



CHEMISTRY

Grade 11

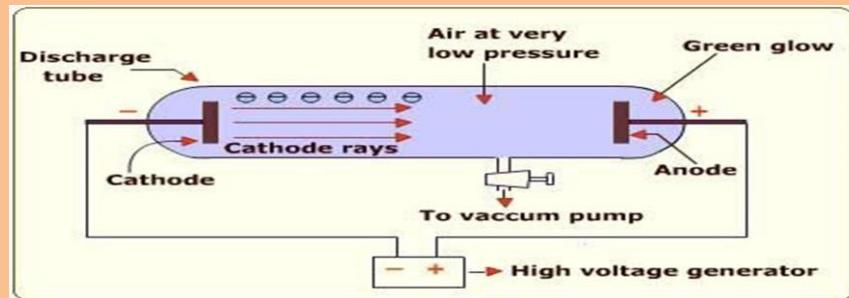


Table of Contents

UNIT 1	6
ATOMIC STRUCTURE AND PERIODIC PROPERTIES OF THE ELEMENTS.....	6
Introduction	6
1.1 Dalton's Atomic Theory and the Modern Atomic Theory.....	6
1.1.1 Postulates of Dalton's Atomic Theory.....	6
1.1.2 Postulates of Modern Atomic Theory.....	9
1.2 Early Experiments to Characterize the Atom.....	10
1.2.1 The Discovery of the Electron	10
Figure: Formation of cathode rays	11
1.2.2 Radioactivity and the Discovery of the Nucleus	12
1.2.3 Discovery of the Neutron	14
1.3 Make - up of the Nucleus.....	14
1.3.1 Subatomic Particles.....	14
1.3.2 Atomic Mass and Isotopes	15
1.4 Electromagnetic Radiation and Atomic Spectra	16
1.4.1 Electromagnetic Radiation	16
1.4.2 The quantum Theory and Photon	19
1.4.3 Atomic Spectra.....	22
1.4.4 The Bohr Model of the Hydrogen Atom	23
1.5 Limitations of the Bohr model	30
1.5.1 The Wave – particle Duality of Matter and Energy.....	30
1.6 The Quantum Mechanical Model of the Atom	31
1.6.1 The Heisenberg's Uncertainty Principle.....	31
1.6.2 The Quantum Numbers	32
1.6.3 Shapes of Atomic Orbitals.....	36
1.7 Electron Configurations and Orbital Diagrams	38
1.7.1 Ground State Electron Configuration of the Elements	38

1.8 Electronic Configuration and the Periodic Table of the Elements	41
1.8.1 The Modern Periodic Table.....	41
1.8.2 Classification of the Elements	41
1.8.3 Periodic Properties.....	41
1.8.4 Advantages of Periodic Classification of the Elements.....	47
UNIT SUMMARY.....	48
REVIEW EXERCISE.....	49
CHAPTER 2	54
CHEMICAL BONDING.....	54
2.1 INTRODUCTION.....	54
2.1.1The Octet Rule	54
2.1.2 Types of Chemical Bonding	54
2.2 Ionic Bonds.....	55
2.2.1 Lewis Electron – Dot Formula	56
2.2.2 Formation of Ionic Bonds.....	58
2.2.3 The Exceptions of the Octet Rule in Ionic Compounds.....	63
2.2.4 Properties of Ionic compounds.....	65
2.3 Covalent Bonds and Molecular Geometry.....	65
2.3.1 Molecular Geometry.....	77
2.3.2 Intermolecular Forces in Covalent Compounds.....	84
2.4 Metallic Bonding	88
2.4.1 Formation of Metallic Bonding	88
2.4.2 Electron sea- Model	88
2.4.3 Properties of Metallic Bonding	89
2.5 Chemical Bonding Theories.....	90
2.5.1 The Valence Bond (VB) Theory	90
2.5.2 Molecular Orbital Theory.....	103
2.6 Types of Crystal	110
UNIT SUMMARY.....	113
REVIEW EXERCISE.....	114

UNIT 3	119
PHYSICAL STATES OF MATTER	119
3.1 INTRODUCTION.....	119
3.2 Kinetic theory and properties of matter.....	121
3.2.1 The kinetic theory of matter	121
3.2.2 Properties of matter	121
3.3 The Gaseous state.....	123
3.3.1 The Kinetic Molecular Theory of Gases	123
3.3.2 The Gas Laws.....	124
3.4 The Liquid State	136
3.4.1 Energy Changes in Liquids.....	137
3.5 The Solid State	142
UNIT SUMMARY.....	145
REVIEW EXERCISE.....	146
UNIT 4	151
CHEMICAL KINETICS	151
4.1 INTRODUCTION.....	151
4.2 The Rate of a Reaction	151
UNIT SUMMARY.....	161
REVIEW EXERCISE.....	162
UNIT 5	167
CHEMICAL EQUILIBRIUM	167
5.1 INTRODUCTION.....	167
5.2 Chemical Equilibrium	167
5.2.1 Reversible and Irreversible Reactions.....	167
5.2.2 Attainment and Characteristics of Chemical Equilibrium	169
5.2.3 Conditions for attainment of Chemical Equilibrium	169
5.2.4 Equilibrium Expression and Equilibrium Constant.....	171
5.2.5 Application of Equilibrium Constant	179
5.2.6 Changing Equilibrium Conditions; Le Chatelier's Principle	185

5.7.2 Equilibrium and Industry.....	189
UNIT SUMMARY.....	194
REVIEW EXERCISE.....	195
UNIT 6	200
SOME IMPORTANT OXYGEN CONTAINING ORGANIC COMPOUNDS	200
6.1 INTRODUCTION.....	200
6.2 Alcohols and Ethers.....	200
6.2.1 Classification of Alcohols.....	201
6.2.2 Nomenclature of Alcohols	203
6.2.3 Physical Properties of Alcohols	204
6.2.4 Preparation of Alcohols.....	205
6.2.5 Chemical Properties of Alcohols	207
6.2.6 Structure and Nomenclature of Ethers.....	210
6.2.7 Physical Properties of Ethers	212
6.2.8 Preparation of Ethers	213
6.2.9 Reactions of Ethers	213
6.3 Aldehydes and Ketones.....	214
6.3.1 Nomenclature	215
6.3.2 Physical Properties Of Aldehydes and Ketones	216
6.4 Carboxylic Acids	218
6.4.1 Structure and Nomenclature of Carboxylic Acids	218
Structure of Carboxylic Acids	218
6.4.2 Physical Properties of Carboxylic Acids.....	226
6.4.3 Chemical Properties of Carboxylic Acids.....	229
6.4.4 Preparation of Carboxylic Acids	231
6.4.5 Fatty Acids.....	233
6.4.6 Uses of Carboxylic Acids.....	234
6.5 Esters.....	235
6.5.1 Source of Esters.....	235
6.5.3 Physical Properties.....	238

6.5.4 Chemical Properties	238
6.5.5. Preparations of Esters	239
6.5.6 Uses of Esters	240
6.6 Fats and Oils	241
6.6.1 Sources of Fats and Oils	241
6.6.2 Structure of Fats and Oils.....	241
6.6.3 Physical properties of fats and oils	243
6.6.4 Hardening of Oils.....	243
6.6.5 Rancidity.....	245
UNIT SUMMARY.....	245
REVIEW EXERCISE.....	246

UNIT 1

ATOMIC STRUCTURE AND PERIODIC PROPERTIES OF THE ELEMENTS

Introduction

- The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter.
- The philosophers of ancient Greece wondered about the composition of matters.
- **Is matter continuously divisible into ever smaller and smaller pieces, or is there an ultimate limit?**
- Most philosophers, Plato and Aristotle, believed that matter is continuous.
- That is, if one proceeded on breaking down a substance, it would be impossible to reach to the last indivisible particle.
- Democritus disagreed.

The Greek philosopher Democritus expressed his own postulate and he states that:

- Matter consists of very small, indivisible particles which are called as **atoms**. Atoms are derived from Greek words **ATOMOS** which mean indivisible into smaller particle.
- Atoms are indivisible particles.
- The early concept of atoms was simply a result of thinking and reasoning on the part of the philosophers, rather than experimental observations.

1.1 Dalton's Atomic Theory and the Modern Atomic Theory

1.1.1 Postulates of Dalton's Atomic Theory

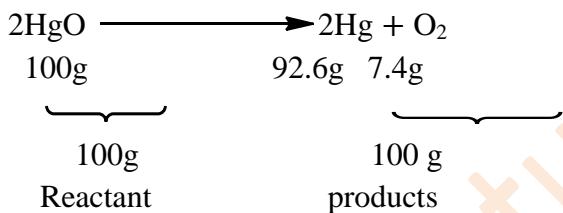
- In 1804, John Dalton developed the first modern theory of atoms and proposed their existence.
- Dalton's atomic theory was based on the ideas of elements and compounds, and on the three laws of chemical combination. The **three** laws are:
 - ✓ The law of conservation of mass
 - ✓ The law of definite proportions
 - ✓ The law of multiple proportions

- i) **The law of conservation of mass states** that matter is neither created nor destroyed. This law is also called the law of indestructibility of matter. It means that the mass of the reactants is exactly equal to the mass of the products in any chemical reaction.

Mass of reactants = Mass of products

There is no loss or gain of substances during a chemical reaction, and mass is conserved.

For example, consider the decomposition of mercury (II) oxide. When 100 g of mercury (II) oxide decomposes by heat, 92.6 g of mercury and 7.4 g of oxygen are formed. Note that the total mass of mercury and oxygen after decomposition is 100 g:



- ii) **The law of definite proportions states** that a pure compound is always composed of the same elements combined in a definite ratio by mass. This means that all pure samples of a compound have the same composition regardless of the source of sample.

For example, sample of water could be obtained from different sources, such as from a river, the ground, or the ocean. But whatever the original source, all forms of pure water contains 11.2% hydrogen and 88.8% oxygen by mass. These percentages represent a ratio of 1.0 to 8.0 (1:8), by mass, of hydrogen to oxygen.

This ratio is constant (fixed) for water. In other words, a compound with a different ratio of hydrogen and oxygen is not water.

- iii) **The law of multiple proportions states** that when two different compounds are formed from the same elements, the masses of one of the elements in the two compounds, compared to a given mass of the other element, is in a small whole number ratio.

For example the two oxides of carbon are carbon monoxide (CO) and carbon dioxide (CO₂). In CO₂, 1.0 g of carbon is combined with 2.67 g of oxygen; whereas in CO, 1.0 g of carbon is combined with 1.33 g of oxygen. By comparing 2.67 g of oxygen with 1.33 g of oxygen, it is found that the masses of oxygen in the two compounds that combine with the same mass of carbon are in the simple whole number ratio, 2:1

$$\frac{2.67\text{g of oxygen in CO}_2}{1.33\text{g of oxygen in CO}} = \frac{2}{1} = 2:1$$

➤ The basic postulates of Dalton's Atomic Theory are summarized as:

- ✓ All elements are made up of small particles called atoms.
- ✓ Atoms are indivisible and indestructible.
- ✓ All atoms of a given element are identical in mass and in all other properties.
- ✓ Atoms are neither created nor destroyed in chemical reactions.
- ✓ Compounds are formed when atoms of more than one element combine.
- ✓ In a given compound, the relative numbers and types of atoms are constant.

✓ Limitations of Dalton's atomic theory

- ✓ Does not include the existence of the nucleus
- ✓ Does not explain the existence of ions or isotopes
- ✓ Does not have any information on subatomic particles (electron, proton and neutron).

Exercise 1

1. List the postulates of Dalton's that continue to have significance (are retained in the modern atomic theory).
2. How does the atomic theory account for the fact that when 1.00 g of water is decomposed into its elements, 0.112 g of hydrogen and 0.888 g of oxygen are obtained regardless of the source of the water?

