

## Chapter 1. Introduction: Matter and Measurement

### 1.1 The Study of Chemistry

- Chemistry is the central science
  - a) study of properties of materials and changes they undergo
  - b) can be applied to all aspects of life (e.g. pharmaceutical )
  - c) has a considerable impact on society

Chemistry involves the study of the properties and behavior of matter

Matter

- a) physical material of the universe
- b) has mass and occupies space
- c) almost 100 elements constitute all matter

### 1.2 Classification of Matter;

Matter is classified by state (solid, liquid or gas) or by composition (element, compound or mixture)

Gas: No fixed volume or shape, conforms the shape of container, compressible. Molecules are far apart, move at high speed, collide often.

Liquid: volume independent of container, no fixed shape, incompressible. Molecules are closer than gas, move rapidly but can slide over each other.

Solid: volume and shape independent of container, rigid, incompressible. Molecules packed closely in definite arrangements.

Pure substances:

- a) Elements : can not be decomposed into simpler substances, i.e. only one kind of atom).
  - 114 known, vary in abundance.
  - Each is given a unique name and a one or two-letter symbol derived from its name
  - Organized in periodic table

b) Compounds: are combination of elements. The compound H<sub>2</sub>O is a combination of elements H and O.

Law of Constant (Definite) Proportions : A compound always consists of the same combination of elements (e.g. water is always 11% H and 89%O)

Mixture is a combination of two or more substances

Heterogeneous (do not have uniform composition, properties and appearance, e.g. sand)

Homogeneous (uniform throughout, e.g. air). Homogeneous mixtures are solutions.

## Separation of Mixtures

- Filtration; remove solid from liquid
- Distillation: Boil off one or more components of the mixture
- Chromatography: Exploit solubility of components.

## Physical and Chemical Changes

- Physical change: substances changes physical appearance without altering its identity ( e.g. change of state)
- Chemical change (or chemical reactions): substances transform into chemically different substances (e.g. decomposition of water)

## 1.4 Units of Measurement

the units most often used for scientific measurement are those of the metric system.

## 1.5 Uncertainty in Measurement

Two types of numbers:

- exact numbers
- inexact numbers

All measurements have some degree of uncertainty or error associated with them.

## Precision and accuracy

- precision: how well measured quantities agree with each other
- accuracy: how well measured quantities agree with the 'true value'.

## Significant Figures

The exactness of a measurement is reflected in the number of significant figures. The number of significant figures is the number of digits known with certainty plus one uncertain digit.( Example; 2.2405 g means we are sure the mass in 2.240 g but we are uncertain about the nearest 0.0001 g).

### Rule

- nonzero numbers and zeros between nonzero numbers are always significant
- zeros before the first nonzero digit are not significant (example:0.0003 has one significant figure.
- zeros at the end of the number before a decimal point are significant.

Numbers are written in scientific notation.  $2.50 \times 10^2$  has 3 s.f.  $1.030 \times 10^4$  has 4 s.f.

## Significant figures in calculations

- Multiplication and Division: report to the least number of significant figures (e.g.  $6.221 \text{ cm} \times 5.2 \text{ cm} = 32 \text{ cm}^2$ )
- Addition and subtraction: report to the least number of decimal places (e.g.,  $20.4 \text{ g} - 1.322 \text{ g} = 19.1 \text{ g}$ )

## 1.6 Dimensional Analysis

Dimensional analysis is a method of calculation utilizing a knowledge of units.

Given units can be multiplied and divided to give the desired units.

Conversion factors are used to manipulate units

$$\text{Desired unit} = \text{given unit} \times (\text{conversion factor})$$

The conversion factor = (desired unit) / (given unit).

We often need to use more than one conversion factor in order to complete a problem.

The final answer must be the correct unit.

Conversions involving volume

Suppose that we wish to know the mass in grams of 2.00 cubic inches of gold given that the density of the gold is  $19.3 \text{ g/cm}^3$

We know the following conversion factors

$$2.54 \text{ cm} = 1 \text{ inch and } 1 \text{ cm}^3 = 19.3 \text{ g}$$

$$(2.00 \text{ in.}^3)(2.54 \text{ cm/in.})^3 (19.3 \text{ g gold} / 1 \text{ cm}^3) = 6.33 \text{ g gold}$$

Summary of dimensional analysis

Three questions

1. What data are we given?
2. What quantity do we need?
3. What conversion factors are available to take us from what we are given to what we need?

## Chapter 2. Atoms, Molecules, and ions.

### 2.1. The Atomic Theory of Matter

- Greek philosophers; Can matter be subdivided into fundamental particles?
- Democritus (460-370 BC); All matter can be divided into indivisible atoms.
- Dalton: Proposed atomic theory with the following postulates;
  - o Elements are composed of atoms
  - o All atoms of an element are identical
  - o In chemical reactions atoms are not changed into different types of atoms. Atoms can neither be created nor destroyed.
  - o Compounds are formed when atoms of element combine.

**Atoms** are the building blocks of matter.

**Law of constant composition:** the relative kinds and numbers of atoms are constant for a given compound.

**Law of conservation of mass (matter):** During a chemical reaction, the total mass before reaction is equal to the total mass after reaction.

Conservation means something can neither be created nor destroyed. It can be applied to both matter and energy,

**Law of multiple proportions:** if two elements A and B combine to form more than one compound, then the mass of B which combines with the mass A is a ratio of small whole number.

### 2.2. The Discovery of Atomic Structure

- By 1850 scientists knew that atoms consisted of charged particles
- Subatomic particles: those particles that make up the atom.
- Recall: The law of electrostatic attraction: like charges repel and opposite charges attract.

### 2.3. The Modern View of Atomic Structure

The atom consists of positive, negative and neutral entities (protons, electrons and neutrons)

The quantity  $1.602 \times 10^{-19}$  C is called electronic charge.

Masses are so small that we define the **atomic mass unit**, amu.

$$1 \text{ amu} = 1.66054 \times 10^{-24} \text{ g.} \quad 1 \text{ g} = 6.02214 \times 10^{23} \text{ amu}$$

The angstrom is convenient non-SI unit of length used to denote atomic dimensions

Since most atoms have radii around  $1 \times 10^{-10}$  m, we define  $1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ .

Isotopes, Atomic Numbers, and Mass Numbers.

An atom of a specific isotope is called **nuclide**.

Examples: Nuclides of hydrogen include

$^1\text{H}$  = hydrogen (protium);  $^2\text{H}$  = deuterium,  $^3\text{H}$  = tritium; tritium is radioactive.

**Radioactivity** is the spontaneous emission of radiation.

### 2.4 Atomic Weights

## Average Atomic Masses

We average the masses of isotopes to give relative atomic masses;

Naturally occurring C consists of 98.892%  $^{12}\text{C}$  (12 amu) and 1.108%  $^{13}\text{C}$  (13.00335).

The average mass of C is:  $(0.98892)(12) + (0.01108)(13.00335) = 12.011$  amu.

Atomic weight (AW) is also known as average atomic mass

Atomic weights are listed on the periodic table

A mass spectrometer is an instrument that allows for direct and accurate determination of atomic (and molecular) weights.

## 2.5 The Periodic Table

**The periodic table** is used to organize the elements in a meaningful way

**Metallic elements** are located in the left-hand side of the periodic table. Most are metals. They tend to be malleable, ductile, and lustrous and are good thermal and electrical conductors.

**Nonmetallic elements** are located in the top right-hand side of the periodic table. They tend to be brittle as solids, dull in appearance, and do not conduct heat or electricity well. Elements with properties similar to both metals and nonmetals are called **metalloids** and are located at the interface between metals and nonmetals. These include the elements B, Si, Ge, As, Sb and Te.

## 2.6 Molecules and Molecular Compounds

A molecule consists of two or more atoms bound together

Molecules and Chemical Formulas

Each molecule has a chemical formula

The chemical formula indicates

1. Which atoms are found in the molecule, and
2. In what proportion they are found

A molecule made up of two atoms is called **diatomic molecule**.

Compounds composed of molecules are **molecular compounds**. These contain at least two types of atoms.

### Molecular and Empirical Formulas

Molecular formulas: Give the actual numbers and types of atoms in a molecule,

Examples,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{O}_2$ , and  $\text{C}_2\text{H}_4$ .

Empirical formula: Give the relative number and types of atoms in a molecule (they give the lowest whole number ratio of atoms in a molecule). Examples:  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{HO}$ ,  $\text{CH}_2$ .

### Picturing Molecules

Molecules occupy three-dimensional space

The structural formula gives the connectivity between individual atoms in the molecule.

Three models can be used

- 1- Perspective drawing uses dashed lines and wedges to represent bonds receding and emerging from the plane of the paper

- 2- Ball-and-stick models show atoms as contracted spheres and the bonds as sticks. The angles are accurate.
- 3- Space-filling models give an accurate representation of the relative size of the atoms and the 3D shape of the molecule.

## 2.7 Ions and Ionic Compounds

If electrons are added to or removed from a neutral atom, an **ion** is formed

When an atom or molecule loses electrons it becomes positively charged

Positively charged ions are called **cations**.

When an atom or molecule gains electrons it becomes negatively charged

Negatively charged ions are called **anions**.

In general, metal atoms tend to lose electrons and nonmetals atoms gain electrons.

When molecules lose electrons, **polyatomic ions** are formed (e.g.  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ).

### Predicting Ionic Charges

An atom or molecule can lose more than one electron.

Many atoms gain or lose enough electrons to have the same number of electrons as the nearest noble gas (group 8A)

The number of electrons an atom loses is related to its position on the periodic table.

### Ionic compounds

A great deal of chemistry involves the transfer of electrons between species

Example:  $\text{Na}^+$  and  $\text{Cl}^-$  form the neutral ionic compound  $\text{NaCl}$ ,  $\text{Mg}_3\text{N}_2$  ( $3 \text{Mg}^{2+}$ ,  $2 \text{N}^{3-}$ ).

Ionic compounds are named cation then anion. Calcium chloride, barium bromide.

### Chemistry of life: Element Required by Living Organism.

Of the 114 elements known, only about 26 are required for life

Water accounts for more than 70% of the mass of the cell

Carbon is the most common solid constituent of cells.

The most important elements of life are H, C, N, O, P and S (red).

The most important ions are  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$  (blue)

The other 15 elements are only needed in trace amounts (green).

## 2.8 Some Simple Organic Compounds.

Organic chemistry is the study of carbon-containing compounds.

Organic compounds are those that contain carbon and hydrogen, often in combination with other elements.

Alkanes are compounds containing only carbon and hydrogen, also called hydrocarbon.

## Chapter 3. Stoichiometry: Calculation with Chemical Formulas and Equations

### 3.1 Chemical Equations.

The quantitative nature of chemical formulas and reactions is called stoichiometry.

