of mathematical functions called wave functions that describe the electron in an atom.

- The wave functions are denoted by the lowercase Greek letter ψ (psi).

- ψ^2 is the probability or electron density. It relates to the probability of finding an electron in a certain region of space at a given instant.

7.17   Electron-Density Distribution in a Hydrogen Atom

- Diagram represents the probability of finding an electron in the ground state of a hydrogen atom.
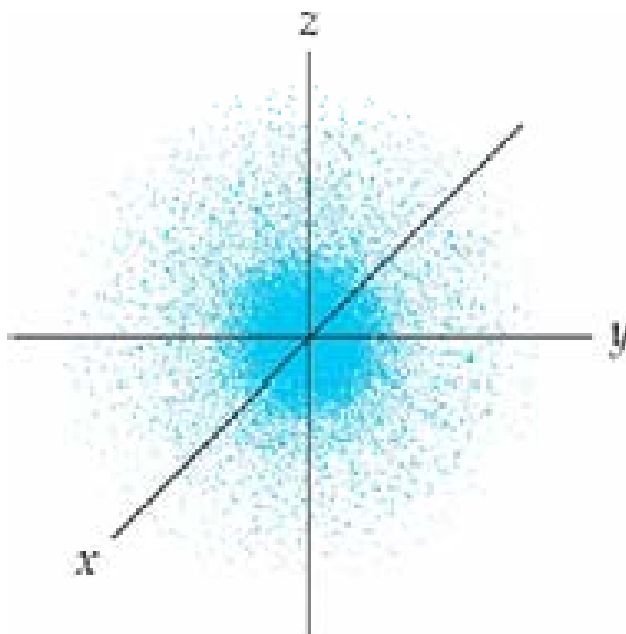

Figure 7.13: Electron-Density Distribution in a Hydrogen Atom

7.18   Orbitals and Quantum Numbers

- The wave function ψ depends on four quantum numbers (n, l, m_l, and m_s)

   Principal quantum number n that can have integral values of 1, 2, 3, ... As n increases, the orbital becomes larger and the electron is further from the nucleus.

- Energy and size of the electron.

Angular momentum quantum number l can take on integral values from 0 to $n - 1$ for each defined value of n.

- Shape of the home

Magnetic quantum number m_l that can take values of $-l$ to $+l$, including 0.

- Orientation

Spin magnetic quantum number m_s are two possible values are $+\frac{1}{2}$ (spin pointing up) and $-\frac{1}{2}$ (spin pointing down).

7.19   Shells and Subshells

Electron Shell A collection of orbitals with the same value of n.

Subshell A set of orbitals that have the same n and l values.

Table 7.2: Value of l, Corresponding Letter Designation and Number of Orbitals in a Subshell

Value of l	Corresponding Subshell Label	Number of Orbitals in Subshell
0	s	1
1	p	3
2	d	5
3	f	7

Table 7.3: Relationship among n, l, and m_l values

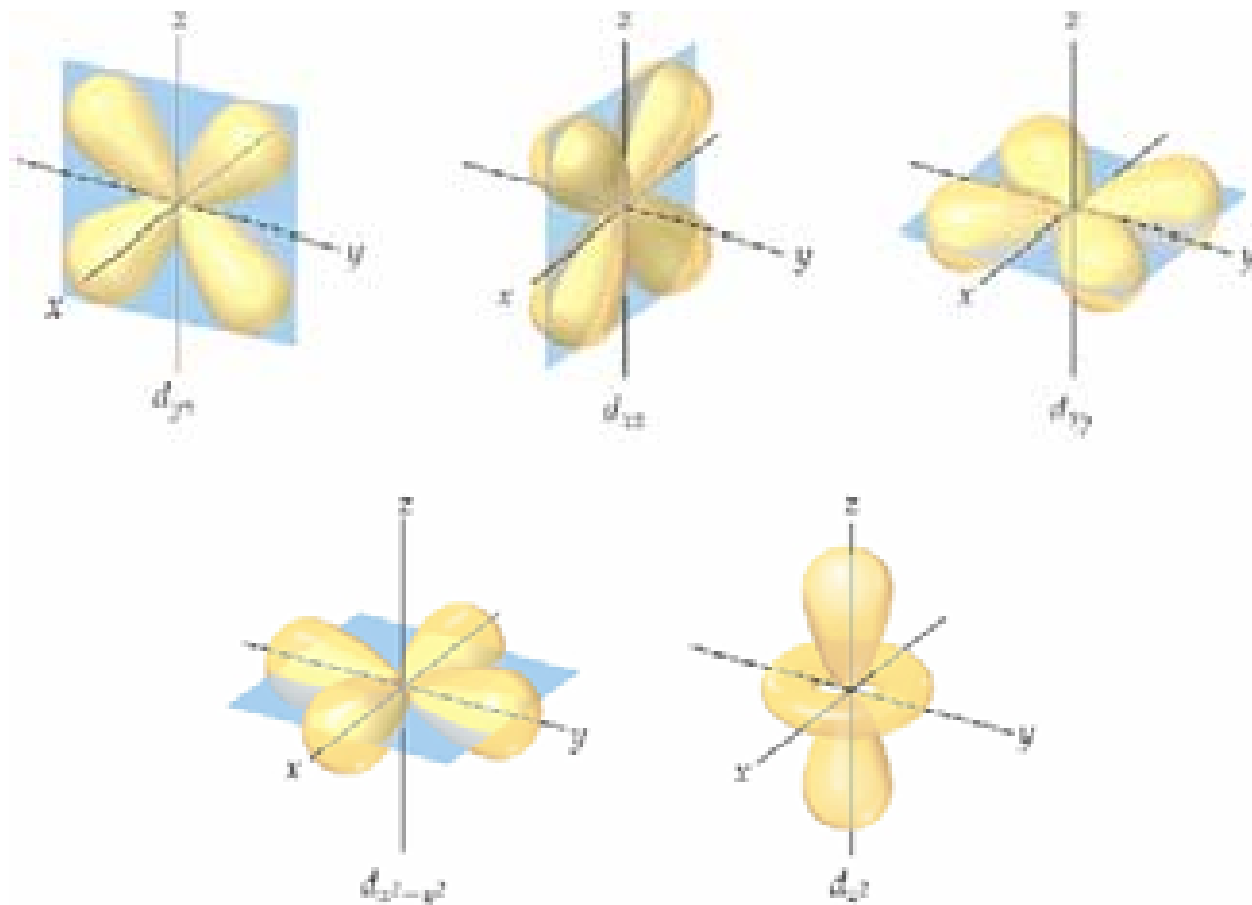| n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	$1s$	0	1	1
2	0	$2s$	0	1	
	1	$2p$	$1, 0, -1$	3	4
3	0	$3s$	0	1	
	1	$3p$	$1, 0, -1$	3	
	2	$3d$	$2, 1, 0, -1, -2$	5	9
4	0	$4s$	0	1	
	1	$4p$	$1, 0, -1$	3	
	2	$4d$	$2, 1, 0, -1, -2$	5	
	3	$4d$	$3, 2, 1, 0, -1, -2, -3$	7	16