Answer to Exercise 1

1. The postulates of Dalton's atomic theory are:

- I. All matter is composed of the indivisible particles called atoms. Atoms of an element cannot be created neither can be destroyed.
- II. All atoms of a given element are identical in mass and in all other properties.
- III. The atoms of the different elements combine in fixed and whole ratios to form different compounds of atoms.
- IV. Atoms of the same element can combine in more than one ratio to form different compounds.
- V. The atom is the smallest indivisible unit of matter which takes part in the chemical

reaction.

2. The law of definite proportions

1.1.2 Postulates of Modern Atomic Theory

- ✓ Most of the experiments conducted during the development of the modern atomic theory.
- ✓ The experiments are presented as postulates of modern atomic theory.
- ✓ Modern atomic theory is generally said to begin with John Dalton.
- ✓ Dalton's work was mainly about the chemistry of atoms – how they combine to form new compounds – rather than about the internal structure of atoms.
- ✓ The modern theories about the physical structure of atoms did not begin until J.J. Thomson discovered the electron in 1897.

➤ **The Modern Atomic Theory can be summarized as follows:**

- ✓ Atoms are the smallest particles of all elements that can take part in a chemical reaction.
- ✓ An atom is divisible. It can be subdivided into electrons, protons, and neutrons. An atom is also indestructible i.e., atoms can neither be created nor destroyed during ordinary chemical reactions.
- ✓ Atoms of the same element may not be identical in mass because of the existence of isotopes.
- ✓ Atoms of the same elements have identical chemical properties.
- ✓ Atoms of different elements have different chemical properties.
- ✓ Atoms of two or more elements combine in simple whole-number ratios to form compounds.

Exercise 2

1. Describe the limitations of Dalton's atomic theory.
2. Explain the postulates of the modern atomic theory.
3. List the three fundamental laws of chemistry.
4. How does the modern atomic theory explain the three fundamental laws of chemistry?

Answer to Exercise 2

1. Limitations of Dalton's atomic theory

- Does not include the existence of the nucleus

- Does not explain the existence of ions or isotopes
 - Does not have any information on subatomic particles (electron, proton and neutron).
2. The postulates of modern atomic theory:
- All matter consists of atoms, tiny indivisible particles of an element that cannot be created or destroyed.
 - Atoms of one element cannot be converted into atoms of another element. In chemical reactions, the atoms of the original substances recombine to form different substances.
 - Atoms of an element are identical in mass and other properties and are different from atoms of any other element.
 - Compounds result from the chemical combination of a specific ratio of atoms of different elements.
3. Modern chemistry is based on several fundamental laws, including the law of multiple proportions, law of definite proportions, and law of conservation of mass.
- **The law of conservation of mass** states that matter is neither created nor destroyed.
 - **The law of definite proportions** states that a pure compound is always composed of the same elements combined in a definite ratio by mass.
 - The law of multiple proportions states that when two different compounds are formed from the same elements, the masses of one of the elements in the two compounds, compared to a given mass of the other element, is in a small whole number ratio.

1.2 Early Experiments to Characterize the Atom

1.2.1 The Discovery of the Electron

Cathode Rays

- One of the first experiments on subatomic particles was carried out by the English physicist J.J. Thomson in 1897.
- Figure: shows emission of cathode rays in a discharge tube which is an experimental apparatus.
- In this apparatus, two electrodes from a high-voltage source are sealed into a glass tube from which the air has been evacuated.
- The negative electrode is called the cathode; the positive one, the anode.
- When the high-voltage current is turned on, the glass tube emits a greenish light.
- Experiments showed that this greenish light is caused by the interaction of the glass with cathode rays, which are rays that originate from the cathode.

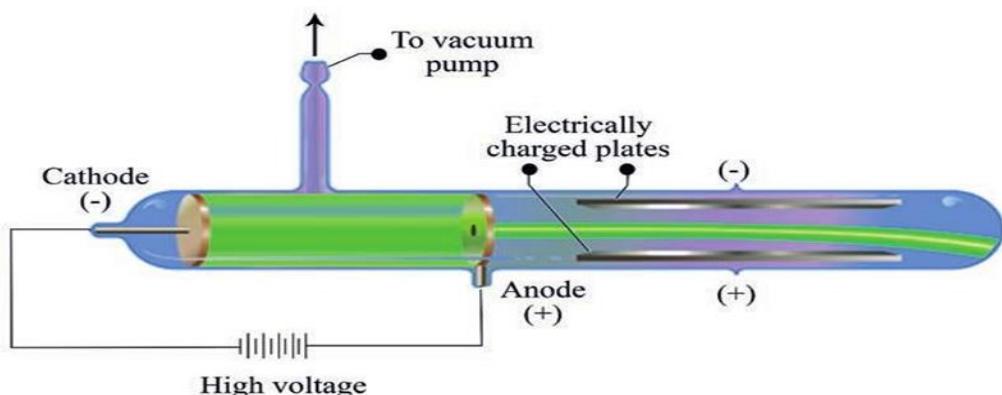


Figure: Formation of cathode rays

After the cathode rays leave the negative electrode, they move toward the anode, where some rays pass through a hole to form a beam.

This beam bends away from the negatively charged plate and toward the positively charged plate.

Thomson showed that the characteristics of cathode rays are independent of the material making up the cathode.

He concluded that a cathode ray consists of a beam of negatively charged particles (or electrons) and that electrons are constituents of all matter.

Cathode rays normally travel in straight lines, but are deflected when a magnet is brought nearby (figure 2).

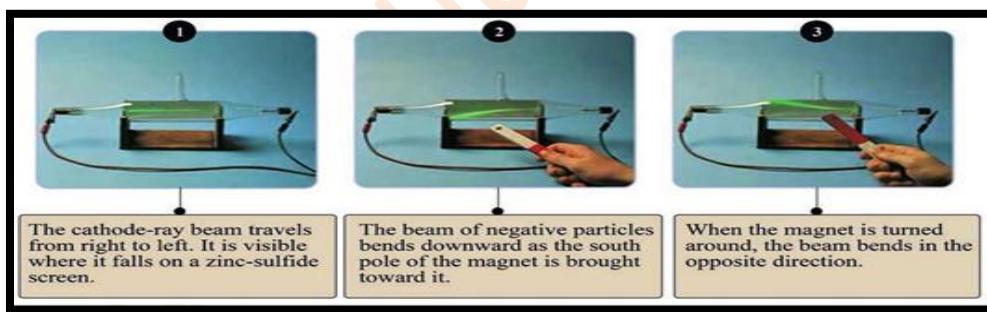


Figure 2: Bending cathode rays using a magnet

By measuring the amount of deflection of a cathode ray beam in electric and magnetic fields of known strengths, Thomson was able to calculate the ratio of the mass of an electron, m_e , to its charge, e , with -5.686×10^{-12} kg C⁻¹ (kilograms per coulomb). However, he could not obtain either the mass or the charge separately.

In 1909, **Robert A. Millikan**, an American physicist, measured the charge

of the electron by measuring the effect of an electrical field on the rate at which charged oil drops fell under the influence of gravity. Based on careful experiments, Millikan established the charge on an electron as $e = -1.602 \times 10^{-19} \text{ C}$.

He used this value and Thomson's mass/charge ratio to calculate an electron's mass to be $9.109 \times 10^{-31} \text{ kg}$.

$$m_e = \frac{me}{e} \times e = -5.686 \times 10^{-12} \text{ kg C}^{-1} \times -1.602 \times 10^{-19} \text{ C}$$

$$= 9.109 \times 10^{-31} \text{ kg}$$

1.2.2 Radioactivity and the Discovery of the Nucleus

Radioactivity

Radioactivity or radioactive decay is the spontaneous emission of particles and/or radiation from the unstable nuclei of certain atoms such as uranium, radium.

After the discovery of radioactivity, three types of rays were identified in the emissions from radioactive substances.

Two are deflected by oppositely charged metal plates.

Alpha (α) rays consist of positively charged particles, called **α particles**.

- ✓ They have a mass of about four times that of a hydrogen atom and a charge twice the magnitude of an electron;
- ✓ They are identical to helium nuclei.

Beta (β) rays, or **β particles**, are electrons coming from inside the nucleus and are deflected by the negatively charged plate.

The third type of radioactive radiation consists of high-energy rays called **gamma (γ) rays**.

- ✓ They have no charge and are not affected by an external electric or magnetic field.

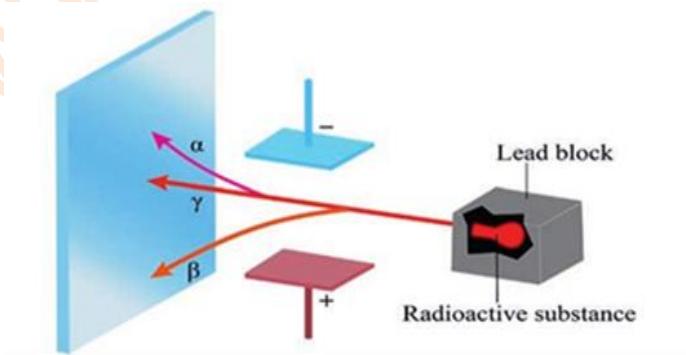


Figure 3: Three types of ray emitted by radioactive elements

The Discovery of the Nucleus

Thomson proposed a “plum-pudding” model (**Figure 4**) for the atom in which the electrons and protons were randomly distributed in a positively charged cloud like plums in a pudding.

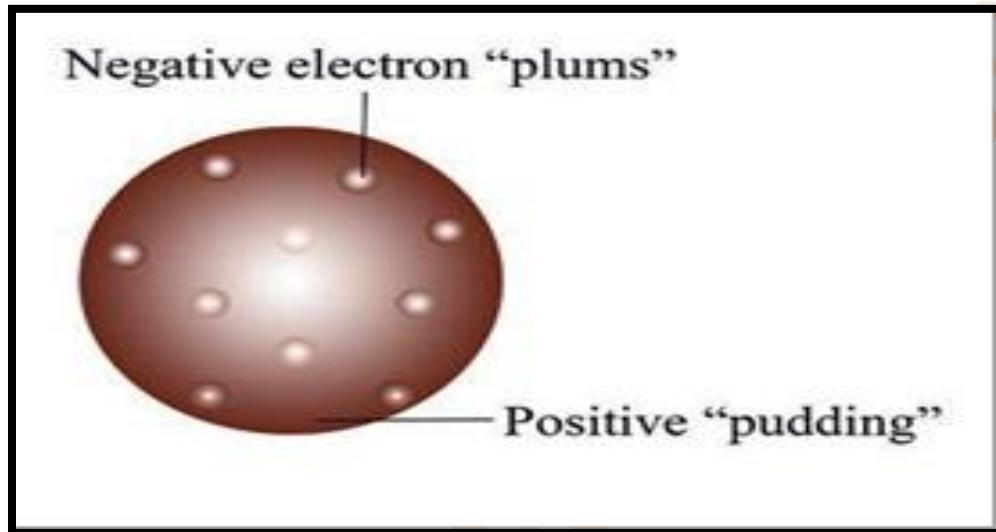


Figure 4: Thomson’s “plum-pudding” model of an atom

In 1911, Ernest Rutherford worked with Thomson to test this model.

In Rutherford’s experiment, positively charged particles were passed at a thin sheet of gold foil (Figure 1.5).

If the Thomson model were correct, the particles would travel in straight paths through the gold foil.

Rutherford was greatly surprised to find that some of the particles were deflected as they passed through the gold foil, and a few particles were deflected so much that they went back in the opposite direction.

He also concluded that the force must be caused by a very densely packed bundle of matter with a positive electric charge.

Rutherford called this small, dense, positive bundle of matter the **nucleus**.

Rutherford's Conclusion

Since most of the α -particles passed through the gold foil undeflected, most of the space in an atom is empty.

Some of the α -particles were deflected by small angles. This indicated the presence of a heavy positive center in the atom, which Rutherford named the nucleus.