Lavoisier observed that mass is conserved in a chemical reaction (**Law of Conservation of Mass**).

Chemical equations give a description of a chemical reaction.

There are two parts to any equation:

**Reactants** (written to the left of the arrow) and

**Products** (written to the right of the arrow);



There are two sets of numbers in a chemical equation

Numbers in the front of the chemical formula (stoichiometric Coefficients). They give the ratio in which the reactant and products exist and

Numbers in the formulas (subscripts). They give the ratio in which the atoms are found in the molecule.

Matter can not be lost in any chemical reactions.

Therefore, we must balance the chemical equation. We adjust the stoichiometric coefficients in front of chemical formula. Subscripts in a formula are never changed.

Example;  $\text{CH}_4 + \text{O}_2 \qquad \text{CO}_2 + \text{H}_2\text{O}$



### 3.2 Some Simple Patterns of Chemical Reactivity

Combination and Decomposition Reactions

In **combination reactions** two or more substances react to form one product.



In **decomposition reactions** one substance undergoes a reaction to produce two or more other substances.



Combustion reactions are rapid reactions that produce a flame and involves the reaction of  $\text{O}_2 (\text{g})$  from air



### 3.3 Formula Weights

**Formula weights** (FW) is the sum of atomic weights for the atoms shown in the chemical formula. Example: FW ( $\text{H}_2\text{SO}_4$ )

$$\begin{aligned} &= 2 \text{ AW (H)} + \text{ AW (S)} + 4 \text{ AW (O)} \\ &= 2 (1.0 \text{ amu}) + 32.0 \text{ amu} + 4 (16.0 \text{ amu}) \\ &= 98.0 \text{ amu} \end{aligned}$$

Molecular weight (MW) is the sum of atomic weights of the atoms in a molecule as shown in the molecular formula: Example: MW (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>)  

$$= 6 (12.0 \text{ amu}) + 12 (1.0 \text{ amu}) + 6 (16 \text{ amu})$$

$$= 180 \text{ amu.}$$

### Percentage Composition from Formula

$$\% \text{ element} = \frac{(\text{number of atoms of that element})(\text{atomic weight of element})(100)}{(\text{Formula weight of compound})}$$

### 3.4 The Mole

The mole ('mol') is a convenient measure of chemical equation

1 mole of something =  $6.0221421 \times 10^{23}$  of that thing.

This number is called **Avogadro's number**.

Thus, 1 mole of carbon atoms =  $6.0221421 \times 10^{23}$  carbon atoms.

Experimentally, a mole of <sup>12</sup>C has a mass of 12 g.

### Molar Mass

The mass in gram of 1 mole of substance is said to be the molar mass of that substance. Molar mass has units of g/mol (g.mol<sup>-1</sup>)

The mass of 1 mole of <sup>12</sup>C = 12 g.

The molar mass of a molecule is the sum of the molar masses of the atoms

Example: the molar mass of N<sub>2</sub> = 2 (molar mass of N) = 2 (14 g) = 28 g.

Molar masses of elements are found in the periodic table.

The formula weight is numerically equal to the molar mass.

### Interconverting Masses, Moles, and Number of Particles

Look at units:

- Mass: g
- Mole: mol
- Molar mass: g/mol
- Number of particles:  $6.022 \times 10^{23} \text{ mole}^{-1}$  (Avogadro's number).
- Note: g/mol x mol = g (i.e. molar mass x mole = mass) and
- Mol x mol<sup>-1</sup> = a number (i.e. moles x Avogadro's number = molecules)

To convert between grams and moles, we use the molar mass

To convert moles and molecules we use Avogadro's number

### Molecular Formula and Empirical Formula

To get the molecular formula from the empirical formula, we need to know the molecular weight (MW).

The ratio of molecular weight (MW) to formula weight (FW) of the empirical formula must be a whole number.



Empirical formulas are routinely determined by combustion analysis.

### Quantitative Information from Balanced Equations.

The coefficients in a balanced chemical equation give the relative numbers of molecules involved in the reaction.

Stoichiometric relations or ratios may be used to convert between quantities of reactants and products in a reaction. It is the ideal proportions in which reactants are needed to form products.

To get the grams of product from grams of reactant

Convert grams of reactant to moles of reactant (use molar mass)

Convert moles of one reactant to moles of other reactants and products (use the stoichiometric ration from the balanced chemical equation),

Convert moles back into grams for desired product (use molar mass)..

### Limiting Reactants

It is not necessary to have all reactants present in stoichiometric amounts

Often, one or more reactants is present in excess

Therefore, at the end of reaction, those reactants present in excess will still be in the reaction mixture,

The one or more reactants, which are completely consumed are called **limiting reactants** or **limiting reagents**.

Reactants present in excess are called excess reactants or excess reagents.

Consider 10 H<sub>2</sub> molecules mixed with 7 O<sub>2</sub> molecules to form water

The balanced chemical equation tells us that the stoichiometric ration of H<sub>2</sub> to O<sub>2</sub> is 2 to 1:



This means that our 10 H<sub>2</sub> molecules require 5 O<sub>2</sub> molecules (2:1).

Since we have 7 O<sub>2</sub> molecules, our reaction is limited by the amount of H<sub>2</sub> we have (the O<sub>2</sub> is present in excess)

So, all 10 H<sub>2</sub> molecules can (and do) react with 5 O<sub>2</sub> molecules producing 10 H<sub>2</sub>O molecules.

At the end of the reaction, 2O<sub>2</sub> molecules remain unreacted.

### Theoretical Yields

The amount of product predicted from stoichiometry taking into account limiting reagents is called the **theoretical yield**.

This is often different from the **actual yield** – the amount of product actually obtained in the reaction (amount of material recovered in the laboratory).

The percent yield relates the actual yield to the theoretical yield:

$$\text{Percent yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

## Chapter 4: Aqueous Reactions and Solution Stoichiometry

### 4.1 General Properties of Aqueous Solutions

A solution is a homogeneous mixture of two or more substances

A solution is made when one substance (the **solute**) is dissolved in another (the **solvent**).

The solute is the substance that is present in smallest amount.

Solutions in which water is the solvent are called **aqueous solutions**.

#### Electrolytic Properties

All aqueous solution can be classified in terms of whether or not they conduct electricity

If substance forms ions in solution, then the substance is an electrolyte, and the solution conduct electricity. Example NaCl

If a substance does not form ions in solution, then the substance is nonelectrolyte, and the solution does not conduct electricity. Example; sucrose.

#### Ionic Compounds in Water

When an ionic compound dissolves in water, the ions are said to dissociate.

Each ion is surrounded by a shell of water molecules

The positive ions have the surrounding oxygen atoms of water pointing towards the ion, negative ions have the surrounding hydrogen atoms of water pointing towards the ion.

The transport of ions through the solution caused electric current to flow through the solution.

#### Molecular Compounds in Water

When a molecular compound (e.g.  $\text{CH}_3\text{OH}$ ) dissolves in water, there are no ions formed.

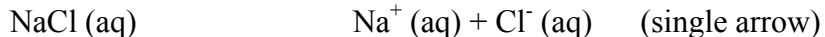
Therefore, there is nothing in the solution to transport electric charge and the solution does not conduct electricity.

#### Strong and Weak Electrolytes

Compounds whose aqueous solutions conduct electricity well are called strong electrolytes.

These substances exist only as ions in solution

Example: NaCl



The single arrow indicates that the  $\text{Na}^+$  and  $\text{Cl}^-$  have no tendency to recombine to form NaCl molecules

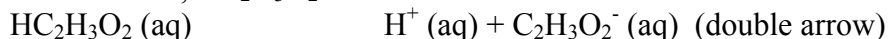
In general soluble ionic compounds are **strong electrolytes**

Compounds whose aqueous solutions conduct electricity poorly are called **weak electrolytes**.

These substances exist as a mixture of ions and un-ionized molecules in solution.

The predominant form of the solute is the un-ionized.

Example: acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$



The double arrow means that the reaction is significant in both directions

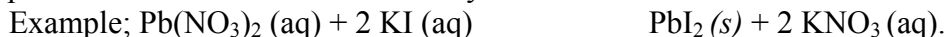
It indicates that there is a balance between the forward and reverse reactions.

This balance produces a state of chemical equilibrium.

#### 4.2. Precipitation Reactions.

Reactions that result in the formation of an insoluble product are known as precipitation reactions.

A precipitate is an insoluble solid formed by a reaction in solution.



Exchange (Metathesis) Reactions

Exchange reactions or metathesis reactions involve swapping ions in solution:



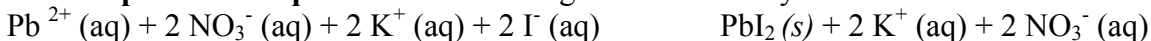
Many precipitation and acid base reactions exhibit this pattern

Ionic Equations

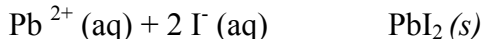
The **molecular equation** lists all species in their molecular forms.



The **complete ionic equation** lists all strong soluble electrolytes in the reactions as ions:



The **net ionic equation** list only those ions which are not common on both sides of the reaction:



Note that spectator ions, ions are present in the solution but play no direct role in the reaction, are omitted in the net ionic equation.

#### 4.3 Acid-Base Reaction

## Acids

Acids are substances that are able to ionize in aqueous solution to form H<sup>+</sup>

Ionization occurs when a neutral substance forms ions in solution.

Example: acetic acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

Common acids are HCl, HNO<sub>3</sub>, vinegar and vitamin C

Acids that ionize to form one H<sup>+</sup> ion are called monoprotic acids.

Acids that ionize to form two H<sup>+</sup> ions are called diprotic acids.

## Bases

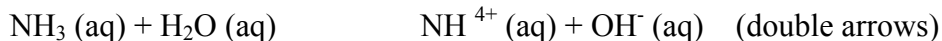
Bases are substances that accept or react with the H<sup>+</sup> ions formed by acids

Hydroxide ions, OH<sup>-</sup> reacts with the H<sup>+</sup> to form water:



Compounds that do not contain OH<sup>-</sup> ions can also be bases

Proton transfer from NH<sub>3</sub> (weak base) and water (weak acid) is an example of an acid-base reaction.



All are present in the solution.

## Strong and Weak Acids and Bases

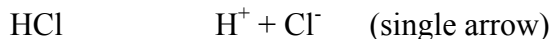
Strong acids and strong bases are strong electrolytes

They are completely ionized in solution

Strong bases include Group 1A metal hydroxide, Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, and Sr(OH)<sub>2</sub>.

Strong acids include; HCl, HBr, HI, HClO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>.