7.20   The p Orbitals

Figure 7.14: The p Orbitals

Note the three different orientations ($m_l : -1, 0, 1$) on a Cartesian coordinate axis system! In each orbital, there are two lobes that are separated by a nodal plane (a point at which the electron density is zero).
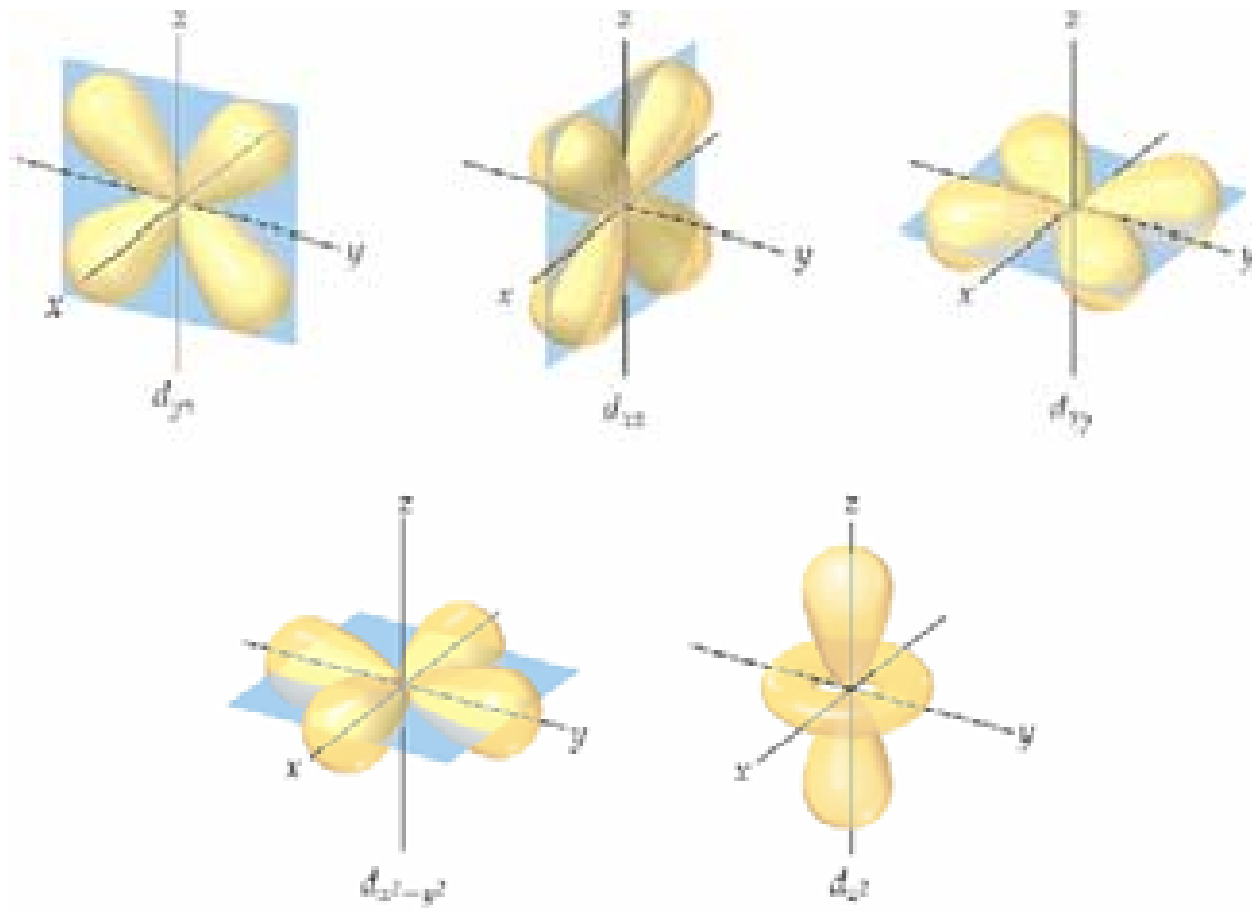
7.21   The d orbitals

Figure 7.15: The d Orbitals

These are the representations of the five d orbitals ($m_l : -2, -1, 0, 1, 2$)

7.22   Many-Electron Atoms - Relative Orbital Energy Levels

The energies follow the order:
$$ns < np < nd < nf$$
$$\text{e.g., } 3s < 3p < 3d$$

7.23   Electron Configurations

- We use the Aufbau Principle for filling electrons from bottom to top.

- Pauli Exclusion Principle – a maximum of two electrons can be placed in an orbital and must have opposite spin.

- **Hunds Rule** – for degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.
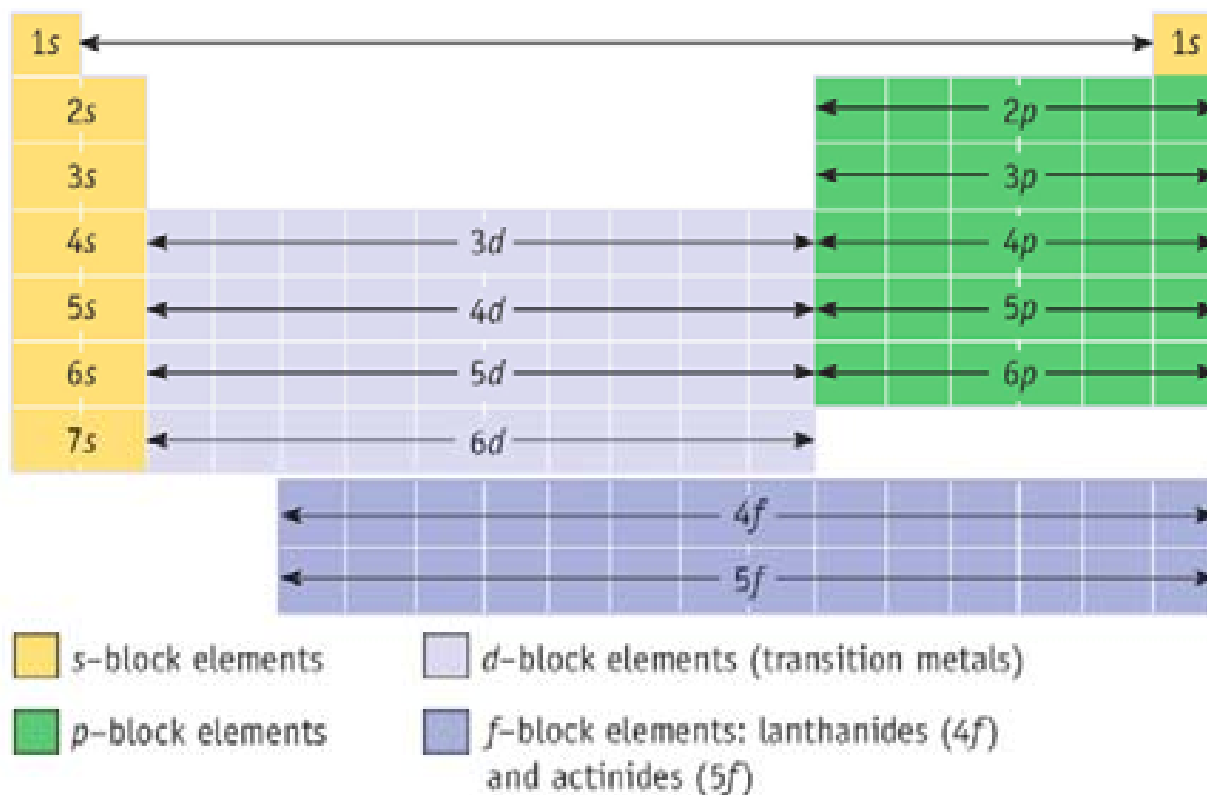
7.24   Subshell Filling Order