Only a few particles (1 in about a million) were either deflected by a very large angle or deflected back. This confirmed that the space occupied by the heavy positive center must be very small.

1.2.3 Discovery of the Neutron

The neutron was discovered by alpha-particle scattering experiments.

When beryllium metal is irradiated with alpha rays, a strongly penetrating radiation is obtained from the metal.

In 1932 the British physicist James Chadwick (1891–1974) showed that this penetrating radiation consists of neutral particles, called neutrons.

The neutron is a nuclear particle having a mass almost identical to that of the proton but with no electric charge.

The mass of a neutron, $m_n = 1.67493 \times 10^{-27}$ kg, which is about 1840 times the mass of an electron.

1.3 Make - up of the Nucleus

1.3.1 Subatomic Particles

In 1919, Rutherford discovered that hydrogen nuclei, or we now call protons, form when alpha particles strike some of the lighter elements, such as nitrogen.

A proton is a nuclear particle having a positive charge equal in magnitude to that of the electron.

A proton has a mass of $m_p = 1.67262 \times 10^{-27}$ kg, which is about 1840 times the mass of electrons.

The protons in a nucleus give the nucleus its positive charge.

Table 1.1: Properties of subatomic particles

Particle	Actual mass (kg)	Relative mass (amu)	Actual charge (C)	Relative charge
Proton (p)	1.672622×10^{-27}	1.007276	1.602×10^{-19}	+1
Neutron (n)	1.674927×10^{-27}	1.008665	0	0
Electron (e^-)	9.109383×10^{-31}	5.485799×10^{-4}	-1.602×10^{-19}	-1

The atomic number (Z): of an element equals the number of protons in the nucleus of each of its atoms.

All atoms of a particular element have the same atomic number, and each element has a different atomic number from that of any other element.

The mass number (A): is total number of protons and neutrons in the nucleus of an atom.

The mass number and atomic number of an element X are written with the symbol.

${}_Z^AX$

Example .the element sodium has atomic number and mass number 11, 23 respectively.

The symbolic representation is ${}_{11}^{23}Na$

1.3.2 Atomic Mass and Isotopes

All atoms of an element are identical in atomic number but not in mass number.

Isotopes of an element are atoms that have different numbers of neutrons and different mass numbers.

Most elements found in nature are mixtures of isotopes.

The **average mass** for the atoms in an element is called the atomic mass of the element and can be obtained as averages over the relative masses of the isotopes of each element, weighted by their observed fractional abundances.

If an element consists of n isotopes, of relative masses $A_1, A_2 \dots A_n$ and fractional abundances of $f_1, f_2 \dots f_n$, then the average relative atomic mass (A) of the element is: $A = A_1f_1 + A_2f_2 + \dots + A_nf_n$.

Example 1, there are two naturally occurring isotopes of silver. Isotope ${}^{107}Ag$ (106.90509amu) accounts for 51.84% of the total abundance, and isotope ${}^{109}Ag$ (108.90476amu) accounts for the remaining 48.16%. Calculate the atomic mass of silver?

Solution:

- ✓ Find the portion of the atomic mass from each isotope:

- ✓ Portion of atomic mass from ^{107}Ag : = isotopic mass \times fractional abundance = $106.90509 \text{ amu} \times 0.5184 = 55.42 \text{ amu}$
- ✓ Portion of atomic mass from ^{109}Ag : = $108.90476 \text{ amu} \times 0.4816 = 52.45 \text{ amu}$
- ✓ Find the atomic mass of silver:
- ✓ Atomic mass of Ag = $55.42 \text{ amu} + 52.45 \text{ amu} = 107.87 \text{ amu}$

Exercise 3

1. How many protons and neutrons are in the nucleus of each of the following atoms?
2. Element X is toxic to humans in high concentration but essential to life at low concentrations. It has four naturally occurring isotopes that contain 24 protons. Identify element X and give the atomic symbol for the isotopes with 26, 28, 29, and 30 neutrons.
3. Naturally occurring boron consists of two isotopes, ^{10}B and ^{11}B , with the isotopic masses 10.013 amu and 11.009 amu, respectively. The observed atomic mass of boron is 10.811 amu. Calculate the abundance of each isotope.
4. The two naturally occurring isotopes of lithium, lithium-6 and lithium-7, have masses of 6.01512 amu and 7.01600 amu, respectively. Which of these two occurs in greater abundance?

Answer to Exercise 3

1. a. 13 protons and 14 neutrons b. 16 protons and 16 neutrons
- c. 30 protons and 34 neutrons d. 82 protons and 125 neutrons
2. **Element X is Cr; $^{50}_{24}\text{Cr}$, $^{52}_{24}\text{Cr}$, $^{53}_{24}\text{Cr}$, $^{54}_{24}\text{Cr}$,**
3. 19.9% boron-10 and 80.1% boron-11
4. Because of the weighted-average atomic mass of lithium, 6.941 amu, is much closer to 7.01600 amu than to 6.01512 amu, lithium-7 must be the more abundant isotope.

1.4 Electromagnetic Radiation and Atomic Spectra

1.4.1 Electromagnetic Radiation

- In 1873, James Clerk Maxwell proposed that light consists of electromagnetic waves.
- According to his theory, an electromagnetic wave has an electric field and magnetic field components.
- These two components vibrate in two mutually perpendicular planes (Figure 1.6).

- EMR is the emission and transmission of energy in the form of electromagnetic waves.

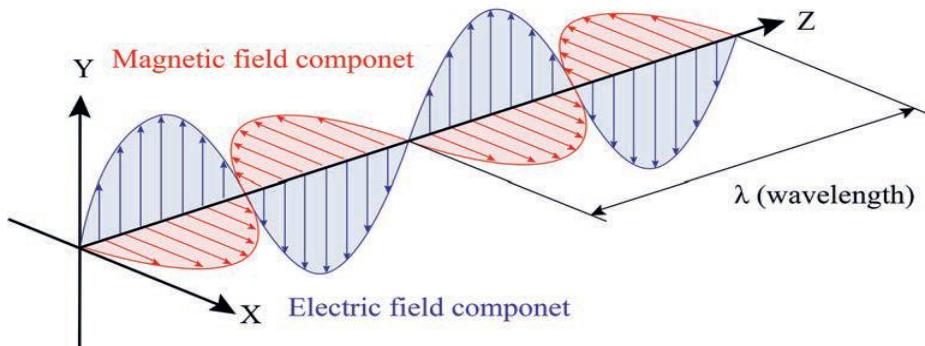


Figure 5: The electric field and magnetic field components of electromagnetic waves

Electromagnetic waves have three primary characteristics: wavelength, frequency and speed.

Wavelength(λ , Greek lambda), is the distance the wave travels during one cycle
It is expressed in meters (m)

For very short wavelengths, in nanometers (nm), Pico meters (pm), or angstrom (\AA).

Frequency (ν , Greek letter nu) is the number of cycles the wave undergoes per second and is expressed in units of 1/second (1/s; also called hertz, Hz).

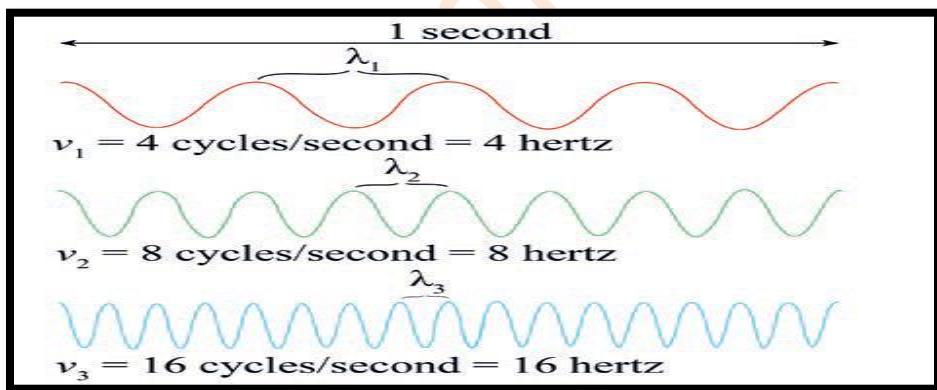


Figure 6: Frequency of waves

Wave has a speed which depends on the type of wave and the nature of the medium through which it is traveling (for example, air, water, or a vacuum).

The speed (c) of a wave is the product of its wavelength and its frequency:

In a vacuum, electromagnetic waves travel at 3×10^8 m/s, which is a physical constant called the **speed of light**.

EMR comes in a broad range of frequencies called the **electromagnetic spectrum** (Figure 1.8).

A rainbow is an example of a continuous spectrum.

Different wavelengths in visible light have different colors from **red** ($\lambda = 750 \text{ nm}$) to **violet** ($\lambda = 380 \text{ nm}$). Radiation provides an important means of energy transfer.

For instance, the energy from the Sun reaches the Earth mainly in the form of visible and ultraviolet radiation.

The glowing coals of a fireplace transmit heat energy by infrared radiation.

In microwave ovens, microwave radiation is used to heat water in foods, causing the food to cook quickly.

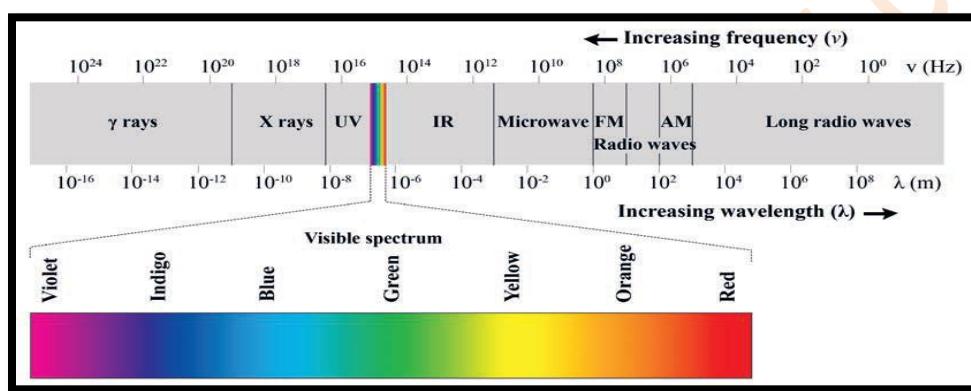


Figure 7: The electromagnetic spectrum

Example 2, Ethiopian National Radio, Addis Ababa station broadcasts its AM signal at a frequency of 2400 kHz. What is the wavelength of the radio wave expressed in meters?

Solution:

We obtain the wavelength of the radio wave by rearranging Equation 1.1 so, $\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{2.4 \times 10^6 \text{ s}} = 125.0 \text{ m}$

Exercise 4

1. The most intense radiation emitted by the Earth has a wavelength of about $10.0 \mu\text{m}$. What is the frequency of this radiation in hertz?
2. Addis Ababa Fana FM radio station, broadcasts electromagnetic radiation at a frequency of 98.1 MHz. What is the wavelength of the radio waves, expressed in meters?

Answer to Exercise 4

$$1.30 \times 10^{13} \text{ s}^{-1} \equiv 3.0 \times 10^{13} \text{ Hz}$$

2. 3.06 m

1.4.2 The quantum Theory and Photon

- In 1900, Max Planck, the German physicist, came to an entirely new view of matter and energy.
 - He made a revolutionary proposal, energy like matter is discontinuous.
 - According to Planck, atoms and molecules could emit or absorb energy only in discrete quantities, like small packages or bundles.
 - Each of these small “packets” of energy is called **a quantum**.

The energy of a quantum is proportional to the frequency of the radiation.

The energy E of a single quantum is given by

$$F \equiv h\nu \quad 12$$

Where \hbar is called Planck's constant and ν is the frequency of radiation.

The value of Planck's constant is 6.63×10^{-34} Js

Since $v = c/\lambda$, Equation 1.2 can also be expressed as:

According to quantum theory, energy is always emitted or absorbed in integral multiples of $h\nu$:

For example, $h\nu$, $2h\nu$, $3h\nu$, etc. A system can transfer energy only in whole quanta.