We write the ionization of HCl as

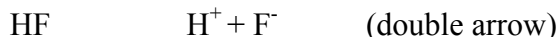


Weak acids and Weak bases are weak electrolytes

Therefore, they are partially ionized in solution.

HF (aq) is a weak acid; most acids are weak acids.

We write the ionization of HF as



## Identifying Strong and Weak Electrolytes

Compounds can be classified as strong electrolytes, weak electrolytes or nonelectrolytes by looking at their solubility

Strong electrolytes

If compound is water soluble and ionic, and is a strong acid or strong base, then it is a strong electrolyte.

Weak electrolytes

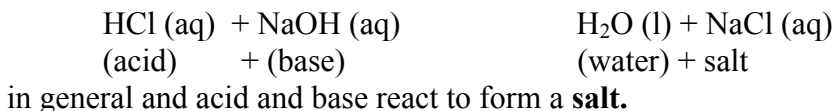
If compound is water soluble and not ionic, and is a weak acid or weak base, then it is a weak electrolyte.

Nonelectrolytes:

Otherwise, the compound is probably a nonelectrolyte.

## Neutralization Reactions and Salts

A **neutralization reaction** occurs when an acid and a base react:



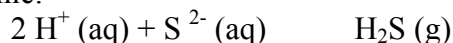
### Acid – Base Reaction with Gas Formation

Reaction of sulfides with acids gives rise to H<sub>2</sub>S (g):

Molecular equation:



Net Ionic:

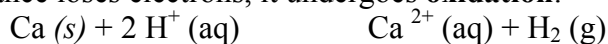


Carbonates and hydrogen carbonate (NaHCO<sub>3</sub>; baking soda) reacts with HCl to form bubbles of CO<sub>2</sub> (g).

## 4.4 Oxidation-Reduction Reactions

Oxidation-reduction or redox reactions involves the transfer of electrons between reactants.

When a substance loses electrons, it undergoes **oxidation**:



The neutral Ca has lost two electrons to 2 H<sup>+</sup> to become Ca<sup>2+</sup>.

We say Ca has been oxidized to Ca<sup>2+</sup>.

When a substance gains electrons, it undergoes **reduction**:



The neutral O<sub>2</sub> has gained electrons from Ca to become O<sup>2-</sup> in CaO.

We say O<sub>2</sub> has been reduced to O<sup>2-</sup>.

In all redox reactions, one species is reduced at the same time as another is oxidized.

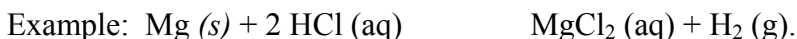
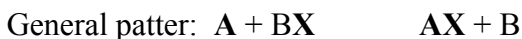
### Oxidation Numbers

**Oxidation numbers** (or oxidation state) help to keep track of electrons during chemical reactions.

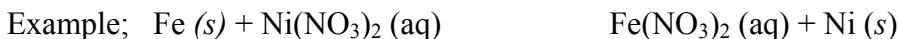
The oxidation of an element is evident by its increase in oxidation number; reduction is accompanied by a decrease in oxidation number.

### Oxidation of Metals by Acids and Salts

The reaction of metal with either an acid or a metal salt is called a displacement reaction;



In the process, the metal is oxidized and the H<sup>+</sup> is reduced.



The net ionic shows the redox chemistry well



In this reaction iron has been oxidized to  $\text{Fe}^{2+}$  while  $\text{Ni}^{2+}$  has been reduced to Ni

Always keep in mind that whenever one substance is oxidized, some other substance must be reduced.

#### 4.5 Concentration of Solutions

The term **concentration** is used to indicate the amount of solute dissolved in a given quantity of solvent or solution.

Molarity

The amount (moles) of solute per liter of solution is the **molarity** (symbol M) of the solution

$$\text{Molarity} = \frac{\text{Mole solute}}{\text{Liters of solution}}$$

By knowing the molarity of a quantity of liters of solution, we can easily calculate the number of moles ( and, by using molar mass, the mass) of solute.

Consider weighed copper sulfate,  $\text{CuSO}_4$  (39.9 g, 0.250 mol) placed in a 250 ml volumetric flask. A little water is added and the flask swirled to ensure the copper sulfate dissolves. After, the flask is filled to the mark with water.

The molarity of the solution is  $0.25 \text{ mol CuSO}_4 / 0.25 \text{ L solution} = 1.00\text{M}$ .

#### Expressing the Concentration of an Electrolyte

When an ionic compound dissolves, the relative concentrations of the ions in the solution depend on the chemical formula of the compound

Example: For a 1.0 M solution of NaCl:

The solution is 1.0 M in  $\text{Na}^+$  ions and 1.0 M in  $\text{Cl}^-$  ions.

Example: For a 1.0 M solution of  $\text{Na}_2\text{SO}_4$ :

The solution is 2.0 M in  $\text{Na}^+$  ions and 1.0 M in  $\text{SO}_4^{2-}$  ions.

#### Interconverting Molarity, Moles, and Volume

The definition of molarity contains three quantities: molarit, moles of solute, and liters of solution.

If we know any two of these, we can calculate the third

Dimensional analysis is very helpful in these calculations.

Dilution

Take a solution of known molarity and dilute it with more solvent (water) to obtain a solution with lower concentration.

Since the number of moles of solute remains the same in the concentrated and dilute forms of the solution we can show:

$$M_{\text{initial}} \times V_{\text{initial}} = M_{\text{final}} \times V_{\text{final}}$$

An alternative form of this equation is

$$M_{\text{concentrated}} \times V_{\text{concentrated}} = M_{\text{dilute}} \times V_{\text{dilute}}$$

#### 4.6 Solution Stoichiometry and Chemical Analysis

In approaching stoichiometry problems:

Recognize that there are two different types of units

Laboratory units (we measure in the lab) and

Chemical units (moles)

Always convert the laboratory units into chemical first.

Convert grams to moles using molar mass.

Convert volume or molarity into moles using  $M = \text{mol/L}$

Use the stoichiometric coefficients to move between reactants and products

This step requires the balanced chemical equations

Convert the laboratory units back into the required units

Convert moles to grams using molar mass

Convert moles to molarity or volume using  $m = \text{mol/L}$

Titration:

A common way to determine the concentration of a solution is via **titration**.

We determine the concentration of one substance by allowing it to undergo a specific chemical reaction, of known stoichiometry, with another substance whose concentration is known (**standard solution**).

Example: suppose we know the molarity of an NaOH solution and we want to find the molarity of an HCl solution

Take a known volume of the HCl solution (i.e. 20.00 mL) and measure the number of milliliters of NaOH required to react completely with HCl solution

The point at which stoichiometrically equivalent quantities of NaOH and HCl are brought together is known as the **equivalence point** of the titration.

In a titration we often use an **acid-base indicator** which change the color at the equivalence point of the titration

What do we get?

Volume of NaOH, since we already have the molarity of the NaOH, we can calculate moles of NaOH.

Next step?

We also know  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

Therefore, we know moles of HCl

Can we finish?

Knowing mol (HCl) and volume of HCl, we can calculate the molarity.

#### Chapter 5. Thermochemistry

## 5.1 The Nature of Energy

**Thermodynamic** is the study of energy and its transformation

**Thermochemistry** is the study of the relationship between chemical reactions and energy changes involving heat.

Kinetic Energy and Potential Energy

**Kinetic energy** ( $E_k$ ) is the energy of motion

**Potential energy** is the stored energy. It is the energy an object possesses by virtue of its position or composition. Example: electrostatic energy.

Potential energy can be converted into kinetic energy.

### Units of Energy

SI unit is the joule, J

From  $E_k = 1/2 m v^2$ ,  $1J = 1 \text{ kg} \times \text{m}^2/\text{s}^2$

Traditionally, we use the **calories** as a unit of energy

1 cal = 4.184 J (exactly)

The nutritional Calorie, Cal = 1,000 cal.

### System and Surroundings

A **system** is the part of the universe we are interested in studying

**Surroundings** are the rest of the universe

Example: if we are interaction between hydrogen and oxygen in a cylinder, then the hydrogen and oxygen in the cylinder form a system

Transferring Energy; work and Heat

From physics;

Force is a push or pull on an object

Work is the energy used to move an object against a force

$$w = F \times d$$

Heat is the energy transferred from a hotter object to a colder one.

Energy is the capacity to do work or to transfer heat.

## 5.2 The First Law of Thermodynamics

The first law of thermodynamics states that energy cannot be created or destroyed

It is the law of conservation of energy.

The energy of (system + surroundings) is constant.

Thus any energy transferred from a system must be transferred to the surrounding (and vice versa).

### Internal Energy

The total energy of a system is called the **internal energy**.

It is the sum of all the kinetic and potential energies of all components of the system.

Absolute internal energy cannot be measured, only changes in internal energy.

Changes in internal energy,  $\Delta E = \Delta E_{\text{final}} - \Delta E_{\text{initial}}$



Negative change in internal energy indicates that the system has lost energy to the surrounding  $\Delta E < 0$

Positive change in internal energy indicates that the system has gained energy from the surrounding  $\Delta E > 0$

### Relating $\Delta E$ to Heat and Work

From the first law of thermodynamics:

When a system undergoes a physical or chemical change, the change in internal energy is given by the heat added to or liberated from the system plus the work done on or by the system:

$$\Delta E = q + w$$

Heat flowing from the surroundings to the system is positive,  $q > 0$ .

Work done by the surroundings on the system is positive,  $w > 0$ .

### Endothermic and Exothermic Processes.

An **endothermic** process is one that absorbs heat from the surroundings.

An endothermic reaction feels cold.

An **exothermic** process is one that transfers heat to the surroundings.

An exothermic reaction feels hot.

### State Functions

A **state function** depends only on the initial and final states of a system.

Example ; the altitude difference between Denver and Chicago does not depend on whether you fly or drive, only on the elevation of the two cities above the sea level.

Similarly, the internal energy of 50 g of  $\text{H}_2\text{O}$  (l) at 25 °C does not depend on whether we cool 50 g of  $\text{H}_2\text{O}$  liquid from 100 °C to 25 °C or heat 50 g of  $\text{H}_2\text{O}$  (l) at 0°C to 25 °C.

A state function does not depend on how the internal energy is used

Example: the same internal energy of a battery is used to produce heat and light in a flashlight, or heat and work in a toy car.

### 5.3 Enthalpy.

The heat transferred between the system and the surroundings during a chemical reaction carried out under constant pressure is called **enthalpy**,  $H$ .

Again, we can only measure the change in enthalpy  $\Delta H$ .

Mathematically,

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = \Delta E + P \Delta V$$

$$w = -P \Delta V; \Delta E = q + w$$

$$\Delta H = \Delta E + P \Delta V = q_p + w - w = q_p.$$

For most reaction  $P \Delta V$  is small, thus  $\Delta H = \Delta E$ .