Figure 7.16: Periodic Table Levels

Chapter 8

Periodic Properties of the Elements

8.1   Outline

- History of the periodic table

- Effective nuclear charge

- Sizes of atoms and ions

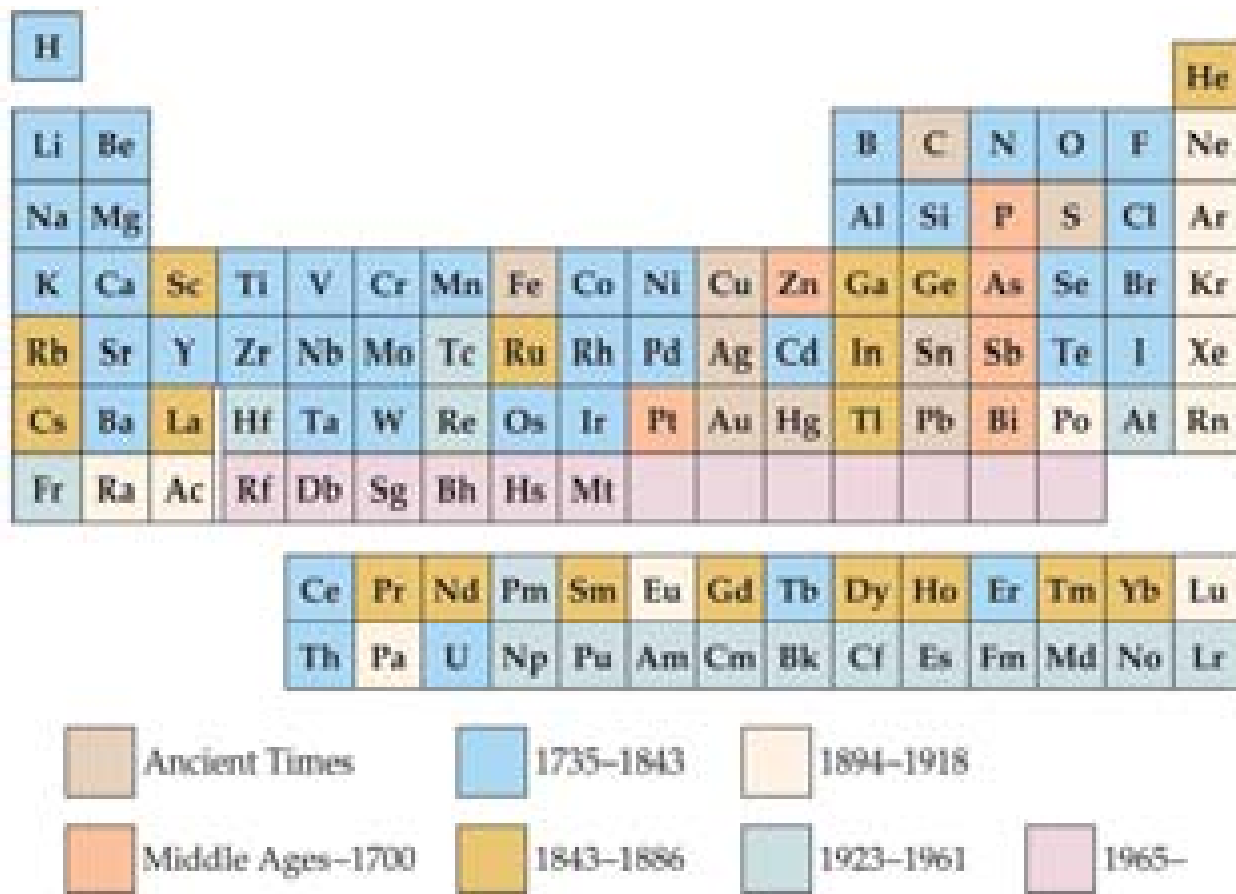- Trends in ionization energies

- Trends in electron affinities

Figure 8.1: Discovery Dates of the Elements

8.2   Development of the Periodic Table

- Mendeleev's insistence that elements with similar properties be listed in the same group lead him to leave several blanks in the periodic table.

- For example, Mendeleev predicted some properties of now what is called Germanium based on the fact that it is in the same group as Silicon. Silicon was discovered almost 100 years before that of Germanium!

- Once germanium was discovered, its observed properties matched exceptionally well with Mendeleev's predictions (see the table on the next slide).

Table 8.1: Comparison of the Properties of Eka-Silicon ("under" silicon) Predicted by Mendeleev with the Observed Properties of Germanium

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat ($J/g \times K$)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84

Periodic law 1860–1870's (Mendeleev and Meyer) – A periodic repetition of physical and chemical properties occurs when the elements are arranged in order of increasing atomic weight [number]

Figure 8.2

8.3   Ordering by Atomic Weight

Inconsistencies in ordering by atomic weight:

- Co (58.93 amu; $Z = 27$) and Ni (58.69 amu; $Z = 28$)

- Ar (39.95 amu; $Z = 18$) and K (39.10 amu; $Z = 19$)

- Te (127.60 amu; $Z = 52$) and I (126.90 amu; $Z = 53$)

However, all of the above are correctly ordered by atomic number, Z (i.e., the number of protons).

8.4　Development of Periodic Table

- Elements in the same group generally have similar chemical properties.

- However, physical properties are not necessarily similar.

- For example, even though Oxygen and Sulfur are in the same group (6A), Oxygen is a colorless gas, while Sulfur is a yellow solid under normal conditions.

8.5　But why do elements in the same group have similar properties?

- Underlying valence electronic structure is the same (almost) for elements of a group:

  - e.g., alkaline earth metals (Group 2) metals are all

  > [Noble Gas] ns^2

  - halogens (Group 17) are all

  > [Noble Gas] ns^{2}np^5

- So, broadly speaking, elements in the same group *should* have similar chemistry

- But why do properties like atomic size, ionization energies and electron affinity vary from group to group?.

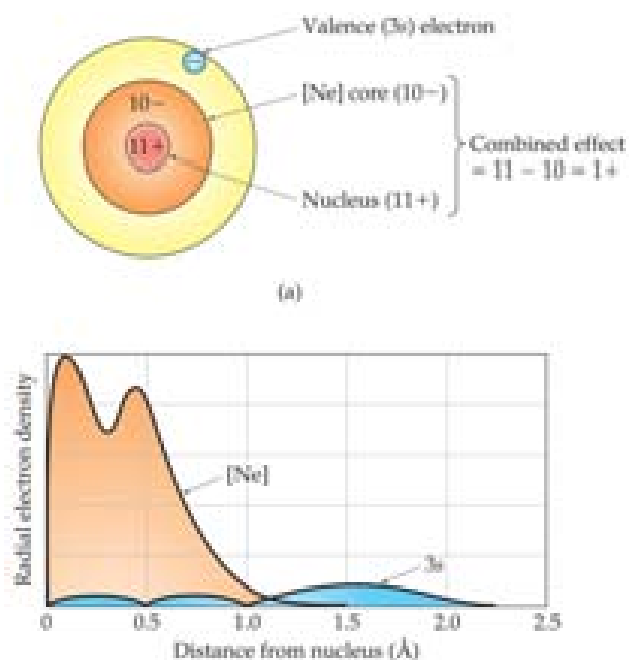## 8.6   Effective Nuclear Charge

Figure 8.3: Effective Nuclear Charge

- In a many-electron atom, electrons are both attracted to the nucleus and repelled by other electrons.