Example 3, The blue color in fireworks is often achieved by heating copper (I) chloride (CuCl) to about $1200\text{ }^{\circ}\text{C}$. Then the compound emits blue light having a wavelength of 600 nm . What is the increment of energy (the quantum) that is emitted at 600 nm by CuCl ?

Solution:

The quantum of energy can be calculated from the **Equation 1.2**:

$$E = h\nu$$

The frequency (v) for this case can be calculated as follows

$$v = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{6.0 \times 10^{-7} \text{ m}} = 0.50 \times 10^{15} \text{ s}^{-1}$$

$$So, E = hv$$

$$= 3.32 \times 10^{-19} \text{ J}$$

The Photoelectric Effect

In 1905, Albert Einstein used the quantum theory to explain the photoelectric effect.

The photoelectric effect is a phenomenon in which electrons are ejected from the surface of certain metals exposed to light of at least a certain minimum frequency, called the threshold frequency, v_0 .

These observations can be explained by assuming that EMR is quantized (consists of photons), and the threshold frequency represents the minimum energy required to remove the electron from the metal's surface. Photons are particles of light or energy packet. The minimum energy required to remove an electron is:

Where E_0 is the minimum energy (of the photon), and ν_0 , the threshold frequency.

A photon with energy less than E_o ($\nu < \nu_o$) cannot remove an electron, or a light with a frequency less than the ν_o produces no electrons.

On the other hand, if a light has $v > v_o$, the energy in excess of that required to remove the electron is given to the electron as kinetic energy (KE):

Where KE_e is the kinetic energy of an electron, m is mass of an electron, v is the velocity of an electron, $h\nu$, is the energy of an incident photon, and $h\nu_0$ is the energy required to remove an electron from the metal's surface.

Intensity of light is a measure of the number of photons present in a given part of the beam:

A greater intensity means that more photons are available to release electrons (as long as $\nu > \nu_0$ for the radiation).

In his theory of relativity in 1905, Einstein derived the famous equation:

Rearranging this equation, we have

$$m = \frac{E}{c^2} \dots \dots \dots \quad (1.7)$$

Where E is energy, m is mass, and c is speed of light

Equation 1.7 tells that energy has mass.

For electromagnetic radiation of wavelength, λ , the energy of each photon is given by the expression:

$$E = \underline{hc}$$

λ 1.8

Then, the apparent mass of a photon of light with wavelength is given by:

$$\triangleright m = \frac{E}{c^2} = \frac{hc/\lambda}{c^2} = \frac{h}{c\lambda} \quad 1.9$$

Energy is **quantized**. It can occur only in discrete units called photon or quanta.

EMR, which was previously thought to exhibit only wave properties, seems to show certain characteristics of particulate matter as well. This phenomenon is sometimes referred to as the dual nature of light and is illustrated **Figure 9**.

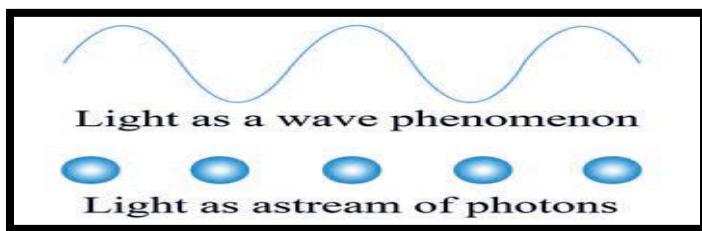


Figure: The dual nature of light

Example 4; The maximum kinetic energy of the photoelectrons emitted from a given metal is $1.5 \times 10^{-20} \text{ J}$ when a light that has a 750 nm wavelength shines on the surface.

Determine the threshold frequency, ν_0 , for this metal. Calculate the corresponding wavelength, λ_0 .

Solution:

a) Determination of the threshold frequency, ν_0

➤ Solve for ν from $c = \nu \times \lambda$

$$\text{Thus, } \nu = c/\lambda = (3.0 \times 10^8 \text{ m/s})/7.5 \times 10^{-7} \text{ m} \\ = 0.4 \times 10^{15} \text{ s}^{-1} = 4.0 \times 10^{14} \text{ s}^{-1}$$

Similarly, rearrange **Equation 1.5** and solve ν_0

$$\nu_0 = \frac{h\nu - KE}{h}$$

$$= \frac{6.63 \times 10^{-34} \text{ J.s} \times 4.0 \times 10^{14} \text{ s}^{-1} - 1.5 \times 10^{-20} \text{ J}}{6.63 \times 10^{-34} \text{ J.s}} \\ = \frac{26.52 \times 10^{-20} \text{ J} - 1.5 \times 10^{-20} \text{ J}}{6.63 \times 10^{-34} \text{ J.s}} = \frac{24.02 \times 10^{-20} \text{ J}}{6.63 \times 10^{-34} \text{ J.s}} \\ = 3.77 \times 10^{14} \text{ s}^{-1}$$

✓ Therefore, a frequency of $3.77 \times 10^{14} \text{ s}^{-1}$ Hz is the minimum (threshold) required to cause the photoelectric effect for this metal.

✓ b) Calculate the corresponding wavelength λ_0

$$\checkmark \lambda_0 = \frac{c}{\nu_0} = \frac{3.0 \times 10^8 \text{ m/s}}{3.77 \times 10^{14} \text{ s}^{-1}} \\ = 0.796 \times 10^{-6} \text{ m} \\ = 796 \text{ nm}$$

Exercise 5

- The following are representative wavelengths in the infrared, ultraviolet, and γ -ray regions of the electromagnetic spectrum, respectively: $1.0 \times 10^{-6} \text{ m}$, $1.0 \times 10^{-8} \text{ m}$, and $1.0 \times 10^{-10} \text{ m}$.

- a. What is the energy of a photon of each radiation?
 - b. Which has the greatest amount of energy per photon?
 - c. Which has the least?
2. A clean metal surface is irradiated with light of three different wavelengths λ_1 , λ_2 , and λ_3 . The kinetic energies of the ejected electrons are as follows: λ_1 : 7.2×10^{-20} J; λ_2 : approximately zero; λ_3 : 5.8×10^{-19} J. Which light has the shortest wavelength and which has the longest wavelength? Determine the threshold frequency, v_o , for this metal.
3. The minimum energy required to cause the photoelectric effect in potassium metal is 3.69×10^{-19} J. Will photoelectrons be produced when visible light, 520 nm and 620 nm, shines on the surface of potassium? What is or are the velocities of the ejected electron/s?

Answer to Exercise 5

1. a. i. $E_{\text{Infrared}} = 19.89 \times 10^{-20} \text{ J} \approx 2.0 \times 10^{-19} \text{ J}$

ii. $E_{\text{ultraviolet}} = 19.89 \times 10^{-18} \text{ J} \approx 2.0 \times 10^{-17} \text{ J}$

iii. $E_{\text{x-ray}} = 19.89 \times 10^{-16} \text{ J} \approx 2.0 \times 10^{-15} \text{ J}$

b. An x-ray has the greatest amount of energy per photon.

c. Infrared has the smallest amount of energy per photon.

2. i. $\lambda_1 = 2.76 \times 10^{-6} \text{ m}$ $\lambda_2 \approx 0$ $\lambda_3 = 3.43 \times 10^{-7} \text{ m}$

ii. λ_2 has the longest wavelength & λ_1 has a shortest wavelength

iii. $v_{o1} = 1.1 \times 10^{14} \text{ Hz}$ $v_{o2} \approx 0$ $v_{o1} = 8.7 \times 10^{14} \text{ Hz}$

3. i. The maximum threshold frequency, $\lambda_o = 539 \text{ nm}$, that means a light with a wavelength greater than the λ_o cannot eject electrons. Thus, photoelectrons cannot be produced when visible light of 620 nm shines on the surface of potassium. But, when a visible light of 520 nm shines on potassium photoelectron can be produced.

ii. Velocity of the ejected electron (v) when 520 nm shines on potassium is 5.4 m/s.

1.4.3 Atomic Spectra

Atomic or line spectra are produced from the emission of photons of electromagnetic radiation (light). Different kinds of spectrum are observed when an electric discharge, or spark, passes through a gas such as hydrogen. The electric discharge is an electric current that excites, or

energizes, the atoms of the gas. More specifically, the electric current transfers energy to the electrons in the atoms raising them to excited states.

The atoms then emit the absorbed energy in the form of light as the electrons return to lower energy states. When a narrow beam of this light is passed through a prism, we do not see a continuous spectrum, or rainbow, as sunlight does. Rather, only a few colors are observed, displayed as a series of individual lines.

This series of lines is called the element's atomic spectrum or emission spectrum. The wavelengths of these spectral lines are characteristic of the element producing them, and used for their identification. For example, the emission (line) spectrum of hydrogen atom is shown in Figure 9.

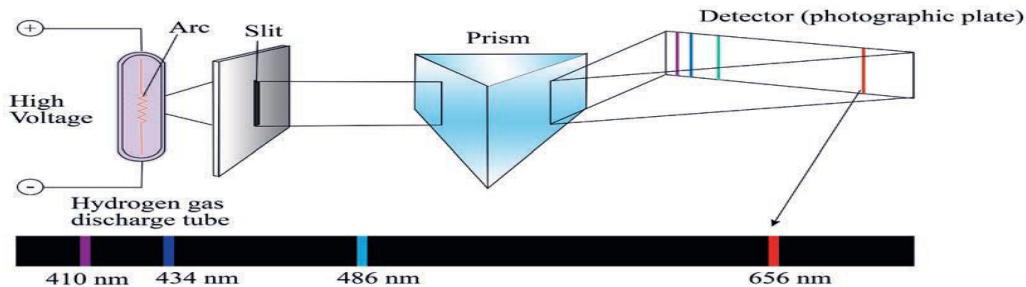


Figure 9: The hydrogen line spectrum, containing only a few discrete wavelengths.

- Changes in energy between discrete energy levels in hydrogen will produce only certain wavelengths of emitted light, as shown in Figure. For example, a given change in energy from a high to a lower level would give a wavelength of light which can be expressed using Planck's equation:
- $\Delta E = h\nu = hc/\lambda$

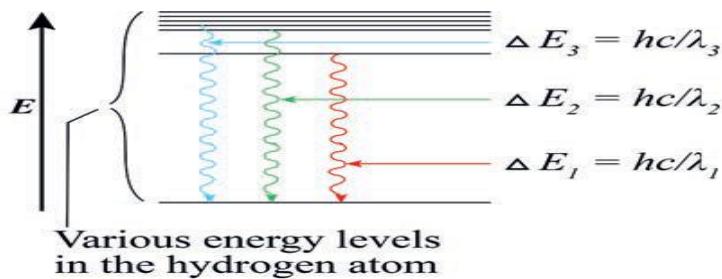


Figure 10: A change between two discrete energy levels emits a photon of light.

1.4.4 The Bohr Model of the Hydrogen Atom

In 1913, Niels Bohr (a Danish physicist) explained why the orbiting electron does not radiate energy as it moves around the nucleus.

He introduced the fundamental idea that the absorption and emission of light by hydrogen atoms was due to energy changes of the electrons within the atoms.

The fact that only certain frequencies are absorbed or emitted by an atom tells us that only certain energy changes are possible.

Thus, energy changes in an atom are **quantized**.

Bohr used Planck's and Einstein's ideas about quantized energy and proposed the following assumptions:

The electron in an hydrogen atom travels around the nucleus in a circular orbit.

The energy of the electron in an atom is proportional to its distance from the nucleus. The further an electron is from the nucleus, the more energy it has.

Only limited number of orbits with certain energies is allowed. This means, the orbits are quantized.

The only orbits that are allowed are those for which the angular momentum of the electron is an integral multiple of $\hbar/2\pi$.