Heat transferred from surroundings to the system has a positive enthalpy (i.e,  $\Delta H > 0$  for an endothermic reaction).

Heat transferred from system to the surroundings has a negative enthalpy (i.e,  $\Delta H < 0$  for an exothermic reaction).

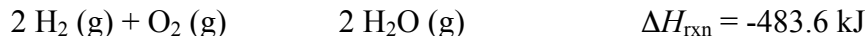
Enthalpy is a state function.

## 5.4 Enthalpies of Reactions

For a reaction,  $\Delta H_{\text{rxn}} = H(\text{products}) - H(\text{reactants})$ .

The enthalpy change that accompanies a reaction is called the enthalpy of reaction or heat of reaction ( $\Delta H_{\text{rxn}}$ ).

Consider the *thermochemical equation* for the production of water:



The equation tells us that 483.6 kJ of energy are released to the surroundings when water is formed. This reaction is exothermic.

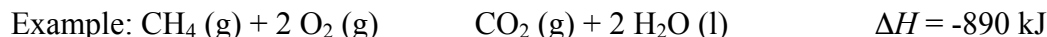
Enthalpy is an extensive property

Therefore, the *magnitude* of enthalpy is directly proportional to the amount of reactant consumed.

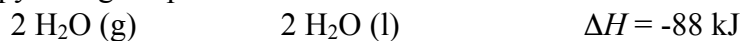
Example: if one mole of  $\text{CH}_4$  is burned in oxygen to produce  $\text{CO}_2$  and water, 890 kJ of heat is released to the surroundings. If two moles of  $\text{CH}_4$  are burned then 1780 kJ of heat is released.

The sign of  $\Delta H$  depends on the direction of the reaction

The enthalpy change for a reaction is equal in magnitude but opposite in sign to  $\Delta H$  for the reverse reaction.



Enthalpy change depends on state:



## 5.5 Calorimetry

**Calorimetry** is a measurement of heat flow

**Calorimeter** is an apparatus that measures heat flow.

### Heat Capacity and Specific Heat

**Heat capacity** is the amount of energy required to raise the temperature of an object by  $1^\circ\text{C}$ .

**Molar heat capacity** is the heat capacity of 1 mole of substance.

**Specific heat**, or specific heat capacity is the heat capacity of 1 g of a substance.

Heat,  $q = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T$

Be careful of the sign of  $q$ .

Constant Pressure Calorimetry

Most common technique; use atmospheric pressure as the constant pressure.

Recall  $\Delta H = q_p$ .

Easiest method: use a coffee cup calorimeter

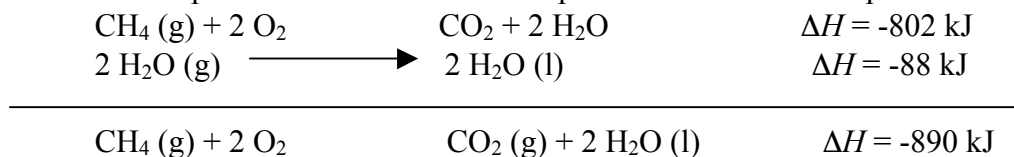
$$q_{\text{soln}} = (\text{specific heat}) \times (\text{grams of substance}) \times \Delta T = -q_{\text{rxn}}$$

For dilute aqueous solution, the specific heat of the solution will be close to that of pure water.

## 5.6 Hess's Law

**Hess's Law:** if a reaction is carried out in a series of steps,  $\Delta H$  for the reaction is the sum of  $\Delta H$  for each of the steps.

The  $\Delta H$  is independent of the number of steps and the nature of the path



$\Delta H$  is sensitive to the states of the reactants and products.

Hess's law allows us to calculate enthalpy data for reactions which are difficult to carry out directly.

### 5.7 Enthalpy of Formation

If a compound is formed from its constituent elements, then the enthalpy change for the reaction is called enthalpy of formation,  $\Delta H_f$

*Standard state* (standard conditions) refers to the substance at 1 atm and 25 °C (e.g standard enthalpy,  $\Delta H^\circ$ )

**Standard enthalpy of formation** of a compound,  $\Delta H^\circ_f$ , is the enthalpy change for the formation of 1 mole of compound with all substances in their standard states.

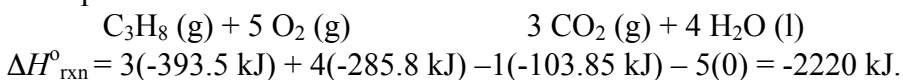
The standard enthalpy of formation of the most stable form of an element is zero.

Using Enthalpy of Formation to Calculate Enthalpies of Reaction

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f(\text{products}) - \sum m \Delta H^\circ_f(\text{reactants}).$$

Where n and m are the stoichiometric coefficients.

Example: calculate the  $\Delta H^\circ$  for



## Chapter 6. Electronic Structure of Atoms

### 6.1 The Wave Nature of Light

The **electronic structure** of an atom refers to the arrangement of electrons.

Visible light is a form of **electromagnetic radiation** or radiant energy

Radiation carries energy through space.

Electromagnetic radiation is characterized by its wave nature.

All waves have a characteristic **wavelength**,  $\lambda$  (lambda), and amplitude,  $A$ .

The **frequency**,  $\nu$  (nu), of a wave is the number of cycles which pass a point in one second.

The units of  $\nu$  are Hertz ( $1 \text{ Hz} = 1 \text{ s}^{-1}$ )

The speed of a wave is given by its frequency multiplied by its wavelength.

For light, speed,  $c = \lambda\nu$

Electromagnetic radiation moves through a vacuum with a speed of approximately  $3.00 \times 10^8 \text{ m/s}$ .

Electromagnetic waves have characteristic wavelength and frequencies.

The electromagnetic spectrum is a display of the various types of electromagnetic radiation arranged in order of increasing wavelength.

Example: visible radiation has wavelength between 400 nm (violet) and 750 nm (red).

### 6.2 Quantized Energy and Photons

Some phenomena can't explain using a wave model of light:

Blackbody radiation: emission of light from hot objects.

The photoelectric effect: emission of electrons from metal surfaces on which light shines.

Emission spectra: emission of light from electronically excited gas atoms.

#### Hot Objects and the Quantization of Energy

Heated solids emit radiation (black body radiation)

The wavelength distribution depends on the temperature (i.e., 'red hot' objects are cooler than 'white hot' object).

Planck investigated black body radiation

He proposed that energy can only be absorbed or released from atoms in certain amounts.

These amounts are called quanta.

A **quantum** is the smallest amount of energy that can be emitted or absorbed as electromagnetic radiation

The relationship between energy and frequency is

$$E = h \nu$$

Where  $h$  is **Planck's constant** ( $6.63 \times 10^{-34} \text{ J.s}$ ).

#### The Photoelectric Effect and Photons

The photoelectric effect provides evidence for the particle nature of light and quantization.

Einstein assumed that light traveled in energy packets called **photons**.

The energy of one photon,  $E = h \nu$   
Light shining on the surface of a metal can cause electrons to be ejected from the metal.  
The electrons will only be ejected if the photons have sufficient energy  
Below the threshold frequency no electrons are ejected.  
Above the threshold frequency, the excess energy appears as the kinetic energy of the electrons.  
Light has wave-like AND particle-like properties.

### 6.3 Line and the Bohr Model

#### Line spectra

Radiation composed of only one wavelength is called monochromatic  
Radiation that spans a whole array of different wavelengths is called continuous.  
When radiation from a light source such as light bulb is separated into its different wavelength components, a **spectrum** is produced.

White light can be separated into **continuous spectrum** of colors (e.g, rainbow)

Not all radiation is continuous

A gas placed in a partially evacuated tube and subjected to a high voltage produces single colors of light.

The spectrum that we see contains radiation of only specific wavelengths; this is called a **line spectrum**.

#### Bohr's Model

Rutherford assumed the electrons orbited the nucleus analogous to planets around the sun.

However, charged particles moving in circular path lose energy. The atom should be unstable, then.

Bohr noticed the line spectra of certain element and assumed that the electrons were confined to specific energy states. These were called orbits and they have specific radii.

Energy is only emitted or absorbed by an electron as it moves from one-allowed energy state to another.

The energy is gained or lost as a photon.

#### The Energy States of the Hydrogen Atom

Colors from excited gases arise because electrons move between energy states in the atom. Since the energy states are quantized, the light emitted from excited atoms must be quantized and appear as line spectra.

Bohr showed mathematically that:

$$E_n = - R_H (1/n^2)$$

Where  $n$  is the principal quantum number (i.e.,  $n = 1, 2, 3, \dots, \infty$ ) and  $R_H$  is the Rydberg constant =  $2.8 \times 10^{-18}$  J.

The first orbit in the Bohr model has  $n = 1$  and is closest of the nucleus.

The furthest orbit in the Bohr model has  $n \rightarrow \infty$  and correspond to  $E = 0$ .

Electrons in the Bohr model can only move between orbits by absorbing and emitting energy in quanta ( $E = h \nu$ ).

The **ground state** = the lowest energy state

An electron in a higher energy state is said to be in **excited state**.

The amount of energy absorbed or emitted on moving between states is given by

$$\Delta E = E_f - E_i = h \nu = R_H \left\{ \frac{1}{n_i^2} - \frac{1}{n_f^2} \right\}$$

When  $n_i > n_f$  energy is emitted and when  $n_f > n_i$  energy is absorbed.

### Limitation of the Bohr Model

The Bohr Model has several limitations;

It cannot explain the spectra of atoms other than hydrogen.

Electrons do not move about the nucleus in circular orbits.

However the model introduces two important ideas:

The energy of an electron is quantized; electrons exist only in certain energy levels described by the quantum numbers.

Energy gain or loss is involved in moving an electron from one energy level to another.

## 6.4 The Wave Behavior of Matter

Knowing that light has a particle nature, it seems reasonable to ask whether matter has a wave nature.

The question was answered by Louis deBroglie.

Using Einstein's and Planck's equations. DeBroglie derived:

$$\lambda = h / m v$$

The **momentum**,  $m v$ , is a particle property, whereas  $\lambda$  is a wave property.

**Matter waves** is the term used to describe the wave characteristics of material particles.

Therefore, in one equation deBroglie summarized the concepts of waves and particles as they apply to low-mass, high-speed objects.

### The Uncertainty Principle

**Heisenberg's uncertainty principle**; We cannot determine the exact position, direction of motion and speed of subatomic particles simultaneously.

For electrons: we cannot determine their momentum and position simultaneously.

## 6.5 Quantum mechanics and Atomic Orbitals

Schrodinger proposed an equation containing both wave and particle terms

Solving the equation leads to **wave functions**,  $\psi$ .