- The nuclear charge that an electron experiences depends on both factors.

- The effective nuclear charge, Z_{eff}, is found this way:

$$Z_{eff} = Z - \sigma \qquad (8.1)$$

  where Z is the atomic number and σ is the screening constant, usually close to the number of inner/core electrons.

- Z_{eff} is always less than Z (atomic number) due to shielding!

- Electrons in the same shell don't screen one another very well.
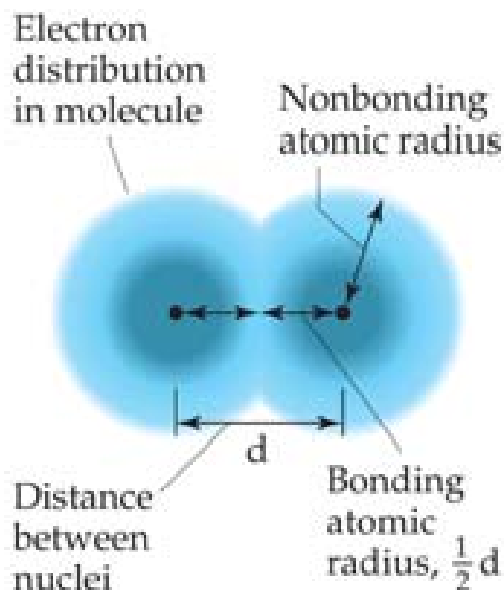
8.7   What is the Size of an Atom?

Figure 8.4: Atom Size

- The bonding atomic radius is defined as $\frac{1}{2}$ of the distance between covalently bonded nuclei.
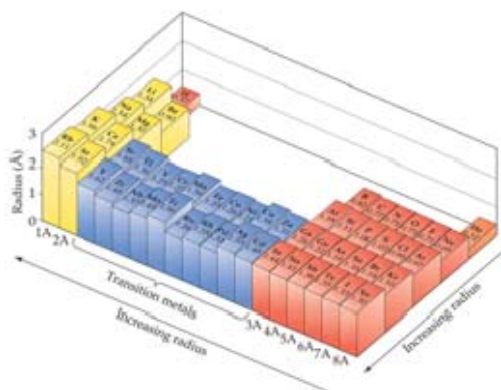
Figure 8.5: Sizes of Atoms

- Bonding atomic radii tend to:

    (A) decrease from left to right across a row (due to increasing Z_{eff}).

    (B) increase from top to bottom of a column (due to increasing value of n).

8.8 Estimating Bond Lengths

- Atomic radii allows one to estimate bond lengths.

- Example, estimate the carbon-chlorine bond length in carbon tetrachloride, CCl_4.
  Atomic radius of C: 0.77 Å
  Atomic radius of Cl: 0.99 Å
  Intenuclear bond length = 0.77 Å + 0.99 Å = 1.76 Å

- The experimentally determined carbon-chlorine bond length in carbon tetrachlroide is actually 1.77 Å.

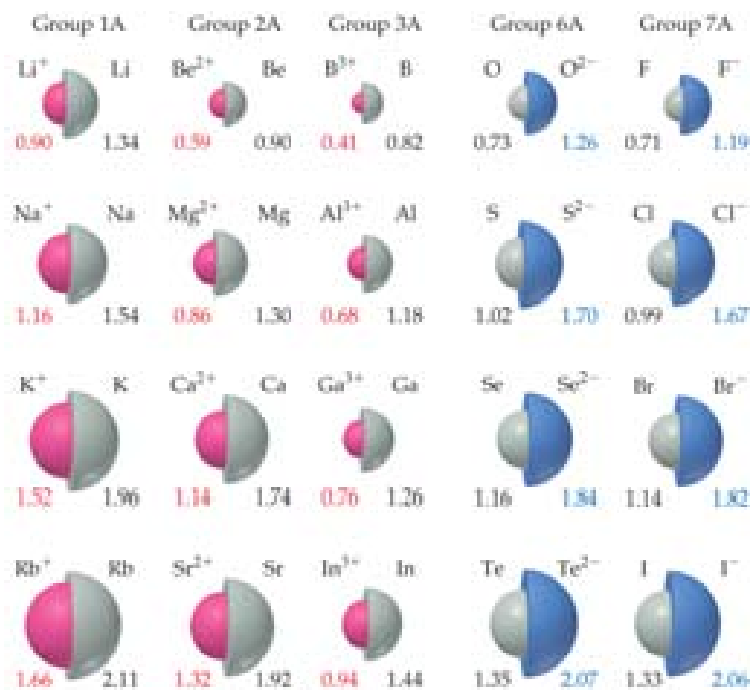# 8.9   Radii of Cations and Anions

Figure 8.6: Radii of Cations and Anions

- Cations are smaller than parent neutral atoms (e.g., Li^+ is smaller than Li.) Why?

- Increased Z_{eff} upon electron removal.

- Anions are larger than parent neutral atoms (e.g., I^- is larger than I.) Why?

- Increased electron-electron repulsions upon electron addition, causing electrons to spread out more in space.

- Ions with the same charge – ion size increases going down a group due to increasing values of n.

- For example, a Sr^{2+} ion (radius = 1.32 Å) is larger than a Ca^{2+} ion (radius = 1.14 Å).

8.10   Sizes of Isoelectronic Ions

- In an isoelectronic series, ions have the same number of electrons.

- Ionic size decreases with an increasing nuclear charge (Z_{eff}).

Figure 8.7: Sizes of Isoelectronic Ions

8.11   Ionization Energy

- Ionization energy – energy required to remove an electron from a gaseuos species.

- The first ionization energy is the energy required to remove the first electron.

- The second ionization energy is the energy required to remove the second electron, etc.

$$Mg \xrightarrow{IE_1=738\frac{kJ}{mol}} Mg^+ \xrightarrow{IE_2=1451\frac{kJ}{mol}} Mg^{2+}$$
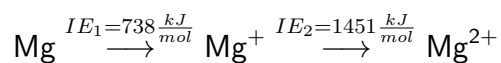
- It requires more energy to remove each successive electron.

- When all valence electrons have been removed, the ionization energy takes a large leap.