As long as an electron stays in a given orbital, it neither gains or losses energy. That means, the atom does not change its energy while the electron moves within an orbit.

The electron moves to a higher energy orbit only by absorbing energy in the form of light, and emitting light when it falls to a lower energy orbit. The energy (photon) of the light absorbed or emitted is exactly equal to the difference between the energies of the two orbits.

Furthermore, Bohr showed that the radii, r , of the permitted orbits or energy levels for an atom of hydrogen atom are related to Planck's constant, \hbar , the electron's charge, e , and its mass, m .

Consider hydrogen atom with an electron with constant speed, v , circulating the nucleus in an orbit of radius, r .

The total energy of the electron is the sum of the kinetic energy (energy of movement) and the potential energy (energy of position):

For an electron to exist in a stable orbit of a constant radius, the centripetal force (attracting the electron to the nucleus), e^2/r^2 , and the centrifugal force (pulling away the electron from the nucleus), mv^2/r must be equal.

Bohr introduced an additional requirement that the angular momentum, mvr , of the electron can take only certain permitted values, that is, an integral multiple of $\hbar/2\pi$. This requirement is called a **quantum condition**:

Solving Equation 1.12 for v gives:

Substituting for v in Equation 1.11 and solving for r gives:

Here, n is positive integer ($n = 1, 2, 3 \dots$) and is called **quantum number**. It is known that h, π, m , and e are constants, thus Equation 1.14 can be simplified to:

According to **Equation 1.15** the only permitted values of the radii of the electron path in the hydrogen atom are those proportional to the square of a whole number, n .

The numerical values of a_o is 0.53 Å. Thus,

$r = (0.53 \text{ \AA})n^2$ For instance, for $n = 1$, $r = 0.53 \text{ \AA}$. This is the first Bohr radius.

The larger the values of n , the further the electron from the nucleus.

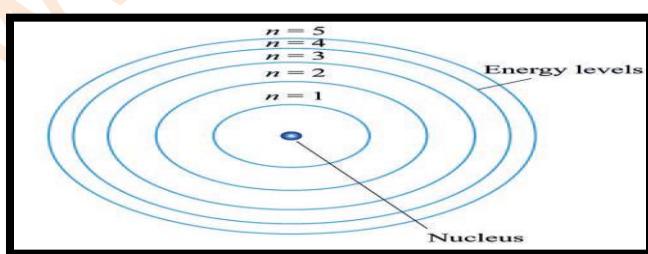


Figure 11: Bohr's energy levels of a hydrogen atom

Bohr showed that the energies that an electron in hydrogen atom can occupy are given by:

Where R_H , the Rydberg constant for the hydrogen atom and has the value 2.18×10^{-18} J. Thus, Equation 1.16 can be written as:

$$E_n = -\frac{2.18 \times 10^{-18} J}{n^2}$$

The negative sign in Equation 1.16 is an arbitrary convention, signifying that the energy of the electron in the atom is lower than the energy of a free electron, which is an electron that is infinitely far from the nucleus.

The energy of a free electron is given a value of zero.

As the electron gets closer to the nucleus (as n decreases), $|En|$ becomes larger in absolute value, but also more negative. The most negative value, then, is reached when $n = 1$, which corresponds to the most stable energy state.

We call this the ***ground state or ground level***, which refers to the lowest energy state of an atom.

The stability of the hydrogen electron diminishes for $n = 2, 3, \dots$. Each of these levels is called an ***excited state, or excited level***, which is higher in energy than the ground state.

A hydrogen electron for which n is greater than 1 is said to be in an excited state.

Using Bohr's Equation 1.16, relating the energy (E_n) and energy level (n) for an electron it is possible to calculate the energy of a single electron in a ground state or excited state, or the energy change when an electron moves between two energy levels.

Example 5, Consider the $n = 5$ state of hydrogen atom. Using the Bohr model, calculate the radius of the electron orbit, the velocity and the energy of the electron.

Solution:

To determine the radius, Equation 1.15 is used:

$$r = (0.53 \text{ \AA}) \times 5^2 = 15.24 \text{ \AA} = 1.524 \text{ nm}$$

Velocity of the electron is determined using **Equation 1.13:**

$$v = \frac{nh}{2\pi mr}$$

Notice that when $nf > ni$, ΔE is positive, indicating that the system has absorbed energy.

But, $ni > nf$, ΔE is negative and this corresponds to emission of energy.

Example 5, Calculate the energy emitted when an electron moves from the $n= 3$ to the $n = 2$ energy level. Determine the wavelength of the emitted energy.

Solution:

to determine the emitted energy, Equation 1.19 is used;

$$\Delta E = h\nu = - 2.18 \times 10^{-18} J \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 3.03 \times 10^{-19} J$$

To obtain λ , **Equation 1.19:**

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$\text{Thus, } \lambda = \frac{hc}{\Delta E} = \frac{6.63 \times 10^{-34} J \cdot s \times 3.0 \times 10^8 m/s}{3.03 \times 10^{-19} J}$$

$$= 6.56 \times 10^{-7} m = 656 nm$$

Exercise 6

- What is the wavelength of a photon (in nanometers) emitted during a transition from the $n= 5$ state to the $n= 2$ state in the hydrogen atom?
- Calculate the frequency of the green line arising from the electron moving from $n= 4$ to $n= 20$ in the visible spectrum of the hydrogen atom using Bohr's theory.

Answer to Exercise 6

- 1.434 m
- $2. 1.97 \times 10^{14} Hz$

Each spectral line in the emission spectrum corresponds to a particular transition in a hydrogen atom.

When we study a large number of hydrogen atoms, we observe all possible transitions and hence the corresponding spectral lines.

For instance, **Figure 1.14** illustrates line spectra of a hydrogen atom

When its electron moves from $n = 4$ to $n = 1$; $n = 3$ to $n = 1$ and $n = 2$ to $n = 1$.

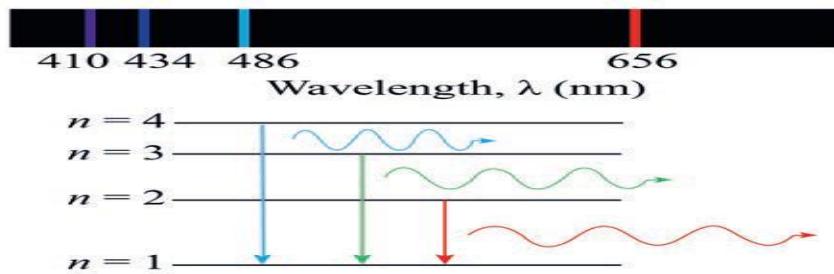


Figure 12: The emission spectrum of a hydrogen atom

- Each horizontal line represents an allowed energy level for the electron in a hydrogen atom. The energy levels are labeled with their principal quantum numbers.
- The emission spectrum of hydrogen includes a wide range of wavelengths from the **infrared to the ultraviolet**.
- Table 1.2 shows the series of transitions in the hydrogen spectrum; they are named after their discoverers.
- The Balmer series was particularly easy to study because some its lines fall in the **visible range**.

Table 1.2: The various series in atomic hydrogen emission spectrum

Series	nf	ni	Spectrum region
Lyman	1	2, 3, 4	Ultraviolet
Balmer	2	3,4,5	Visible and ultraviolet
Paschen	3	4,5,6	Infrared
Brackett	4	5,6,7	Infrared

- For a larger orbit radius (i.e. a higher atomic energy level), the further the electron drops, the greater is the energy (higher v , shorter λ) of the emitted photon.

Exercise 7

- Calculate the energies of the states of the hydrogen atom with $n= 2$ and $n= 3$, and calculate the wavelength of the photon emitted by the atom when an electron makes a transition between these two states.
- What is the wavelength of a photon emitted during a transition from the $n_i= 10$ state to the $n_f = 2$ state in the hydrogen atom?

Answer to Exercise 7

- i. $E_n = 2 = -5.45 \times 10^{-19} \text{ J}$
- ii. $E_n = 3 = -2.42 \times 10^{-19} \text{ J}$
- $6.6 \times 10^{-8} \text{ m} = 66 \text{ nm} \quad \lambda = 3.6 \text{ nm}$

1.5 Limitations of the Bohr model

- The Bohr Model was an important step in the development of atomic theory.
- He introduced the idea of quantized energy states for the electron in a hydrogen atom.
- The model explains atoms and ions containing only one electron such as H, He^+ and Li^{2+} .
- However, the model has several **limitations**:
 - It doesn't explain the atomic spectra of more complicated atoms and ions, even that of helium, the next simplest element.
 - It doesn't explain about further splitting of spectral lines in the hydrogen spectra on application of a magnetic field.
 - It considers electrons to have both known radius and orbit, which is impossible according to Heisenberg's uncertainly principle.

1.5.1 The Wave – particle Duality of Matter and Energy

- Bohr's model assumed that an atom has only certain allowable energy levels in order to explain the observed line spectrum. However, his assumption had no basis in physical theory.
- In 1924, Louis de Broglie, the French physicist, proposed a surprising Reason for fixed energy levels: if energy is particle-like, perhaps matter is wavelike.
- De Broglie reasoned that if electrons have wavelike motion and are restricted to orbits of fixed radii that would explain why they have only certain possible frequencies and energies.
- By combining Einstein's equation for the quantity of energy equivalent to a given amount of mass ($E = mc^2$) with Planck's equation for the energy of a photon ($E = h\nu = hc/\lambda$), de

Broglie derived an equation for the wavelength of any particle of mass, m , whether a planet, ball, or electron-moving at speed, v .

- $\lambda = \frac{h}{mv}$ 1.20
- According to this Equation 1.20, **matter and energy** show **both wave and particle properties**.
- This dual character of matter and energy is known as the **wave-particle duality**.
- **Example 6**, Calculate the de Broglie wavelength of an electron that has a velocity of 1.00×10^6 m/s. (electron mass, $m_e = 9.11 \times 10^{-31}$ kg; $h = 6.63 \times 10^{-34}$ J.s)
- **Solution:** $\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ kgm/s}^2 \cdot \text{s}}{9.11 \times 10^{-31} \text{ kg} \times 1.00 \times 10^6 \text{ m/s}}$
 $= 0.73 \times 10^{-9} \text{ m} = 0.728 \text{ nm}$
- What is the speed of an electron that has a de Broglie wavelength of 1.00 nm
- **Solution:** $v = \frac{h}{m\lambda} = \frac{6.63 \times 10^{-34} \text{ kgm/s}^2}{9.11 \times 10^{-31} \text{ kg} \times 1.00 \times 10^{-9} \text{ m}}$
 $= 0.728 \times 10^6 \text{ m/s} = 7.28 \times 10^5 \text{ m/s}$

Exercise 8

1. What is the characteristic wavelength of an electron (in nm) that has a velocity of 5.97×10^6 m/s ($m_e = 9.11 \times 10^{-31}$ kg)?
2. Calculate the wavelength (in nanometers) of an H atom (mass = 1.67×10^{-27} kg) moving at 7.00×10^2 cm/s.
3. Calculate the wavelength (in nm) of a photon emitted when a hydrogen atom undergoes a transition from $n=5$ to $n=2$.

Answer to Exercise 8

1. 0.122 nm
2. 56.7 nm
3. 434 nm

1.6 The Quantum Mechanical Model of the Atom

- The Bohr model of an electron orbiting around the nucleus, looking like a planet around the Sun, doesn't explain properties of atoms.
- The planetary view of one charged particle orbiting another particle of opposite charge does not match some of the best-known laws of classical physics.

1.6.1 The Heisenberg's Uncertainty Principle

- Discovery of the wave properties of matter raised a new and very interesting question.