The wave function gives the shape of the electron's orbital.

The square of wave function,  $\psi^2$ , gives the probability of finding the electron.

That is,  $\psi^2$  gives the electron density for the atom

$\psi^2$  is called the **probability density**.

**Electron density** is another way of expressing probability

A region of high electron density is none where there is a high probability of finding an electron.

## Orbitals and Quantum Numbers

If we solve the Schrodinger equation, we get wave functions and energies for the wave functions.

We call  $\psi$  **orbitals**.

Schrodinger's equation requires three quantum numbers:

*Principal quantum number, n.* this is the same as Bohr's  $n$ .

As  $n$  becomes larger, the atom becomes larger and the electron is further from the nucleus.

*Azimuthal quantum number, l.* this quantum number depends on the value of  $n$ .

The values of  $l$  begins at 0 and increase to  $n - 1$ .

We usually use letters for  $l$  ( $s, p, d,$  and  $f$  for  $l = 0, 1, 2,$  and  $3$ ). Usually we refer to the  $s, p, d,$  and  $f$  orbitals.

This quantum number defines the shape of the orbital.

*Magnetic quantum number,  $m_l$ .*

This quantum number depends on  $l$ .

The magnetic quantum number has integer values between  $-l$  and  $+l$ .

The magnetic quantum number gives the three-dimensional orientation of each orbital.

A collection of orbitals with the same value if  $n$  is called **electron shell**.

A set of orbitals with the same  $n$  and  $l$  is called **subshell**.

Each subshell is designated by a number and a letter.

For example,  $3p$  orbitals have  $n = 3$  and  $l = 1$ .

Orbitals can be ranked in terms of energy to yield an Aufbau diagram

Note that this Aufbau diagram is for a single electron system.

As  $n$  increases note that the spacing between energy levels becomes smaller.

## 6.6 Representation of Orbitals

### The $s$ Orbitals

All  $s$  orbitals are spherical

As  $n$  increases, the  $s$  orbitals get larger

As  $n$  increases, the number of nodes increases

A **node** is a region in space where the probability of finding an electron is zero.

$$\psi^2 = 0 \text{ at a node}$$

For an  $s$  orbital the number of nodes is given by  $n-1$ .

### The $p$ Orbitals

There are three  $p$  orbitals,  $p_x,$   $p_y,$  and  $p_z$ .

The three  $p$  orbitals lie along the  $x-,$   $y-,$  and  $z-$ axes of a Cartesian system

The letters correspond to allowed values of  $m_l$  of  $-1, 0$  and  $+1$ .

The orbitals are dumb-bell shaped; each has *two lobes*.

As  $n$  increases, the  $p$  orbitals get larger

All  $p$  orbitals have a node at the nucleus.

### The $d$ and $f$ Orbitals

There are five  $d$  and seven  $f$  orbitals.

Three of the  $d$  orbitals lie in a plane bisecting the  $x-,$   $y-,$  and  $z-$ axes.

Two of the  $d$  orbitals lie in a plane aligned along the  $x$ -,  $y$ -, and  $z$ -axes.  
Four of the  $d$  orbitals have four lobes each  
One  $d$  orbital has two lobes and a collar.

## 6.7 Many-Electron Atoms

### Orbitals and Their Energies

In many-electron atom, for a given value of  $n$ ,

The energy of an orbital increases with increasing value of  $l$ .

Orbitals of the same energy are said to be **degenerate**

For  $\geq 2$ , the  $s$  and  $p$  orbitals are no longer degenerate.

Therefore, the Aufbau diagram looks slightly different for many-electron systems.

### Electron Spin and the Pauli Exclusion Principle

Line spectra of many-electron atoms show each line as a closely spaced pair of lines  
Stern and Gerlach designed an experiment to determine why.

A beam of atoms was passed through a slit and into a magnetic field and the atoms were then detected.

Two spots were found: one with the electrons spinning in one direction and one with the electrons spinning in the opposite direction.

Since **electron spin** (electron as a tiny sphere spinning on its own axis) is quantized

We define  $m_s = \text{spin magnetic quantum number} = \pm 1/2$ .

**Pauli's exclusion principle** states that no two electrons can have the same set of 4 quantum numbers.

Therefore, two electrons in the same orbit must have opposite spins.

## 6.8 Electron Configurations

**Electron configurations** tell us how the electrons are distributed among the various orbitals of an atom.

The most stable configuration or ground state is that in which the electrons are in the lowest possible energy state.

When writing ground-state electronic configurations:

Electrons fill orbitals in order of increasing energy with no more than two electrons per orbital.

No two electrons can fill one orbital with the same spin (Pauli)

For degenerated orbitals, electrons fill each orbital singly before any orbital gets a second electron.

How do we show spin?

An arrow pointing upwards has  $m_s = + 1/2$

An arrow pointing downward has  $m_s = -1/2$

### Hund's Rule

**Hund's rule:** for degenerated orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized

Thus electrons fill each orbital singly with their spin parallel before any orbital gets a second electron.



By placing electrons in different orbitals, electron-electron repulsion are minimized.

### Condensed Electron Configurations

Electron configurations may be written using shorthand notation (*condensed electron configuration*):

Write **valence electrons** explicitly

**Valence electrons:** electrons in the outer shell.

These electrons are gained and lost in reactions.

Write **core electrons** corresponding to the filled noble gas in square brackets

**Core electrons:** electrons in the inner shells.

These are generally not involved in bonding.

Example:

P;  $1s^2 2s^2 2p^6 3s^2 3p^3$

But Ne is  $1s^2 2s^2 2p^6$

Therefore, P:  $[\text{Ne}] 3s^2 3p^3$

### Transition Metals

After Ar the d orbitals begin to fill

After the 3d orbitals are full the 4p orbitals begin to fill

The ten elements between Ti and Zn are called the **transition metals** or **transition elements**.

The 4f orbitals begin to fill with Ce.

Note: the electron configuration of La is  $[\text{Xe}] 6s^2 5d^1 4f^0$

The 4f orbitals are filled for the elements Ce-Lu which are called **Lanthanide elements** (or *rare earth elements*)

The 5f orbitals are filled for the elements Th-Lr, which are called **actinide elements**.

Most actinides are not found in nature.

## 6.9 Electron Configurations and the Periodic Table.

The periodic table can be used as a guide for electron configurations.

The period number is the value of  $n$ .

Groups 1A and 2A have their  $s$  orbitals being filled.

Groups 3A – 8A have their  $p$  orbitals being filled.

The  $s$ -block and  $p$ -block of the periodic table contain the representative or main-group elements

The lanthanides and actinides have their  $f$  orbitals being filled

The actinides and lanthanide elements are collectively referred to as the **f-block** metals.

Note that the 3d orbitals fill after the 4s orbital. Similarly, the 4f orbitals fill after the 5d orbitals.

## Chapter 7: Periodic Properties of the Elements.

### 7.1 Development of the Periodic Table

the periodic table is the most significant tool that chemists use for organizing and recalling chemical facts.

Elements in the same column contain the same number of outer-shell electrons or **valence electrons**.

The majority of the elements were discovered between 1735 and 1843.

In the first attempt Mendeleev and Meyer arranged the elements in order of increasing atomic weight.

Modern periodic table: Elements are arranged in order of *increasing atomic number*.

## 7.2 Effective Nuclear Charge

**Effective nuclear charge** is the net positive charge experienced by an electron on a many-electron atom.

The effective nuclear charge is not the same as the charge on the nucleus because of the effect of the inner electrons.

The electrons is attracted to the nucleus, but repelled by the inner-shell electrons that shield or screen it from the full nuclear charge.

This shielding is called the screening effect;

The nuclear charge experienced by an electron depends on its distance from the nucleus and the number of electron in the spherical volume out the electron in question.

As the average number of screening electrons ( $S$ ) increases, the effective nuclear charge ( $Z_{eff}$ ) decreases

$$Z_{eff} = Z - S$$

As the distance from the nucleus increases,  $S$  increases and  $Z_{eff}$  decreases.

## 7.3 Size of Atoms and Ions

Periodic Trends in Atomic Radii

Atomic size varies consistently through the periodic table.

As we move down a group the atoms become larger.

As we move across a period atoms become smaller.

There are two factors at work:

The principal quantum number,  $n$  and

The effective nuclear charge,  $Z_{eff}$

As the principal quantum number increases (i.e, we move down a group), the distance of the outermost electron from the nucleus becomes larger. Hence the atomic radius increases.

As we move across the periodic table, the number of core electrons remains constant, however, the nuclear charge increases. Therefore, there is an increased attraction between the nucleus and the outermost electrons. This attraction causes the atomic radius to decrease.

### Trends in the Size of Ions

Just as the atomic size is periodic, ionic size is also periodic

In general:

Cations are smaller than their parent atoms.

Electrons have been removed from the most spatially extended orbital.

The effective nuclear charge has increased.

Therefore, the cation is smaller than the parent atom.

Anions are larger than their parent atoms.

Electrons have been added to the most spatially extended orbital.

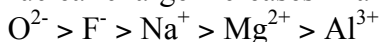
This means total electron-electron repulsion has increased.

Therefore, anions are larger than the parent atoms.

For ion with the same charge, ionic size increases down a group

All the members of an **isoelectronic series** have the same number of electrons

As the nuclear charge increases in an isoelectronic series the ions become smaller



#### 7.4 Ionization Energy

the ionization energy of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atoms or ion.

The first ionization energy,  $I_1$ , is the amount of energy required to remove an electron from a gaseous ion:



The second ionization energy,  $I_2$ , is the amount of energy required to remove a second electron from a gaseous ion:



The larger the ionization energy, the more difficult it is to remove the electrons.

There is a sharp increase in ionization energy when a core electron is removed.

#### Variation in Successive Ionization Energies.

Ionization energies for an element increase in magnitude as successive electrons are removed .

As each successive electron is removed, more energy is required to pull an electron away from an increasingly more positive ion.

A sharp increase ionization energy occurs when an inner-shell electron is removed.

#### Periodic Trends in First ionization Energies.

Ionization energy decreases down a group.

This means that the outermost electron is more readily removed as we go down a group.

As the atom gets bigger, it become easier to remove an electron from the most spatially extended orbital.

Example: for the noble gases the ionization energies follow the order



Ionization energy generally increases across a period.

As we move across a period  $Z_{\text{eff}}$  increases, making it more difficult to remove an electron.

[[Two exceptions: removing the first  $p$  electron and removing the fourth  $p$  electron.

The  $s$  electrons are more effective at shielding than  $p$  electrons. So, forming the  $s^2 p^0$  configuration is more favorable.