- Ionization energies for all elements can be found at: https://www.webelements.com

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4562	(inner-shell electrons)				
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

Figure 8.8: Ionization Energy

8.12   Trends in First Ionization Energies
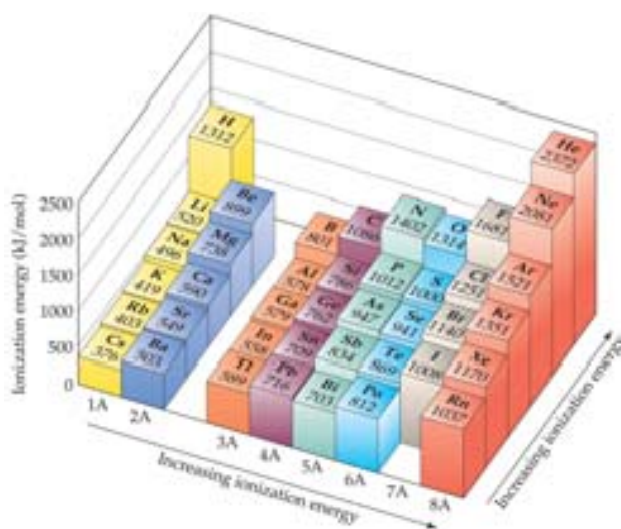
- As one goes down a group, less energy is required to remove the first electron.

    - For atoms in the same group, Z_{eff} is essentially the same, but the valence electrons are farther from than nucleus (i.e., increasing value of n).

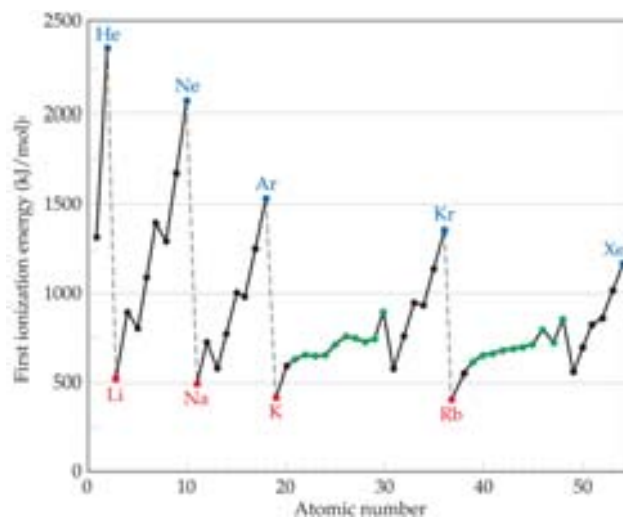Figure 8.9: Periodic Table Ionization Energies
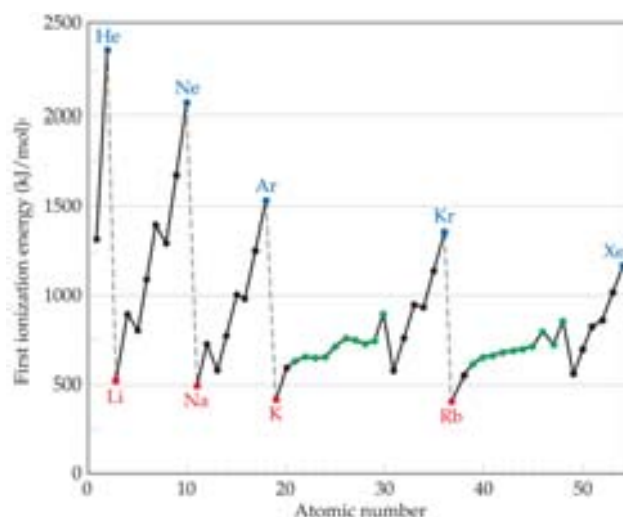
Figure 8.10: Trends in Ionization Energy

- Generally, as one goes across a row/period, it becomes more difficult to remove an electron.

  - As you go from left to right $\Rightarrow Z_{eff}$ increases!

- However, there are two apparent discontinuities in this trend.

- The first occurs between Groups IIA (2) and IIIA (13).

- In this case, the electron is removed from a p-orbital rather than an s-orbital.

  - The electron removed is further from the nucleus.

 - There is also a small amount of repulsion by the s electrons.

- The second occurs between Groups VA (15) and VIA (16).

  - The electron removed comes from a doubly occupied orbital.

  - Repulsion from the other electron in the orbital aids in the removal.

Figure 8.11: Discontinuities in Trends in Ionization Energy

8.13   Electron Affinity

Electron affinity is the energy change accompanying the addition of an electron to a gaseous atom:

$$CL\,(g) + e^- \longrightarrow Cl^-(g) \qquad E_a = -349\frac{kJ}{mol}$$
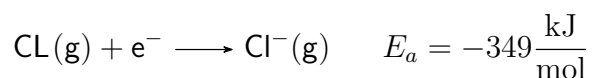
Energy is typically released when an electron is added to a gaseous atom. The process is said to be exothermic, so the energy has a negative sign associated with it.

The electron affinity of lithium is a negative value, whereas the electron affinity of Beryllium is a positive value. Use electron configuration to account for this observation.

8.14   Trends in Electron Affinity

Figure 8.12: Trends in Electron Affinity

- In general, electron affinities become more exothermic/more negative as you go from left to right across a period.

Figure 8.13: Discontinuities in Trends in Electron Affinity

- However, there are two discontinuities in this trend.

- This first occurs between Groups IA and IIA.
    - The added electron must go in a p-orbital, not an s-orbital.
    - The electron is farther from nucleus and feels repulsion from the s-electrons.

- The second occurs between Groups IVA and VA.
    - Group VA has no empty orbitals.
    - The extra electron must go into an already occupied orbital, creating repulsion.

Chapter 9

Basic Concepts of Chemical Bonding

9.1   Outline

- Lewis symbols and valence electrons

- Ionic bonding - electrostatic attractions between ions of opposite charge

- Covalent bonding - sharing of one or more electron pairs between atoms

- Bond polarity and electronegativity

- Drawing Lewis structures

- Resonances structures, exceptions to the octet rule, and strengths of covalent bonds

9.2   Chemical Bonds

Chemical bond – a strong attractive fource that exists between atoms in a molecule.
The three types of chemical bonds are as follows:

ionic bond a bond between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons.

covalent bond a bond formed between two or more atoms by sharing of electrons.

metallic bond Bonding, usually in solid metals, in which bonding electrons are relatively free to move throughout the three-dimensional structure.

9.3   Lewis Symbols

- The valence electrons, those that reside in the outermost shell of an atom, are responsible for chemical bonding.

- Lewis symbol (electron dot symbol) The chemical symbol for an element, with a dot for each valence electron.

- Dots are placed on the four sides of the chemical symbol, where each side can accommodate up to two electrons.

Table 9.1: Lewis Symbols

Electron	Electron Configuration	Lewis Symbol	Electron	Electron Configuration	Lewis Symbol
Li	$[He]2s^1$	Li·	Na	$[Ne]3s^1$	Na·
Be	$[He]2s^2$	·Be·	Mg	$[Ne]3s^2$	·Mg·
B	$[He]2s^22p^1$	·Ḃ·	Al	$[Ne]3s^23p^1$	·Ȧl·
C	$[He]2s^22p^2$	·Ċ·	Si	$[Ne]3s^23p^2$	·Ṡi·
N	$[He]2s^22p^3$	·N̈:	P	$[Ne]3s^23p^3$	·P̈:
O	$[He]2s^22p^4$	:Ö:	S	$[Ne]3s^23p^4$	:S̈:
F	$[He]2s^22p^5$	·F̈:	Cl	$[Ne]3s^23p^5$	·C̈l:
Ne	$[He]2s^22p^6$	:N̈e:	Ar	$[Ne]3s^23p^6$	:Ȧr:

9.4   Ionic Bonding

- The combination of sodium metal and chlorine gas results in a violent reaction. The product of this very exothermic reaction is sodium chloride ($NaCl$).