- If a subatomic particle can exhibit the properties of a wave, is it possible to say precisely where that particle is located.
- A wave extends in space, so its location is not defined precisely.
- In 1927, Werner Heisenberg, the German physicist, proposed the Heisenberg uncertainty principle, stating that it is not possible to know with great certainty both an electron's position and its momentum p (where $p = mv$) at the same time.
- Heisenberg was able to show that if Δp is the uncertainty in the momentum and Δx is the uncertainty of the position of the electron, then:
 - $(\Delta x)(\Delta p) \geq \frac{\hbar}{4\pi}$ or $(\Delta x)(mv) \geq \frac{\hbar}{4\pi}$
 - This equation shows that if we measure the momentum of a particle precisely (i.e., if Δp is very small), then the position will be correspondingly less precise (i.e., Δx will become larger).
 - In simpler terms, if we know precisely where a particle is, we cannot know precisely where it has come from or where it is going.
 - If we know precisely how a particle is moving, we cannot know precisely where it is.
 - The Heisenberg uncertainty principle has no practical consequence in everyday objects in the macroscopic world.
 - However, it has very significant consequences when applied to atomic and subatomic particles.

1.6.2 The Quantum Numbers

- The quantum mechanical description of the atom is based on the assumption that there are waves associated with both matter and radiations.
- The mathematical description of such wave provides information about the energy of electrons and their position.
- Erwin Schrödinger (1927), suggested that an electron or any other particle exhibiting wavelike properties can be described by a mathematical equation called a **wave function** (denoted Greek latter **psi**, ψ).
- The equation is very complex. However, it leads to series of solutions that describe the allowed energy states of electrons.
- The square of a wave function, ψ^2 , gives the probability of finding an electron in a certain region of a space.
- The results of a quantum mechanics indicate that the electron may be visualized as being in a rapid motion within a given region of space around the nucleus.
- Although we cannot determine the precise position of an electron, the probability of the electron being at a definite location can be calculated.
- The region in which an electron is most likely found is called an **orbital**.

- The electron may occupy anywhere within an orbital at any instant in time. So, an electron can be considered as a particle that can rapidly move from place to place, behaving like an “electron cloud” whose density varies within the orbital.
- In quantum mechanics, each electron in an atom is described by **four quantum numbers**.
- Three of the quantum numbers specify the wave function that gives the probability of finding an electron at various places in space.
- The fourth one is used to describe the spin (magnetic property) of the electrons that occupy the orbitals.
- The four quantum numbers are:
 - ✓ The principal quantum number
 - ✓ The angular momentum quantum number
 - ✓ The magnetic quantum number
 - ✓ The electron spin quantum number

1. The principal quantum number (n);

- Describes the main energy level, or shell, an electron occupies.
- It may be any positive integer, $n = 1, 2, 3, 4$, etc.
- It describes the size and energy of the shell.
- It tells maximum number of electrons present in any shell (by the formula $2n^2$).

2. The angular momentum quantum number (ℓ);

- Designates the shape of the atomic orbitals.
- Within a shell different sublevels or subshells are possible, each with a characteristic shape.
- It takes values from 0 to $n-1$.
- Orbitals of the same n , but different ℓ are said to belong to different subshells.
- It is also called azimuthal quantum number or subsidiary quantum number.
- A given energy level, n , has n^2 total number of orbitals.
- For example, in $n = 4$, ℓ has values of 0, 1, 2, and 3.
- Each value of ℓ corresponds to an orbital label and an orbital shape.

The following letters are usually used to denote the values of ℓ :

Value of ℓ	Corresponding subshell
0	S
1	P
2	D
3	F

Example 7, What do “4” and “d” represent in 4d?

- **Solution;** the number 4 gives the principal quantum number ($n = 4$) and the letter d gives the type of orbital ($\ell = 2$).

3. The magnetic quantum number ($m\ell$);

- also called the orbital-orientation quantum number.
- It has integral values between $-\ell$ and ℓ , including **0**.
- The value of $m\ell$ is related to the orientation of the orbital in space relative to the other orbitals in the atom.
- The number of possible $m\ell$ values or orbitals for a given ℓ value is $2\ell+1$.

4. The electron spin quantum number (m_s);

- Refers to the spin of an electron and the orientation of the magnetic field produced by this spin.
- For every set of n , ℓ , and $m\ell$ values, m_s can take the value $+\frac{1}{2}$ or $-\frac{1}{2}$.
- Each atomic orbital cannot accommodate more than two electrons, one with $m_s = +\frac{1}{2}$ and another with $m_s = -\frac{1}{2}$.

Exercise 9

1. What are the values of n and ℓ for the following subshells?

- a. 1s b. 3p c. 4s d. 3d e. 4f

2. Write the subshell notations that correspond to

- | | |
|-----------------------|-----------------------|
| a. $n=3$ and $\ell=0$ | c. $n=7$ and $\ell=0$ |
| b. $n=3$ and $\ell=1$ | d. $n=3$ and $\ell=2$ |

Answer to Exercise 9

1. a. $n = 1, \ell = 0$ b. $n = 3, \ell = 1$ c. $n = 4, \ell = 0$ d. $n = 3, \ell = 2$ e. $n = 4, \ell = 3$

2. a. 3s b. 3p c. 7s d. 3d

➤ **Example 8,** What values of the angular momentum quantum number (ℓ) and magnetic quantum number ($m\ell$) are allowed for a principal quantum number, $n = 3$? How many orbitals are allowed for $n = 3$?

➤ Solution:

➤ Determining ℓ values:

- For $n = 3, \ell = 0, 1, 2$

➤ Determining $m\ell$ for each ℓ value:

- For $\ell = 0, m\ell = 0$

- For $\ell = 1$, $m\ell = -1, 0, +1$
 - For $\ell = 2$, $m\ell = -2, -1, 0, +1, +2$
- Number of orbitals in $n = 3$ is $n^2 = 3^2 = 9$ orbitals
- These orbitals are:
- 3s: 1 orbital,
 - 3p: 3 orbitals,
 - 3d: 5 orbitals,
- ❖ Total = 9 orbitals

Exercise 10

1. What are the allowed values of the quantum numbers through $n=4$?
2. Write an orbital designation corresponding to the quantum numbers:
 - a. $n=4, \ell=2, m\ell=0$
 - c. $n=5, \ell=1, m\ell=-1$
 - b. $n=3, \ell=1, m\ell=1$
 - d. $n=4, \ell=3, m\ell=-3$
3. What values ℓ and $m\ell$ are allowed for a principal quantum number (n) of 3? How many orbitals are allowed for $n = 3$?
4. Can an orbital have the quantum number $n=2, \ell=2, m\ell=2$
5. For an orbital with $n=3$ and $m\ell=1$, what is (are) the possible value(s) ℓ ?
6. Which of the following orbitals do not exist: 1p, 2s, 2d, 3p, 3d, and 3f?

Answer to Exercise 10

1.

n	ℓ	$m\ell$	ms
	0 (2s)	0	$\pm\frac{1}{2}, -\frac{1}{2}$
	1 (4p)	-1, 0, 1	$\pm\frac{1}{2}$ for each value of $m\ell$
4	2 (4d)	-2, -1, 0, 1, 2	$\pm\frac{1}{2}$ for each value of $m\ell$
	3 (4f)	-2, -1, 0, 1, 2	$\pm\frac{1}{2}$ for each value of $m\ell$

2. a. 4d b. 3p c. 5p d. 4f

3. i.

n	ℓ	$m\ell$
----------	--------------------------	---------------------------

	0	0
3	1	-1, 0, 1
	2	-2, -1, 0, 1, 2

ii) $n = 3$ has $3^2 = 9$ orbitals

4. No, for $n = 2$, the values of ℓ and $m\ell$ cannot be 2.
5. Possible values of ℓ are 1 and 2.
6. 1p, 2d and 4f orbitals do not exist.

1.6.3 Shapes of Atomic Orbitals

- The three-dimensional aspects of the orientation of the atomic orbitals are usually represented by drawing a boundary surface diagram that encloses the highest probability (about 90%) of the total electron density in an orbital.
- Figure 1.14, shows that the region of the greatest probability of finding an s electron is in a spherically symmetrical space whose origin is the atomic nucleus.
- The 1s orbital is the smallest; the 2s orbital is larger than 1s and so on. Regardless of their principal quantum numbers, all s orbitals are spherical.

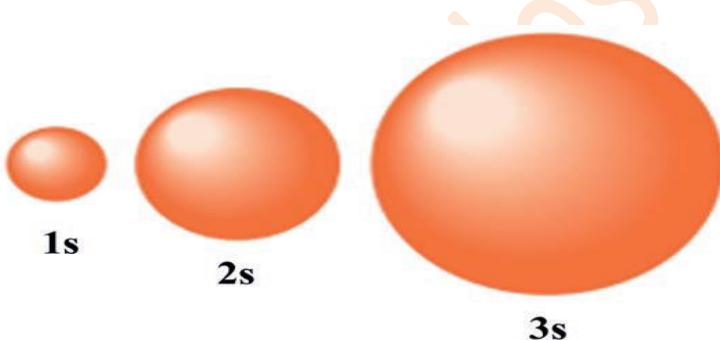


Figure 14: The three S-orbitals

- The p orbitals of any principal quantum number are arranged along three mutually perpendicular axes, x, y, and z, so that the region of the highest electron density are in dumb bell-shaped boundary surface (Figure 15).
- The three 2p orbitals are designated as $2p_x$, $2p_y$ and $2p_z$.

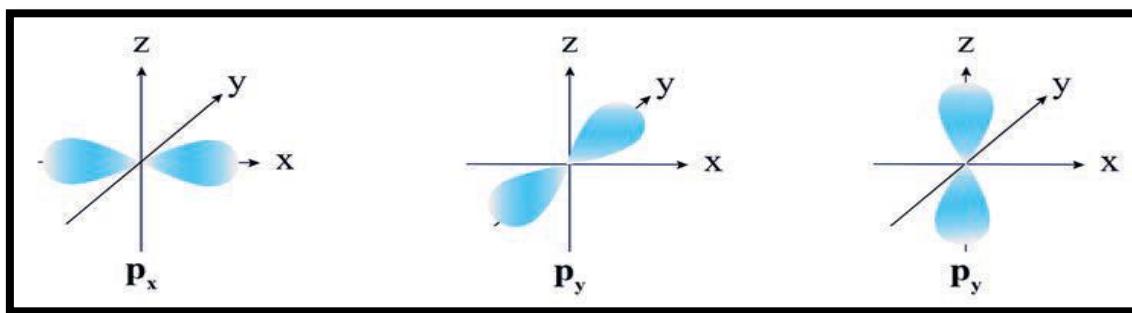


Figure 15: The three p – orbitals

Two lobes of each p orbital lie along a line with the nucleus at their center. For instance, the three 2p orbitals are classified as 2px, 2py and 2pz.

Higher principal energy levels ($n > 3$) have five d orbitals in addition to, one s - orbital, three 3p- orbitals.

The special orientations of d orbitals are much more complex in shape than p orbitals. Figure 1.16 shows the different distribution of the five d atomic orbitals.