When a second electron is placed in a  $p$  orbital, the electron-electron repulsion increases. When this electron is removed, the resulting  $s^2 p^3$  configuration is more stable than the starting  $s^2 p^4$  configuration. Therefore, there is a decrease in ionization energy.]]

### Electron Configurations of Ions.

These are derived from the electron configurations of elements with the required number of electrons added or removed from the most accessible orbital.

Li:  $[\text{He}] 2s^1$  becomes  $\text{Li}^+$ :  $[\text{He}]$

F:  $[\text{He}] 2s^2 2p^5$  becomes  $\text{F}^-$ :  $[\text{He}] 2s^2 2p^6 = [\text{Ar}]$

Transition metals tend to lose the valence shell electrons first and then as many  $d$  electrons as are required to reach the desired charge on the ion.

Thus electrons are removed from  $4s$  **before** the  $3d$ , etc.

### 7.5 Electron Affinities.

Electron affinity is the energy change when a gaseous atom gains an electron to form a gaseous ion:

Electron affinity:  $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$   $\Delta E = -349 \text{ kJ/mol}$

Ionization energy:  $\text{Cl}(\text{g}) \rightarrow \text{Cl}^+(\text{g}) + \text{e}^-$   $\Delta E = 1251 \text{ kJ/mol}$

Electron affinity can either be exothermic (as above example) or endothermic:

$\text{Ar}(\text{g}) + \text{e}^- \rightarrow \text{Ar}^-(\text{g})$   $\Delta E > 0$

Electron configuration helps to determine whether electron affinity is positive or negative.

### 7.6 Metal, Nonmetals and Metalloids

Metallic character refers to the extent to which the element exhibits the physical and chemical properties of metals.

Metallic character increases down a group.

Metallic character decreases from left to right across a period.

#### Metals

Metals are shiny and lustrous, malleable and ductile.

Metal are solids at room temperature (exception; mercury is liquid at room temperature, gallium and cesium melt just above room temperature) and have very high melting temperature.

Metal tend to have low ionization energies and tend to form cations easily

Metals tend to be oxidized when they react.

Compounds of metals with nonmetals tend to be ionic substances.

Most metal oxides are basic:

Metal oxide + water  $\rightarrow$  metal hydroxide

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

Metal oxides are able to react with acids to form salts and water.

Metal oxide + acid  $\rightarrow$  salt + water

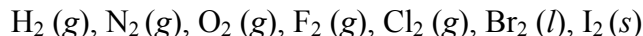
$\text{MgO}(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ .

#### Nonmetals

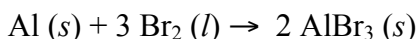
Nonmetals are more diverse in their behavior than metals.

In general, nonmetals are nonlustrous, are poor conductors of heat and electricity, and exhibit lower melting point than metals.

Seven nonmetallic elements exist as diatomic molecules under ordinary conditions.

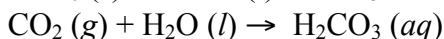
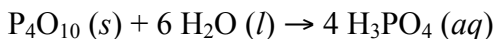
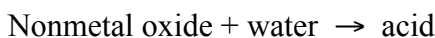


When nonmetals react with metals, nonmetals tend to gain electrons:

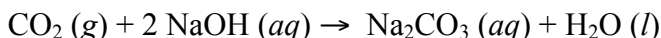
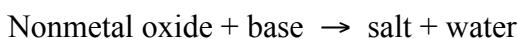


Compounds entirely of nonmetals are molecular substances.

Most nonmetal oxides are acidic:



Nonmetal oxides react with bases to form salts and water:



Metalloids

Metalloids have properties that are intermediate between those of metals and nonmetals (Si)

Metalloids have found fame in the semiconductor industry

## 7.7 Group Trends for the Active Metals

the alkali metals (group 1A) and the alkaline earth metals (group 2A) are often called the active metals.

### Group 1A: The Alkali Metals.

The alkali metals are in Group 1A

Alkali metals are all soft.

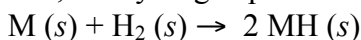
Their chemistry is dominated by the loss of their single s electron



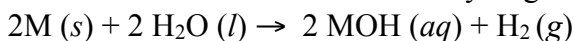
Reactivity increases as we move down a group

Alkali metals react with hydrogen to form hydrides.

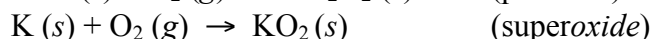
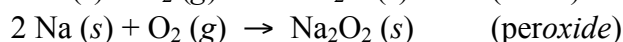
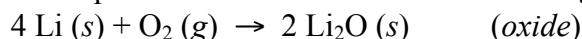
In hydrides, the hydrogen present as H<sup>-</sup>, called the **hydride ion**.



Alkali metals react with water to form MOH and hydrogen gas:



Alkali metals produce different oxides when reacting with O<sub>2</sub>:



Alkali metals emit characteristic colors when placed in a high-temperature flame.

The s electron is excited by the flame and emits energy when it returns to the ground state.

The Na line occurs at 589 nm (yellow), characteristic of the 3P → 3s transition.

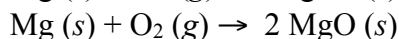
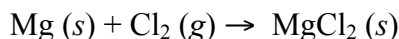
The Ni line is crimson red (2P → 2s)

The K line is lilac (4P → 4s)

### Group 2A: The Alkaline Earth Metals

Alkaline earth metals are harder and denser than the alkali metals

Their chemistry is dominated by the loss of two *s* electrons:

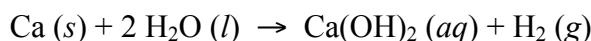


Reactivity increases down the group

Be does not react with water

Mg will only react with steam

Ca and the elements below it react with water at room temperature as follows:



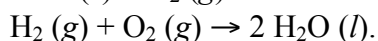
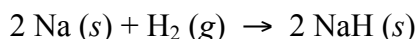
### 7.8 Group Trends for Selected Nonmetals

#### Hydrogen

Hydrogen is a unique element.

It most often occurs as a colorless diatomic gas, H<sub>2</sub>.

It can either gain another electron to form the hydride ion, H<sup>-</sup>, or lose its electron to become H<sup>+</sup>:



H<sup>+</sup> is a proton

The aqueous chemistry of hydrogen is dominated by H<sup>+</sup> (aq).

#### Group 6A: The Oxygen Group

As we move down the group the metallic character increases.

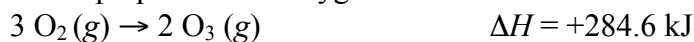
O<sub>2</sub> is a gas, Te is a metalloid, Po is a metal

There are two important forms of oxygen; O<sub>2</sub> and **ozone**, O<sub>3</sub>.

O<sub>2</sub> and O<sub>3</sub> are allotropes

Allotropes are different forms of the same element in the same state (in this case, gaseous)

Ozone can be prepared from oxygen:



Ozone is pungent and toxic

Oxygen (or dioxygen, O<sub>2</sub>) is a potent oxidizing agent since the O<sup>2-</sup> ion has a noble gas configuration.

There are two oxidation states for oxygen (e.g., H<sub>2</sub>O) and -1 (e.g., H<sub>2</sub>O<sub>2</sub>)

Sulfur is another important member of this group.

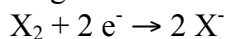
The most common form of sulfur is yellow S<sub>8</sub>.

Sulfur tends to form S<sup>2-</sup> in compounds (sulfides).

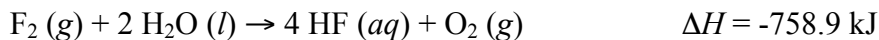
#### Group 7A: The halogens

Group 7A elements are known as the **halogens** ('salt formers').

The chemistry of the halogens is dominated by gaining an electron to form an anion:



Fluorine is one of the most reactive substances known;



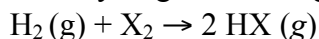
All halogens consist of diatomic molecules,  $\text{X}_2$ .

Chlorine is the most industrially useful halogen

The reaction between chlorine and water produces hypochlorous acid ( $\text{HOCl}$ ), which is used to disinfect swimming pool water:



Halogens react with hydrogen to form gaseous hydrogen halide compounds.



Hydrogen compounds of the halogens are all strong acids with the exception of  $\text{HF}$ .

### Group 8A; The Noble Gases

The group 8A elements are known as the **noble gases**.

These are all nonmetals and monoatomic.

They are notoriously unreactive because they have completely filled  $s$  and  $p$  subshells.

In 1962 the first compounds of the noble gases were prepared:  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$ .

## Chapter 8; Basic Concepts of Chemical Bonding

### 8.1 Chemical Bonds, Lewis Symbols, and the Octet Rule

When atoms or ions are strongly attracted to one another, we say that there is a **chemical bond** between them.

In chemical bonds, electrons are shared or transferred between atoms.

Types of chemical bonds include:

**Ionic bonds** (electrostatic forces that hold ions together, e.g.,  $\text{NaCl}$ );

**Covalent bonds** (result from sharing electrons between atoms, e.g.,  $\text{Cl}_2$ )

**Metallic bonds** (refers to metal nuclei floating in a sea of electrons, e.g.  $\text{Na}$ ).

### Lewis Symbols

The electrons involved in bonding are called *valence electrons*.

Valence electrons are found in the incomplete, outermost shell of an atom.

We represent the electrons as dots around the symbol for the element.

The number of valence electrons available for bonding are indicated by unpaired dots.

These symbols are called **Lewis symbols** or Lewis electron-dot symbols.

We generally place the electrons on four sides of a square around the element's symbol.

### The Octet Rule

Atoms tend to gain, lose or share electrons until they are surrounded by eight valence electrons; this is known as the **octet rule**.

An octet consists of full  $s$  and  $p$  subshells.

We know that  $s^2 p^6$  is a noble gas configuration.

We assume that an atom is stable when surrounded by eight electrons (four electron pairs).

## 8.2 Ionic Bonding

consider the reaction between sodium and chlorine;



The reaction is violently exothermic

We infer that the NaCl is more stable than its constituent elements.

Sodium has lost an electron to become  $\text{Na}^+$  and chlorine has gained the electron to become  $\text{Cl}^-$ .

Note that  $\text{Na}^+$  has an Ne electron configuration and  $\text{Cl}^-$  has an Ar configuration

That is, both  $\text{Na}^+$  and  $\text{Cl}^-$  have an octet of electrons.

Note that the ions are packed as closely as possible.

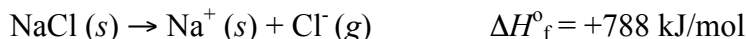
Note that it is not easy to find a molecular formula to describe the ionic lattice.