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s) \qquad \Delta H_f = -410.9\,kJ$$
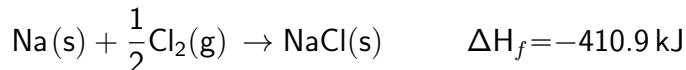
- Sodium chloride is comprised of Na^+ and Cl^- ions (see Figure 9.1).

- Recall that metals (e.g., Na) have a tendency to lose electrons to form cations, whereas nonmetals (e.g., Cl) gain electrons to become anions.

$$Na· + ·\ddot{C}l: \longrightarrow Na^+ + \left[:\ddot{C}l:\right]^-$$
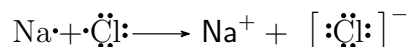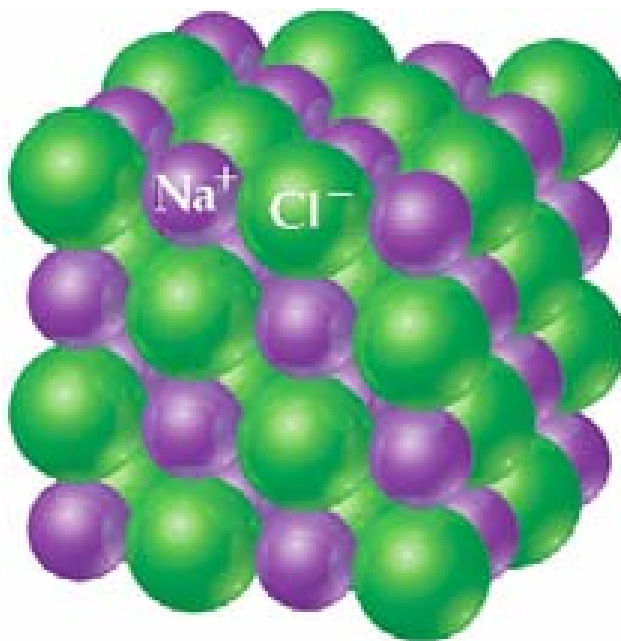
9.5 Structure of Sodium Chloride (NaCl)

Figure 9.1: Structure of Sodium Chloride (NaCl)

In this three-dimensional array of ions, each Na^+ ion is surrounded by siz Cl^- ions, and each Cl^- ion is surrounded by six Na^+ ions.

9.6 Formation of NaCl

- What drives the reaction between Na (s) and Cl_2 (g) to form NaCl?

- Na has a relatively low first ionization energy (i.e., it is perfectly happy to give up its valence electron). Ask yourself, what is the electron configuration of the resulting Na^+ cation?

- Cl has a strong tendency to gain an electron, which is manifested in its large negative electron affinity ($E_a = -349\frac{kJ}{mol}$). Ask yourself, what is the electron configuration of the resulting Cl^- cation?

- In addition, as the Na^+ and Cl^- ions are drawn together to form NaCl, a substantial amount of energy is released, known as the lattice energy.

9.7 Lattice Energy

- Lattice energy – The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

- Lattice energies are positive as energy is required to overcome attractive forces between oppositely charged ions. For example,

$$NaCl(s) \longrightarrow Na^+(g) + Cl-(g) \qquad \Delta H_{lattice} = +788 \, \frac{kJ}{mol}$$
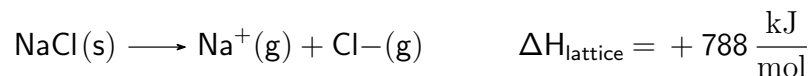
- The energy associated with electrostatic interactions is governed by Coulomb's Law:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d} \qquad (9.1)$$

- Lattice energy increases with the charge on the ions.

- It also increases with decreasing size of ions.

- See the worked example entitled Magnitudes of Lattice Energies.

9.8   Magnitudes of Lattice Energies

Which substance would you expect to have the greatest lattice energy, MgF_2, CaF_2, or ZrO_2?

$$MgF_2(s) \longrightarrow Mg^{2+}(g) + 2\,F^-(g)$$

Because the product of the charge, $Q_1 Q_2$, appears in the numerator of the equation above, the lattice energy will increase dramatically when the charges of the ions increase. Thus,

$$MgF_2 \quad Q_1 = {}^+2 \quad Q_2 \quad = -1$$
$$CaF_2 \quad Q_1 = {}^+2 \quad Q_2 \quad = -1$$
$$ZrO_2 \quad Q_1 = {}^+4 \quad Q_2 \quad = -2$$

$$CaF_2 < MgF_2 < ZrO_2$$

Table 9.2: Lattice Energies for Some Ionic Compounds

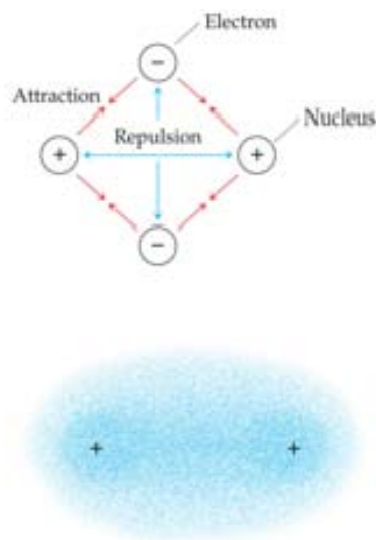| Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2326
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KFCl	701		
KBr	671		
CsCl	657		
CsI	600		

9.9 Covalent Bonding

- In covalent bonds, atoms share electrons.

- There are several electrostatic interactions in these bonds:

  - Attractions between electrons and positive nuclei.
  - Repulsions between electrons
  - Repulsions between nuclei
 - Attractive forces must outweigh the repulsive ones

Figure 9.2: Covalent Bonding

9.10 Lewis Structures

- Consider two Hydrogen atoms coming together to form a covalently bonded H_2 molecule:

$$H\cdot + \cdot H \longrightarrow H\!:\!H$$
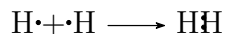
- The H_2 molecule on the right, with its two electrons, exhibits the noble-gas configuration of Helium. The shared pair of electrons can be represented by a single bond, as shown below¿
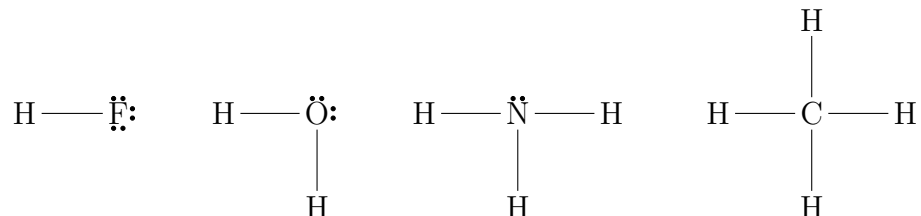
$$H\!:\!H = H \!-\!\!-\! H$$
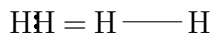
- Consider two chlorine atoms coming together to form a covalently bonded Cl_2 molecule:

$$:\!\ddot{C}\!l\cdot + \cdot\ddot{C}\!l\!: \longrightarrow :\!\ddot{C}\!l\!:\!\ddot{C}\!l\!:$$
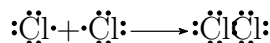
- Each chlorine atom on the right now has a *complete octet* of electrons by sharing the bonding electron pair. It achieves the noble gas configuration of argon (Ar). Again, the shared pair of electrons can be represented by a single bond, as shown below.
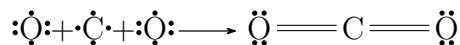
9.11   Typical Bonding Motifs