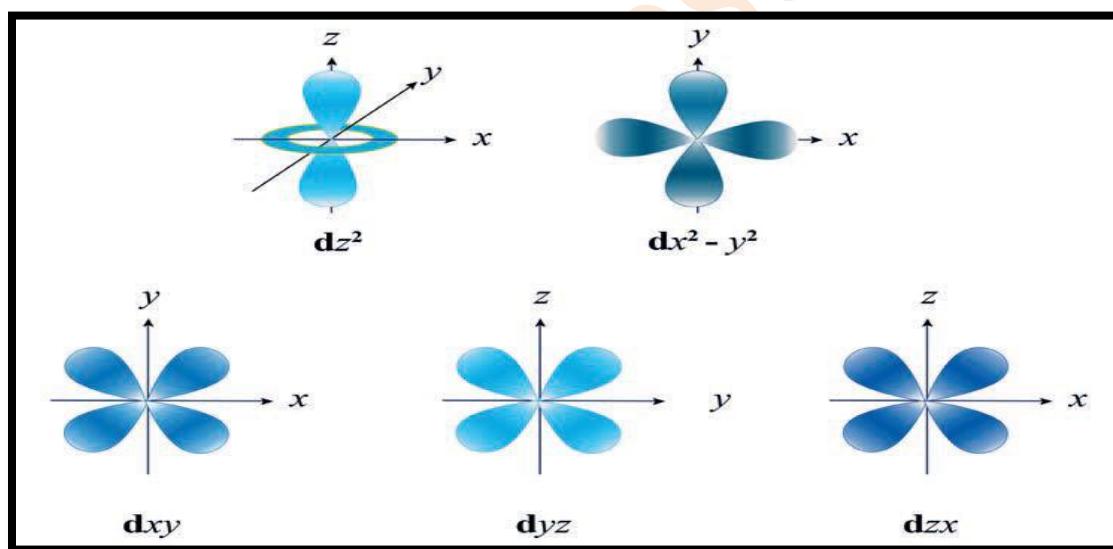


Figure 16: The five d orbitals

- The principal energy level whose values are $n \geq 4$ have additional fourth sublevels.
- For instance, in $n = 4$, there are a 4s subshell with one orbital, a 4p subshell with three orbitals, a 4d subshell with five orbitals, and a 4f subshell with seven orbitals.
- The f orbitals have more complex shapes than the d orbitals.

1.7 Electron Configurations and Orbital Diagrams

- The electron configuration for any atom is governed by the following three principles:

1. Aufbau(building up) Principle

- In general, electrons occupy the lowest-energy orbital available before entering the higher energy orbital.
- Accordingly, the ground state electron configurations of atoms are obtained by filling the subshell in the following order; 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, and so on.

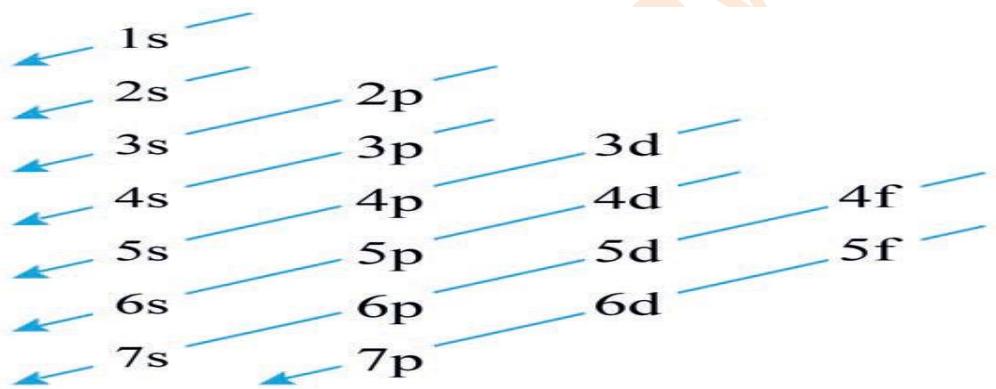


Figure 17: The order of filling orbitals

1. Hund's Principle:

- Equal energy orbitals (degenerate orbitals) are each occupied by a single electron before the second electrons of opposite spin enters the orbital.
- In other words, each of the three 2p orbitals (2px, 2py and 2pz) will hold a single electron before any of them receives a second electron.

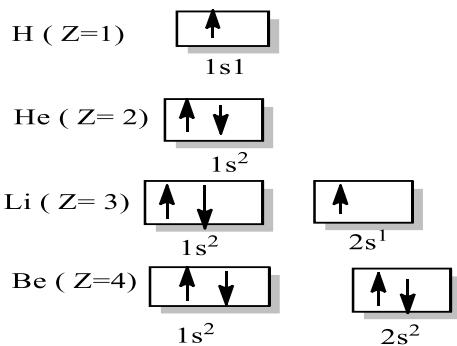
2. Pauli's Exclusion Principle:

- No two electrons can have the same four quantum numbers.
- That means, they must differ in at least one of the four quantum numbers.

1.7.1 Ground State Electron Configuration of the Elements

- The electronic configuration of an atom describes the distribution of the electrons among atomic orbitals in the atom.
- Two general methods are used to denote electron configurations.

- ❖ The subshell (sublevel) notation uses numbers to designate the principal energy levels and the letters *s*, *p*, *d* and *f* to identify the sublevels.
- A superscript number following a letter indicates the number of electrons (*e*) in the designated subshell.
- The designation can be written as *nl^e*.
- For instance, the ground state electron configuration of H (*Z*=1) is $1s^1$.
- The orbital diagrams for the first four elements are:



Exercise 11

1. Write the expected electron configuration for these atoms:

- a. Na (*Z*= 11) d. V (*Z* = 23)
 b. Al (*Z* = 13) e. Mn (*Z* = 25)
 c. P (*Z* =15) f. Fe (*Z* = 26)

2. Indicate the total number of:

- a. p electrons in N (*Z* = 7) c. 3d electrons in S (*Z* = 16)
 b. s electrons in Si (*Z* = 14)

3. Indicate which of the following sets of quantum numbers in an atom are unacceptable and explain why:

- a. (1, 0, $\frac{1}{2}$, $\frac{1}{2}$) d. (2, 2, 1, $+\frac{1}{2}$)
 b. (3, 0, 0, $+\frac{1}{2}$) e. (4, 3, -2, $+\frac{1}{2}$)
 c. (3, 2, 1, 1)

Answer to Exercise 1.11

1. a) $1s^2 2s^2 2p^6 3s^1$ or [Ne]3s¹ d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ or [Ar] 4s²3d³
 b) $1s^2 2s^2 2p^6 3s^2 2p^1$ or [Ne] 3s²3p¹ e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$ or [Ar] 4s²3d⁵
 c $1s^2 2s^2 2p^6 3s^2 3p^3$ or [Ne] 3s²3p³ f) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ or [Ar] 4s²3d⁶
 2. a) N (*Z* = 7): $1s^2 2s^2 2p^3$: 3 p electrons
 b) Si (*Z* = 14): $1s^2 2s^2 2p^6 3s^2 3p^2$: 6 s electrons

- c) S ($Z = 16$): $1s^2 2s^2 2p^6 3s^2 3p^4$: No d electron
 3. c is unacceptable, because the value of m_s can't be 1.
 d. c is unacceptable, because for $n = 2$, ℓ value can't be 2

Table 3: Ground state electron configurations of some atoms

Atom	Atomic number (Z)	Electron configuration
H	1	$1s^1$
He	2	$1s^2$
Be	4	$1s^2 2s^2$ or $[He]2s^2$
O	8	$1s^2 2s^2 2p^4$ or $[He]2s^2 2p^4$
Ne	10	$1s^2 2s^2 2p^6$ or $[He]2s^2 2p^6$
Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$ or $[Ne] 3s^2 3p^5$
Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or $[Ar]4s^2$
Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$ or $[Ar]4s^2 3d^1$
Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ or $[Ar]4s^1 3d^5$

➤ Notice that in the electron configuration of an atom, the electrons in the outermost principal quantum level of an atom are called **valence electrons**. For example, the valence electrons of the Be atom, are the 2s electrons. For the Ne atom, the valence electron is the electrons are in the 2s and 2p electrons.

- Valence electrons are the most important electrons to chemists since they are involving in **bonding**.
- The inner electrons are known as **core electrons**.
- Examine the electron configurations of chromium and copper.
- The expected configurations, those based on the Aufbau principle, are not the ones observed through the emission spectra and magnetic properties of these elements.

➤ Expected Observed

Cr ($Z = 24$) $[Ar]4s^2 3d^4$ $[Ar]4s^1 3d^5$

Cu ($Z = 29$) $[Ar]4s^2 3d^9$ $[Ar]4s^1 3d^{10}$

- The reason for these exceptions to the Aufbau principle are not completely understood, but it seems that the half-filled 3d subshell of chromium ($3d^5$) and the fully filled 3d subshell of copper ($3d^{10}$) lends a special stability to the electron configurations.
- Apparently, having a half-filled 4s subshell and a half-filled 3d subshell gives a lower energy state for a Cr atom than having a filled 4s subshell.

1.8 Electronic Configuration and the Periodic Table of the Elements

1.8.1 The Modern Periodic Table

- Elements are arranged in the modern periodic table in a specific pattern that helps to predict their properties and to show their similarities and differences.
- Periodic relationships can be summarized by the general statement called the **periodic law**.
- In its modern form, the periodic law states that certain sets of physical and chemical properties repeat at regular intervals (periodically) when the elements are arranged according to increasing atomic number.

1.8.2 Classification of the Elements

- The periodic classification follows as a logical consequence of the electronic configuration of atoms.
- Elements are grouped according to their outer-shell electron configurations, which account for their similar chemical behavior.
- The period indicates the value of n for the outermost or valence shell.
- There are 18 groups and 7 periods in the modern periodic table.
- A metalloid is an element that has properties that are between those of metals and non-metals.
- For example boron, germanium and silicon.

1.8.3 Periodic Properties

- The electron configurations of the atoms display a periodic variation with increasing atomic number (nuclear charge). As a result, the elements show periodic variations of physical and chemical behavior.
- In this section you will examine some periodic atomic properties like atomic radii, ionization energies, electron affinities, electronegativity, and metallic character.

Atomic Size (Atomic Radii)

- Exact size of an isolated atom cannot be measured because the electron cloud surrounding the atom does not have a sharp boundary.
- However, an estimate of the atomic size can be made by measuring the distance between the nuclei of two adjacent atoms.
- This property is called the **atomic radius**.
- One of the most common methods to determine the atomic radius is to assume that atoms are spheres touching each other when they are bonded together.

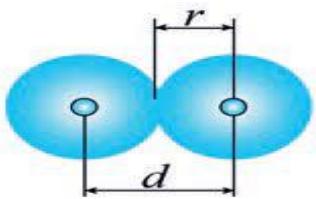


Figure 18: Atomic radius for a diatomic molecule

$$r = \frac{d}{2}$$

- Atomic size varies within both a group and a period of the main-group elements.
- These variations in atomic size are the result of two opposing influences: changes in the principal quantum number (n) and changes in the effective nuclear charge (Z_{eff}) the nuclear charge an electron actually experiences.
- The net effect of these depends on the shielding of the increasing nuclear charge by the inner electrons.
- Atomic radius generally increases in a group from top to bottom but it decreases in a period from left to right.
- These trends hold well for the main-group elements. but not as for the transition elements (electrons enter an inner electron shell, not the valence shell).
- As we move from left to right, size shrinks through the first two or three transition elements because of the increasing nuclear charge. But, from then on, the size remains relatively constant because shielding by the inner d electrons cancels out the usual increase in Z_{eff} .
- For instance, vanadium (V; $Z = 23$), the third Period 4 transition metal, has the same atomic radius as zinc (Zn; $Z = 30$), the last Period 4 transition metal.

Exercise 12

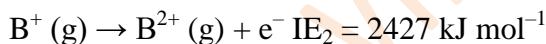
1. What are the factors affecting the size of an atom of an element? Explain your answer using examples.
2. Using the periodic table, rank each set of main-group elements in order of decreasing atomic size:
 - a. Ca, Mg, Sr b. K, Ga, Ca c. Br, Rb, Kr d. Sr, Ca, Rb
3. Why is the difference in atomic radius between the elements $Z= 11$ (Na; 186 pm) and $Z = 12$ (Mg; 160 pm) so large, whereas between $Z = 24$ (Cr; 125 pm) and $Z = 25$ (Mn; 124 pm) the difference is very small. (Note that "pm" is picometers.).