### Energetic of Ionic bond Formation

The heat of formation of NaCl (s) is exothermic:



Separation of the NaCl into sodium and chloride ions is endothermic:



The energy required to separate one mole of a solid ionic compound into gaseous ions is called the lattice energy,  $\Delta H_{\text{lattice}}$

Lattice energy depends on the charge on the ions and the size of the ions.

The stability of the ionic compound comes from the attraction between ions of unlike charge.

The specific relationship is given by Coulomb's equation

$$E = k \frac{Q_1 Q_2}{D}$$

Where  $Q_1$  and  $Q_2$  are the charges on the particles,  $d$  is the distance between their center, and  $k$  is a constant.

As  $Q_1$  and  $Q_2$  increase,  $E$  increases, and as  $d$  increases,  $E$  decreases.

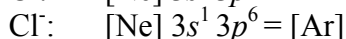
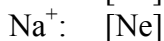
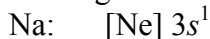
### **Calculation of the Lattice Energy: The Born-Harber Cycle.**

The **Born-Harber cycle** is a thermodynamic cycle that analyzes lattice energy precisely.

Electron Configuration of Ions of the Representative Elements.

These are derived from the electron configuration of elements with the required number of electrons added or removed from the most accessible orbital.

Electron configuration of ions can predict stable ion formation:



### Transition-Metal Ions

Lattice energy compensate for the loss of up to three electrons

We often encounter cations with charges of  $1^+$ ,  $2^+$  or  $3^+$  in ionic compounds



However, transition metals can not attain noble gas conformation ( $> 3$  electrons beyond a noble gas core).

Transition metals tend to lose the valence shell electrons first and then as many  $d$  electrons as are required to reach the desired charge on the ion.

Thus electrons are removed from  $4s$  **before** the  $3d$ , etc.

### **Polyatomic Ions**

Polyatomic ions are formed when there is an overall charge on a compound containing covalent bonds

Example:  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$

In polyatomic ions, two or more atoms are bound together by predominantly covalent bonds.

### **8.3 Covalent Bonding**

The majority of chemical substances do not have characteristics of ionic compounds.

A chemical bond formed by sharing a pair of electrons is called a covalent bond.

Both atoms acquire noble-gas electronic configurations.

This is the 'glue' to bind atoms together.

### **Lewis Structures**

Formation of covalent bonds can be represented using Lewis symbols.

The structures are called **Lewis structures**.

We usually show each electron pair shared between atoms as a line and show unshared electrons as dots.

Each pair of shared electrons constitutes one chemical bond.

Example;  $\text{H} \cdot + \text{H} \cdot \rightarrow \text{H}:\text{H}$  has electrons on a line connecting the two H nuclei;  
 $\text{H}-\text{H}$ .

### **Multiple Bonds**

It is possible for more than one pair of electrons to be shared between two atoms (e.g **multiple bonding**):

One shared pair of electrons is a **single bond** (e.g.,  $\text{H}_2$ );

Two shared pairs of electrons is a **double bond** (e.g.,  $\text{O}_2$ )

Three shared pairs of electrons is a **triple bond** (e.g.,  $\text{N}_2$ )

Generally, bond distance decrease as we move from single through double to triple bonds.

### **8.4 Bond Polarity and Electronegativity**

the electron pairs shared between two different atoms are usually unequally shared.

Bond polarity describes the sharing of the electrons in a covalent bond.

Two extremes:

In a **nonpolar covalent bond**, the electrons are shared equally.

Example: bonding between identical atoms (example:  $\text{Cl}_2$ ).

In a **nonpolar covalent bond**, one of the atoms exerts a greater attraction for bonding electron than the other (example:  $\text{HCl}$ ).

If the difference is large enough, an ionic bond forms (example:  $\text{NaCl}$ ).

## Electronegativity

The ability of an atom in a molecule to attract electrons to itself is its electronegativity. The electronegativity of an element is related to its ionization energy and electron affinity.

Pauling electronegativity scale: from 0.7 (Cs) to 4.0 (F).

Electronegativity increases across a period and decreases down a group.

## Electronegativity and Bond Polarity

Electronegativity difference close to zero result in nonpolar covalent bonds.

The electrons are equally or almost equally shared.

The greater the difference in electronegativity between two atoms, the more polar the bond (polar covalent bond).

There is no sharp distinction between bonding types.

## Dipole Moments

Molecules like HF have centers of positive and negative charge that do not coincide.

These are **polar molecules**.

We indicate the polarity of a molecule in two ways

The positive end (or pole) in a polar bond may be represented with a “ $\delta^+$ ” and the negative with a “ $\delta^-$ ”.

We can also place an arrow over the line representing the bond.

The arrow points toward the more electronegative element and shows the shift in electron density toward that atom.

We can quantify the polarity of the molecule.

When charges are separated by a distance, a **dipole** is produced.

The **dipole moment** is the quantitative measure of the magnitude of the dipole ( $\mu$ )

$$\mu = Q r$$

The magnitude of the dipole moment is given in Debyes.

## 8.5 Drawing Lewis Structures

Some simple guidelines for drawing Lewis structures:

Add up all of the valence electrons in all atoms.

For an anion, add electrons equal to the negative charge.

For a cation, subtract electrons equal to the positive charge.

Identify the central atom.

When the central atom has other atoms bound to it, the central atom is usually written first.

Example: in  $\text{CO}_2$ , the central atom is carbon.

Place the central atom in the center of the molecule and add all other atoms around it.

Place one bond (two electrons) between each pair of atoms

Complete the octets for all atoms connected to the central atom (exception: hydrogen can only have two electrons).

Complete the octet for the central atom; use multiple bonds if necessary.

## Formal Charge

Sometimes it is possible to draw more than one Lewis structure with the octet rule obeyed for all the atoms.

To determine which structure is the most reasonable, we use formal charge.

The **formal charge** of an atom is the charge that an atom (in a molecule) would have if all of the atoms had the same electronegativity.

To calculate the formal charge, electrons are assigned as follows:

All nonbonding (unshared) electrons are assigned to the atom on which they are found.

Half of the bonding electrons are assigned to each atom in a bond.

Formal charge is the number of valence electrons in the isolated atom, minus the number of electrons assigned to the atom in the Lewis structure.

For example; consider CN<sup>-</sup> (cyanide ion):

For carbon:

There are four valence electrons (from periodic table).

In the Lewis structure, there are two nonbonding electrons and three electrons from the triple bond.

There are five electrons from the Lewis structure.

Formal charge:  $4 - 5 = -1$ .

For nitrogen:

There are five valence electrons (from periodic table).

In the Lewis structure, there are two nonbonding electrons and three electrons from the triple bond.

There are five electrons from the Lewis structure.

Formal charge:  $5 - 5 = 0$ .

Using formal charge calculations to distinguish between alternative Lewis structures:

The most stable structure has the smallest formal charge on each atom and

The most negative formal charge on the most electronegative atoms.

It is important to keep in mind that formal charges Do NOT represent REAL charges on atoms.

## 8.6 Resonance Structure

Some molecules are not well described by a single Lewis structure.

Typically, structures with multiple bonds can have similar structures with the multiple bonds between different pairs of atoms.

Example: experimentally, ozone has two identical bonds whereas the Lewis structure requires one single (longer) and one double bond (shorter).

**Resonance structures** are attempts to represent the real structure that is a mix between several extreme possibilities.

Resonance structures are Lewis structures that differ only with respect to placement of the electrons.

The “true” arrangement is a blend or hybrid of the resonance structures.

Example; in ozone the extreme possibilities have one double and one single bond.

The resonance structure has two identical bonds of intermediate character.

We use a double-headed arrow ( $\leftrightarrow$ ) to indicate resonance.

Common example: O<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, SO<sub>3</sub>, NO<sub>2</sub> and benzene.

### Resonance in Benzene

Benzene belongs to an important category of organic molecules called *aromatic* compounds.

Benzene (C<sub>6</sub>H<sub>6</sub>) is a cyclic structure.

There are alternative double and single bonds between the carbon atoms

Experimentally, the C-C bonds in benzene are all the same length.

Experimentally, benzene is planar.

To emphasize the resonance between the two Lewis structures, we often represent benzene as a hexagon with a circle in it.

### 8.7 Exception to the Octet Rule.

There are three classes of exceptions to the octet rule:

Molecules with an odd number of electrons

Molecules in which one atom has less than an octet.

Molecules in which one atom has more than an octet.

#### [Odd Number of Electrons

Most molecules have an even number of electrons and complete pairing of electrons occurs although some molecules have an odd number of electrons.

Example: ClO<sub>2</sub>, NO and NO<sub>2</sub>.]

#### Less than an Octet

Molecules with less than an octet are also relatively rare.

Most often encountered in compounds of boron or beryllium

A typical example is BF<sub>3</sub>.

#### More than an Octet.

This is the largest class of exceptions.

Atoms from the third period on can accommodate more than an octet.

Example; PCl<sub>5</sub>, SF<sub>6</sub>, AsF<sub>6</sub><sup>-</sup> and ICl<sub>4</sub><sup>-</sup>.

Elements from the third period and beyond have unfilled *d* orbitals that can be used to accommodate additional electrons.

Size also plays a role.

The larger the central atom, the larger the number of atoms that can surround it.

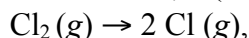
The size of the surrounding atoms is also important.

Expanded octets occur often when the atoms bound to the central atom are the smallest and most electronegative (e.g., F, Cl, O)

### 8.8 Strengths of Covalent Bonds.

The energy required to break a covalent bond is called the bond **enthalpy**, *D*.

That is for the Cl<sub>2</sub> molecule, *D*(Cl-Cl) is given by  $\Delta H$  for the reaction:



When more than one bond is broken:



The bond enthalpy is a fraction of  $\Delta H$  for the atomization reaction:

$$D(\text{C-H}) = 1/4 \Delta H = 1/4 (1660 \text{ kJ}) = 415 \text{ kJ.}$$

The bond enthalpy is always a positive quantity.

### **Bond Enthalpies and the Enthalpies of Reactions**

We can use bond enthalpies to calculate the enthalpy for a chemical reaction.

We recognize that in any chemical reaction bonds need to be broken and then new bonds form.

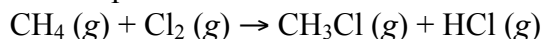
The enthalpy of the reaction is given by:

The sum of bond enthalpies for bonds broken less the sum of bond enthalpies for bonds formed.

Where  $\Delta H_{\text{rxn}}$  is the enthalpy for a reaction

$$\Delta H_{\text{rxn}} = \Sigma D(\text{bonds broken}) - \Sigma D(\text{bonds formed})$$

We illustrate the concept with the reaction between methane,  $\text{CH}_4$  and chlorine:



In this reaction one C-H bond and one Cl-Cl bond are broken while one C-Cl bond and one H-Cl bond are formed.

$$\text{So } \Delta H_{\text{rxn}} = [D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})] = -104 \text{ kJ.}$$

The overall reaction is exothermic which means that the bonds formed are stronger than the bonds broken.