Typical bonding motifs above: hydrogen and halogens typically form one bond, oxygen two bonds, nitrogen three bonds, and carbon four bonds.
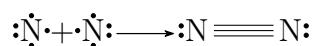
$$
H\!-\!\ddot{\underset{\displaystyle\cdot\cdot}{F}}\colon \qquad H\!-\!\underset{\displaystyle\overset{|}{H}}{\ddot{O}}\colon \qquad H\!-\!\underset{\displaystyle\overset{|}{H}}{\ddot{N}}\!-\!H \qquad H\!-\!\underset{\displaystyle\overset{|}{H}}{\overset{\displaystyle\overset{H}{|}}{C}}\!-\!H
$$

9.12   Multiple Bonds

- Double bonds in CO_2:

$$
:\!\ddot{O}\!:\,+\,\cdot\dot{C}\cdot\,+\,:\!\ddot{O}\!: \longrightarrow \ddot{O}\!=\!C\!=\!\ddot{O}
$$

- Triple bond in N_2:

$$
:\!\dot{\ddot{N}}\cdot\,+\,\cdot\dot{\ddot{N}}\!: \longrightarrow :\!N\!\equiv\!N\!:
$$

9.13   Bond Polarity and Electronegativity

- Molecules such as H_2, N_2, Cl_2, etc are said to be **nonpolar**.

- A nonpolar covalent bond is one in which the electrons are shared equally between two atoms.

- On the other hand, a polar covalent bond is one in which one of the atoms exerts a greater attraction for the bonding electrons than the other.

- In other words, there exists a bond between atoms of different electronegativities (e.g., O-H, C-H, N-H, etc.).

9.14   Electronegativity

- Electronegativity – the ability of atoms in a molecule to attract electrons to themselves.

- On the periodic table, electronegativity increases as you go. . .

    - from left to right across a row
    - from bottom to the top of a column.

Figure 9.3: The Electronegativities of Selected Elements

9.15 Polar Covalent Bonds

- Though atoms often form compounds by sharing electrons, the electrons are not always shared equally.

- Fluorine pulls harder on the electrons it shared with Hydrogen than Hydrogen does.

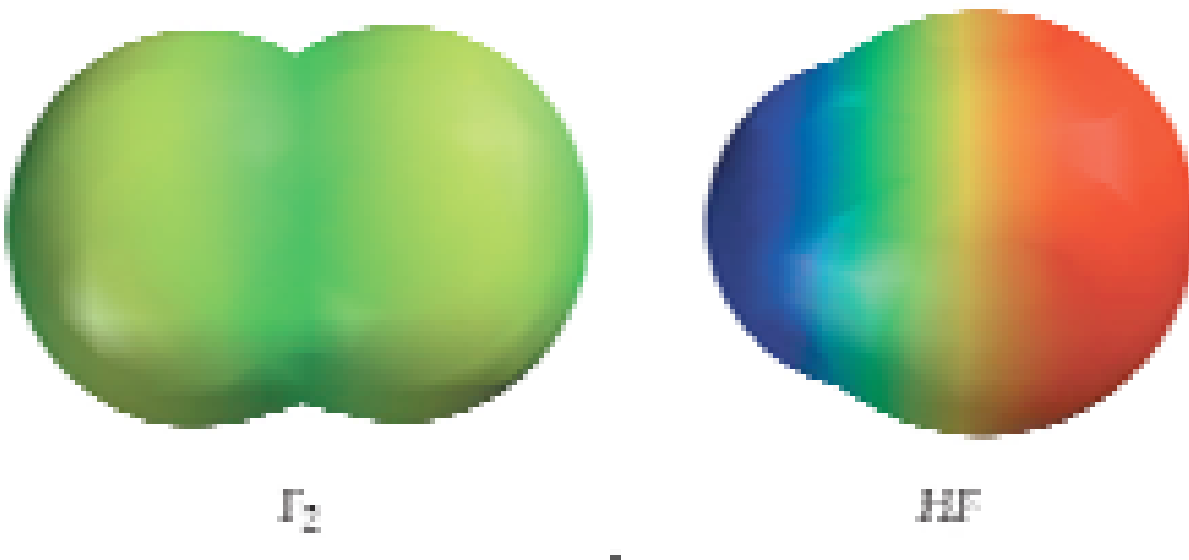- Therefore, the Fluorine end of the molecule has more electron density than the hydrogen end.

Figure 9.4: Polar Covalent Bonds

Table 9.3: Electronegativity and Bond Polarity

Compound	F_2	HF	LiF
Electronegativity	4.0 - 4.0 = 0	4.0 - 2.1 = 1.9	4.0 - 1.0 = 3.0
Type of bond	Nonpolar covalent	Polar covalent	Ionic

- When two atoms share electrons unequally, a bond dipole results.

- The dipole moment, μ, produced by two equal but opposite charges separated by a distance r is calculated as:

$$\mu = Qr \tag{9.2}$$
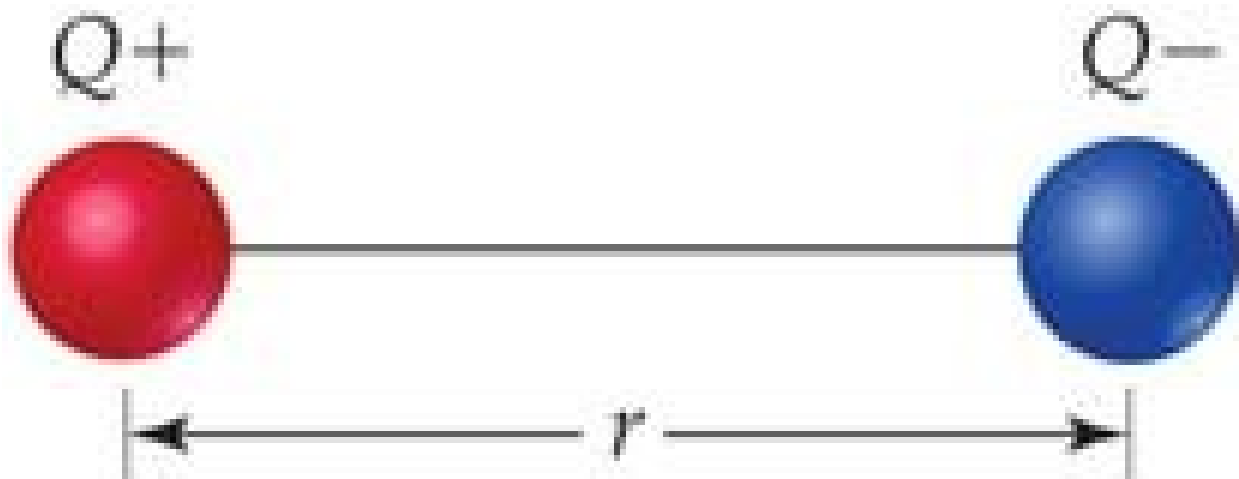
- The dipole is measured in debye (D) units.