The above result is consistent with Hess's law.

### **Bond Enthalpy and Bond Length**

The distance between the nuclei of the atoms involved in a bond is called **bond length**.

Multiple bonds are shorter than single bonds

We can show that multiple bonds are stronger than single bonds.

As the number of bonds between atoms increases, the atoms are held closer and more tightly together.

## Chapter 10. Gases.

### 10.1 Characteristics of Gases.

All substances have three phases; solid, liquid and gas.

Substances that are liquids or solids under ordinary conditions may also exist as gases.

These are often referred to as **vapors**.

Many of the properties of gases differ from those of solids and liquids.

Gases are highly compressible and occupy the full volume of their containers.

When a gas is subjected to pressure, its volume decreases

Gases always form homogeneous mixtures with other gases.

Gases only occupy a small fraction of the volume of their containers.

As a result, each molecule of gas behaves largely as though other molecules were absent.

### 10.2 Pressure.

**Pressure** is the force acting on an object per unit area:

$$P = F / A$$

#### Atmospheric Pressure and the Barometer

SI units of pressure are **pascals**.

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

$$1 \text{ N} = 1 \text{ kg.m/s}^2$$

A related unit is the **bar**, which is equal to  $10^5$  Pa

Gravity exerts a force on the Earth's atmosphere

A column of air  $1 \text{ m}^2$  in cross section extending to the top of atmosphere exerts a force of  $10^5$  N.

Thus, the pressure of a column of air  $1 \text{ m}^2$  in cross section extending to the top of atmosphere exerts a force of 100 kPa or 1 bar.

Atmospheric pressure is measured with a barometer

If a tube is completely filled with mercury and then inverted into a container of mercury open to the atmosphere, the mercury will rise 760 mm up the tube.

**Standard atmospheric pressure** is the pressure required to support 760 mm of Hg in a column.

Important non-SI units used to express gas pressure include:

**Atmospheres** (atm)

*Millimeter of mercury* (mm Hg) or **Torr**.

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa.}$$

### 10.3 The Gas Laws.

The equations that express the relationships among  $T$  (temperature),  $P$  (pressure),  $V$  (volume), and  $n$  (number of moles) are known as *gas laws*.

#### The Pressure-Volume Relationship: Boyle's Law

Weather balloons are used as a practical application of the relationship between pressure and volume of a gas

As the weather balloon ascends, the volume increases.

As the weather balloon gets further from Earth's surface, the atmospheric pressure decreases.

**Boyle's law:** the volume of a fixed quantity of gas, at constant temperature, is inversely proportional to its pressure.

Mathematically:

$$V = \text{constant} \times 1/P \quad \text{or} \quad PV = \text{constant}$$

A plot of  $V$  versus  $P$  is a hyperbola

Similarly, a plot of  $V$  versus  $1/P$  must be a straight line passing through the origin.

The working of lung illustrates this:

As we breathe in, the diaphragm moves down, and the ribs expand.

Therefore, the volume of the lungs increases.

According to Boyle's law, when the volume of the lungs increases, the pressure decreases. Therefore the pressure inside the lungs is less than atmospheric pressure.

Atmospheric pressure then forces air into the lungs until the pressure once again equals atmospheric pressure.

As we breathe out, the diaphragm moves up and the ribs contract.

Therefore, the volume of the lungs decreases.

By Boyle's law, the pressure increases and air is forced out.

### **The Temperature-Volume Relationship: Charles's Law**

We know that hot-air balloons expand when they are heated

**Charles's law:** The volume of a fixed quantity of gas at constant pressure is directly proportional to its absolute temperature.

Mathematically:

$$V = \text{constant} \times T \quad \text{or} \quad V/T = \text{constant}$$

Note that the value of the constant depends on the pressure and number of moles of gas.

A plot of  $V$  versus  $T$  is a straight line.

When  $T$  is measured in  $^{\circ}\text{C}$ , the intercept on the temperature axis is  $-273.15^{\circ}\text{C}$ .

We define absolute zero,  $0 \text{ K} = -273.15^{\circ}\text{C}$ .

### **The Quantity-Volume Relationship: Avogadro's Law**

Gay-Lussac's law of combining volumes; At a given temperature and pressure the volume of gases that react with one another are ratios of small whole numbers.

**Avogadro's hypothesis:** Equal volumes of gases at the same temperature and pressure contain the same number of molecules.

**Avogadro's law:** The volume of gas at a given temperature and pressure is directly proportional to the number of moles of gas.

Mathematically:

$$V = \text{constant} \times n$$

We can show that 22.4 L of any gas at 0°C and 1 atmosphere contains  $6.02 \times 10^{23}$  gas molecules.

## 10.4 The Ideal-Gas Equation

Summarizing the Gas Laws

$$\text{Boyle: } V \propto 1/P \quad (\text{constant } n, T)$$

$$\text{Charles: } V \propto T \quad (\text{constant } n, P)$$

$$\text{Avogadro: } V \propto n \quad (\text{constant } P, T)$$

$$\text{Combined: } V \propto nT/P$$

**Ideal gas equation:**  $PV = nRT$

An ideal gas is a hypothetical gas whose  $P$ ,  $V$ , and  $T$  behavior is completely described by the ideal-gas equation.

$$R = \text{gas constant} = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$$

Define **STP (standard temperature and pressure)** = 0°C, 273.15 K, 1 atm.

The molar volume of a mol of an ideal gas at STP is 22.4 L.

Relating the Ideal-Gas Equation and the Gas Laws

If  $PV = nRT$  and  $n$  and  $T$  are constant, then  $PV$  is constant and we have the Boyle's law.

Other laws can be generated similarly.

In general, if we have a gas under two sets of conditions, then

$$P_1V_1/T_1 = P_2V_2/T_2$$

We often have a situation in which  $P$ ,  $V$ , and  $T$  all change for a fixed number of moles of gas.

For this set of circumstances,

$$PV/T = nR = \text{constant.}$$

## 10.5 Further Application of the Ideal-Gas Equation

### Gas Densities and Molar Masses

Density has units of mass over volume.

Rearranging the ideal-gas equation with  $M$  as molar mass we get

$$n/V = P/RT$$

$$nM/V = PM/RT$$

$$m/V = PM/RT$$

$$\therefore d = PM/RT$$

the molar mass of a gas can be determined as follows:

$$M = dRT/P$$

### Volumes of Gases in Chemical Reactions

The ideal-gas equation relates  $P$ ,  $V$ , and  $T$  to number of moles of gas.

The  $n$  can be used in stoichiometric calculations.



## 10.6 Gas Mixtures and Partial Pressures.

Since gas molecules are so far apart, we can assume that they behave independently. Dalton observed:

The total pressure of a mixture of gases equals the sum of the pressures that each would exert if present alone.

**Partial pressure** is the pressure exerted by a particular component of a gas mixture.

**Dalton's law of partial pressures:** In a gas mixture the total pressure is given by the sum of partial pressures of each component:

$$P_1 = P_1 + P_2 + P_3 + \dots$$

Each gas obeys the ideal gas equation.

Thus,

$$P_1 = (n_1 + n_2 + n_3 + \dots) RT/V = n_t RT/V$$

### Partial Pressures and Mole Fractions

Let  $n_1$  be the number of moles of gas 1 exerting a partial pressure  $P_1$ , then

$$P_1 = X_1 P_t$$

Where  $X_1$  is the number of **mole fraction** ( $n_1/n_t$ )

Note that a mole fraction is a dimensionless number.

### Collection Gases over Water

It is common to synthesize gases and collect them by displacing a volume of water.

To calculate the amount of gas produced, we need to correct for partial pressure of the water:

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{water}}$$

The vapor pressure of water varies with temperature

Values can be found in Appendix B.

## 10.7 Kinetic-Molecular theory

The kinetic molecular theory was developed to *explain* gas behavior

Summary

Gases consist of a large number of molecules in constant random motion.

The volume of individual molecules is negligible compared with the volume of the container.

The intermolecular forces (forces between gas molecules) are negligible.

The collisions are perfectly elastic.

The average kinetic energy of the gas molecules is proportional to the absolute temperature.

Kinetic molecular theory gives us an *understanding* of pressure and temperature on the molecular level.

The pressure of a gas results from the collisions with the walls of the container.

The magnitude of the pressure is determined by how often and how hard the molecules strike.

The absolute temperature of a gas is a measure of the average kinetic energy.

As the temperature increases, the average kinetic energy of the gas molecules increases.

As kinetic energy increases, the velocity of the gas molecules increases.

**Root-mean-square (rms) speed**,  $u$ , is the speed of a gas molecules having average kinetic energy.

Average kinetic energy,  $\epsilon$ , is related to rms speed;

$$\epsilon = 1/2 mu^2$$

Where  $m$  is the mass of the molecule.

### Application to the Gas-Laws

We can understand empirical observations of gas properties with the framework of the kinetic-molecular theory.

Effect of an increase in volume (at constant temperature)

As volume increases at constant temperatures, the average kinetic of gas remains constant.

Therefore,  $u$  is constant.

However, volume increases, so the gas molecules have to travel further to hit the walls of the container.

Therefore, pressure decreases.

Effect of an increase in temperature (at constant volume)

If temperature increases at constant volume, the average kinetic of the gas molecules increases.

There are no more collisions with the container walls.

Therefore,  $u$  increases

The change in momentum in each collision increases (molecules strike harder).

Therefore, pressure increases.

### 10.8 Molecular Effusion and Diffusion

The average kinetic energy of a gas is related to its mass:

$$\epsilon = 1/2 mu^2$$

Consider two gases at the same temperature; the lighter gas has a higher rms speed than the heavier gas.

Mathematically;

$$u = \sqrt{3RT/M}$$

The lower the molar mass,  $M$ , the higher the rms speed for that gas at a constant temperature.

Two consequences of the dependence of molecular speeds on mass are:

**Effusion** is the escape of gas molecules through a tiny hole into an evacuated space.

**Diffusion** is the spread of one substance throughout a space or throughout a second substance.

### **Graham's Law of Effusion**

The rate of effusion can be quantified.

Consider two gases with molar masses  $M_1$  and  $M_2$  with effusion rates,  $r_1$  and  $r_2$ , respectively;

The relative rate of effusion is given by **Graham's law**;

$$r_1 / r_2 = M_1 / M_2$$

Only those molecules which hit the small hole will escape through it.

Therefore, the higher the rms speed the more likely that a gas molecule will hit the hole.

We can show

$$r_1 / r_2 = u_1 / u_2 = M_1 / M_2$$