Figure 9.5: Dipole Moment μ

Table 9.4: Polar Covalent Bonds

Compound	Bond Length (Å)	Electronegativity	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

The greater the difference in electronegativity, the more polar the bond is.

9.16   Writing Lewis Structures

$$\text{H} \longrightarrow \text{H} \qquad \ddot{\text{:}\text{Cl}} \longrightarrow \ddot{\text{Cl}}\text{:}$$

- Lewis structures are representations of molecules showing all electrons, bonding and nonbonding.

1. Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.

    - If it is an anion, add one electron for each negative charge.
    - If it is a cation, subtract one electron for each positive charge.
    - Total number of valence electrons for PCl_3 is:____ $5 + (7*3) = 26$

2. The central atom is the least electronegative element that isn't Hydrogen. Connect the other atoms to it by single bonds.

3. Fill the octets of the outer atoms.

    - How many electrons have you accounted for in the above structure? 24
    - How many do you have left? 2

- Fill in the octet of the central atom.
- If you run out of electrons before the central atom has an octet: form multiple bonds until it does

$$\text{H}\!-\!\!-\!\text{C}\!-\!\!-\!\ddot{\underset{\cdot\cdot}{\text{N}}}\!: \longrightarrow \text{H}\!-\!\!-\!\text{C}\!\equiv\!\text{N}\!:$$
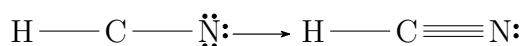
- Then assign formal charges.

- For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.

- Subtract that from the number of valence electrons for that atom: the difference is its formal charge (see (9.3)).

formal charge $=$ # of valence electrons$-$# of lone-pair electrons$-\dfrac{1}{2}$ # of bonding electrons

(9.3)
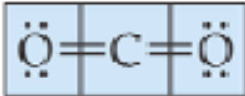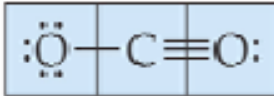
	$\ddot{\text{O}}\!=\!\text{C}\!=\!\ddot{\text{O}}$			$:\!\ddot{\text{O}}\!-\!\text{C}\!\equiv\!\text{O}:$		
Valence electrons:	6	4	6	6	4	6
$-$(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	-1	0	$+1$

Figure 9.6: Formal Charges for CO_2

.

- The best Lewis structure...

    - ... is the one with the fewest charges.
    - ... puts a negative charge on the most electronegative atom.
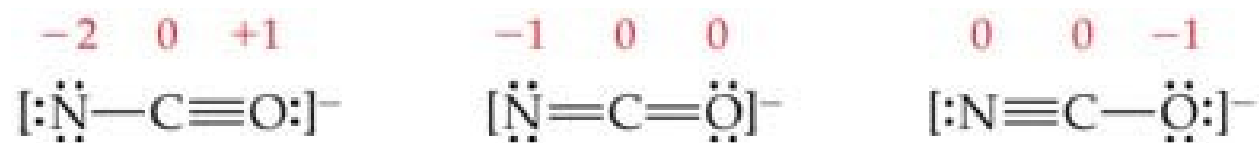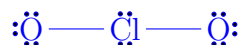

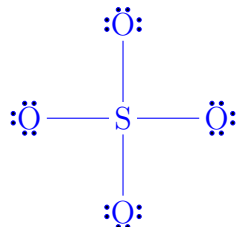Figure 9.7: Choosing the best formal charge for CON.

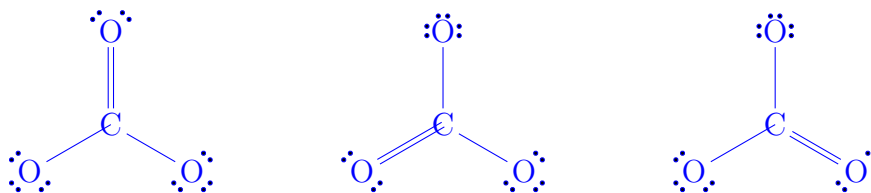## 9.17   Lewis Structures for Polyatomic Ions

Draw the Lewis structures for:

(a) ClO_2^- $7 + 2(6) + 1 = 20$ valence electrons

$$:\ddot{O}\!-\!\ddot{C}l\!-\!\ddot{O}:$$

(b) SO_4^{2-} $6 + 4(6) + 2 = 32$ valence electrons

$$:\ddot{O}:$$
$$|$$
$$:\ddot{O}\!-\!S\!-\!\ddot{O}:$$
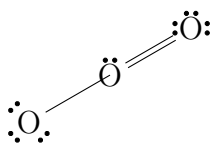$$|$$
$$:\ddot{O}:$$

(c) CO_3^{2-} $4 + 3(6) + 2 = 24$ valence electrons

9.18   Resonance

• One possible Lewis structure of the ozone (O_3) molecule is depicted below.

• But this is not consistent with the observed structure of ozone, whereby. . .

    – both $O-O$ bonds are the same length.

• One Lewis structure cannot accurately describe a molecule like ozone.

• We use multiple structures (i.e. resonance structures) to describe the molecule.

• Placement of atoms remain the same, but the placement of electrons are different.

• A double headed arrow is used to indicate that the real molecule is described by an average of the resonance structures.

9.18.1   An Analogy to Color Mixing

Just as green is a *blend* of blue and yellow... the real structure of ozone is a *blend* of the two resonance structures.

# 9.19   Exceptions to the Octet Rule

- The three types of systems that don't follow the octet rule are as follows:

  - Ions or molecules with an odd number of electrons
  - Ions or molecules with less than an octet
  - Ions or molecules with more than eight valence electrons (an expanded octet)

9.19.1   Odd Number of Electrons

Ions and molecules with an odd number of electrons (e.g., ClO_2, NO, NO_2, and O_2).

$$\ddot{N}\!=\!\!=\!\ddot{O} \text{ and } \ddot{N}\!=\!\!=\!\ddot{O}$$

9.19.2   Fewer than Eight Electrons
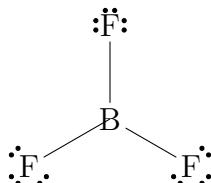
- Consider BF_3

  - Notice how the central boron does not have a complete octet?
 - What about resonance?
  - See worked example below:

Draw the Lewis structure for boron trifluoride, BF_3, and explain why it does not obey the octet rule.

These resonance structures are less important than the first because they put positive charge on the most electronegative fluorine atoms!

9.19.3   More than Eight Electrons

- The only way PCl_5 can exist is if phosphorus has 10 valence electrons around it.

- It is allowed to expand the octet of atoms on or below the 3rd row/period.

- Ask yourself, does NCl_5 exist? No.

- Most likely the *d* orbitals in these atoms participate in bonding.

9.20   Covalent Bond Strength

$$:\ddot{\underset{..}{C}}l \!-\!\!-\!\! \ddot{\underset{..}{C}}l\!:(g) \longrightarrow 2 \cdot \ddot{\underset{..}{C}}l\!:(g)$$
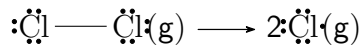
- The strength of a bond is measured by determining how much energy is required to break the bond.

- This is the bond enthalpy.

- The bond enthalpy for a Cl-Cl bond is measured to be 242 kJ/mol.

Chapter 10

Valence Bond Theory