Answer to Exercise 12

1. There are three main factors that affect the size of the atoms: the nuclear charge of the atom, the shielding effect, and the number of energy levels that hold the electrons.
2. a. Sr > Ca > Mg. These three elements are in Group IIA(2), and size decreases up the group.
b. K > Ca > Ga. These three elements are in Period 4, and size decreases across a period.
c. Rb > Br > Kr. Rb is largest because it has one more energy level and is farthest to the left. Kr is smaller than Br because Kr is farther to the right in Period 4.
d. Rb > Sr > Ca. Ca is smallest because it has one fewer energy level. Sr is smaller than Rb because it is farther to the right.
3. In a series of transition elements, electrons join the core electrons, not valence shell electrons. As a result, the effective nuclear charge for Cr and Mn remains more or less constant instead of increasing.

Ionization Energy (IE)

- The ionization energy (IE) is the energy (in kJ) required for the complete removal of 1mol of electrons from 1 mol of gaseous atoms or ions.
- Multi-electron atoms can lose more than one electron, so the ionization energies required to remove each electron are numbered in sequence from the ground-state atom. For instance, boron atom has
- five electrons, two in an inner core ($1s^2$) and three valence electrons ($2s^22p^1$).
- The five ionization steps and their ionization energies, IE1 through IE5, are:



- **The first ionization energy (IE₁)** of an atom is the **minimum energy** needed to remove the **first electron** from the outermost shell of a gaseous atom to produce a gaseous ion.
- Atom (g) \rightarrow Ion⁺(g) + e⁻ $\Delta E = IE_1 > 0$
- **The second ionization energy (IE₂)** removes the second electron. Since the electron is being pulled away from a positively charged ion, IE₂ is always larger than IE₁:
- Ion⁺(g) \rightarrow Ion²⁺(g) + e⁻ $\Delta E = IE_2 (\text{always } > IE_1)$

- The first ionization energy is a key factor in an element's chemical reactivity because; atoms with a low IE₁ tend to form **cations** during reactions, whereas those with a high IE₁, (except the noble gases) often form **anions**.
- Ionization energies display a periodic variation when plotted against atomic number, Within any period, values tend to increase with atomic number.
- Thus, the lowest values in a period are found for the Group IA elements
- (Alkali metals). It is characteristic of reactive metals such as these to lose electrons easily.
- The largest ionization energies in any period occur for the noble-gas elements.
- This general trend increasing ionization energy with atomic number in a given period is due to the fact that as we move across a period, Z_{eff} generally increases so atomic radii become smaller. As a result, the attraction between the nucleus and the outer electrons increases, so an electron becomes more difficult to remove.
- Small deviations from this general trend occur.
- A Group IIIA element (ns^2np^1) has a smaller ionization energy than the preceding Group IIA element (ns^2).
- Apparently, the np electron of the Group IIIA element is more easily removed than one of the ns electrons of the preceding Group IIA element.
- Also note that a Group VIA element (ns^2np^4) has a smaller ionization energy than the preceding Group VA element. As a result of electron repulsion, it is easier to remove an electron from the doubly occupied np orbital of the Group VIA element than from a singly occupied orbital of the preceding Group VA element.

Exercise 13

1. Choose the element with the higher ionization energy from each pair:
 - a. As or Bi b. As or Br c. Al or In d. K or Ge
2. The first and second ionization energies of potassium, K, are 419 kJ mol⁻¹ and 3052 kJ mol⁻¹ and those of calcium, Ca, are 590 kJ mol⁻¹ and 1145 kJ mol⁻¹, respectively. Compare their values and comment on the differences.
3. Based on their positions in the periodic table, predict which atom of the following pairs will have the larger first ionization energy:
 - a. Ga or Ge b. Br or Sb c. K or Cr d. Mg or Sr e. O or Ne
4. Name the period 3 element with the following ionization energies (in kJ/mol), and write its electron configuration:

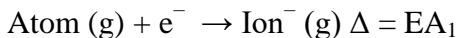
IE1	IE2	IE3	IE4	IE5	IE6
1012	1903	2910	4956	6278	22,330

Answer to Exercise 13

1. a . As b. Br c. Al d. G
2. Potassium ($Z=19$) and electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ removes its 4s electron with great ease, attaining the noble gas configuration (Ar), and it is extremely difficult to remove the second electron from a stable configuration.
- Calcium ($Z=20$) and electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ removes the two electrons to become like that of a noble gases in its configuration. This is the reason why the energy difference between 1st and 2nd is small as compared to potassium.
3. a. Ga < Ge b. Sb < Br c. K < Cr d. Sr < Mg e. O < N.
4. The exceptionally large jump occurs after IE5, indicating that the element has five valence electrons and, thus, is in Group VA (15). This Period 3 element is (P; $Z=15$). Its electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^3$

Electron Affinity (EA)

The electron affinity is the energy change for the process of adding an electron to a neutral atom in the gaseous state to form a negative ion:



An electron approaching a neutral atom experiences an attraction for the positively charged nucleus. Repulsion of the incoming electron by electrons already present in the atom tends to offset this attraction. Still, in many cases the incoming electron is absorbed by the atom and energy is evolved in the process.

Thus, **first electron affinity (EA₁)** is usually negative.

The **second electron affinity (EA₂)**, however, is always positive because energy must be absorbed to overcome electrostatic repulsions and add another electron to a negative ion.

For example, the EA₁ and EA₂ of an oxygen atom can be written as

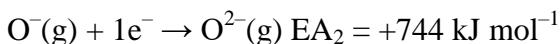


Figure 1.19 gives the electron affinities of the main-group elements. Negative values indicate that energy is released when the anion forms. Positive values, which occur in Group VIIA

(18), indicate that energy is absorbed to form the anion; in fact, these anions are unstable and the values are estimated.

IA (1)							VIIIA (18)
H	IIA (2)						He (0.0)
Li -59.6	Be ≤ 0	III A (13) -26.7	IV A (14) -122	V A (15) +7	VI A (16) -144	VII A (17) -328	Ne (+29)
Na -52.9	Mg ≤ 0	Al -42.5	Si -134	P -72	S -200	Cl -349	Ar (+35)
K -48.4	Ca -2.37	Ga -28.9	Ge -119	As -78.2	Se -195	Br -325	Kr (+39)
Rb -46.9	Sr -5.03	In -28.9	Sn -107	Sb -103	Te -190	I -295	Xe (+41)
Cs -45.5	Ba -13.95	Ti -19.3	Pb -35.1	Bi -91.3	Po -183	At -270	Rn (+41)

Figure 19: Electron affinities of the main-group elements (in kJ/mol)

The general trend is toward more negative electron affinities from left to right in any period.

Electronegativity

Electronegativity indicates the extent of attraction by which the electrons of the bond pair are attracted by an atom linked by this bond.

Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. This is known as the Pauling scale.

Approximate values for the electronegativity of a few elements are given in Table 4.

Table 4: (a) Electronegativity values (on Pauling scale) across the periods

Atom (period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Table 4: (b) Electronegativity values (on Pauling scale) down a group

Atom(Group IA)	Electronegativity	Atom(Group VIIA)	Electronegativity
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	As	2.2

- Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decreases down a group (say from fluorine to astatine) in the periodic table.
- The attraction between the valence electrons and the nucleus increases as the atomic radius decreases in a period. The electronegativity also increases.
- On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization energy.

Metallic character

- Metallic character refers to the chemical properties associated with elements classified as metals. These properties arise from the elements' ability to lose electrons.
- Metallic character decreases as you move across a period in the periodic table from left to right.
- This occurs as atoms more readily accept electrons to fill a valence shell than lose them to remove the unfilled shell.
- Metallic character increases as you move down an element group in the periodic table. This is because electrons become easier to lose as the atomic radius increases, where there is less attraction between the nucleus and the valence electrons because of the increased distance between them.

1.8.4 Advantages of Periodic Classification of the Elements

Some of the advantages of periodic classification of elements are:

1. The classification of elements is based on the atomic number, which is a fundamental property of an element.
2. Isotopes are averaged in one place, as the classification is on the basis of atomic number (For example, chlorine (atomic number 17) is given the atomic mass 35.5.)
3. It explains the periodicity of the properties of the elements and relates them to their electronic configurations.
4. The position of the elements that were misfits on the basis of mass number (anomalous pairs like argon and potassium) could be justified on the basis of atomic number.

5. The lanthanides and actinides are placed separately at the bottom of the periodic table.
6. The table is a simple, systematic and an easy way of remembering the properties of various elements, as it is based on the electronic configuration.

UNIT SUMMARY

- Modern chemistry began with eighteenth century discoveries leading to the formulation of two basic laws of chemical combination: the law of conservation of mass and the law of constant composition (definite proportions). Dalton proposed another law of chemical combination, the law of multiple proportions.
- The first clues to the structure of atoms came through the discovery and characterization of cathode rays (electrons). Key experiments were those that established the mass-to-charge ratio and then the charge on an electron.
- The principal types of radiation emitted by radioactive substances are alpha particles, beta particles, and gamma rays.
- Studies on the scattering of particles by thin metal foils (Rutherford's atomic model) led to the concept of the nuclear atom – a tiny, but massive, positively charged nucleus surrounded by lightweight, negatively charged electrons.
- Electromagnetic radiation is characterized by its wavelength (λ), frequency (v), and speed ($c = 3.0 \times 10^8$ m/s), which are related by the formula:

$$c = \lambda v$$

- Electromagnetic radiation can be viewed as a stream of "particles" called photons, each with energy hv , where h is Planck's constant (6.63×10^{-34} J.s).
- When light strikes a metal surface, electrons are emitted.
- Analysis of the kinetic energy and numbers of the emitted electrons led Einstein to suggest that electromagnetic radiation can be viewed as a stream of photons.
- The photoelectric effect is the emission of an electron from the surface of a metal, caused by electromagnetic radiation of a certain minimum energy; the resulting current increases with increasing intensity of radiation.
- Bohr's theory requires the electron in a hydrogen atom to be in one of a discrete set of energy levels. The fall of an electron from a higher to a lower energy level releases a discrete amount of energy as a photon of light with a characteristic frequency.
- Bohr's theory accounts for the observed atomic spectrum of hydrogen atom.
- An emission spectrum is the spectrum associated with the emission of electromagnetic radiation by atoms (or other species) resulting from electron transitions from higher to lower energy states.
- The electron in a hydrogen atom can be viewed as a matter-wave enveloping the nucleus.

- The matter-wave is represented by a wave equation, and solutions of the wave equation are wave functions.
- Each wave function is characterized by the value of four quantum numbers: the principal quantum number, n ; the angular momentum quantum number ℓ ; the magnetic quantum number, $m\ell$; and the spin quantum number, ms .
- According to Heisenberg's Uncertainty Principle, it is impossible to determine both the momentum and position of an electron.
- An orbital describes a region in an atom that has a high probability of containing an electron or a high electron charge density.
- Orbitals with the same value of n are in the same principal energy level.
- Orbitals with the same value of n and of ℓ are in the same sublevel.
- The shape of orbitals depend on the values of ℓ . Thus, the s orbital ($\ell=0$) is spherical and the p orbital ($\ell=1$) is dumbbell-shaped.
- The n , ℓ and $m\ell$ quantum numbers define an orbital, but a fourth quantum number, ms , is also required to characterize an electron in an orbital.
- The Aufbau ("building up") Principle is a guide for predicting the order in which electrons fill subshells and shells in atoms.
- According to Pauli's Exclusion Principle, no two electrons in the same atom may have identical sets of four quantum numbers.
- Hund's Rule states that each orbital of a given subshell is occupied by a single electron before pairing begins.
- Electron configuration refers to the distribution of electrons among orbitals in an atom. Introduced here are the subshell notations (or s, p, d, and f) and the orbital diagram.
- Elements with similar valence-shell electron configurations fall in the same group of the periodic table. The period number is the same as the highest number of principal shell containing electrons (the outer shell).
- Certain atomic properties vary periodically, when atoms are arranged in terms of increasing atomic number. These include atomic size, metallic character, ionization energy, and electron affinity.

REVIEW EXERCISE

Part I: Multiple Choice Questions:

Choose the correct answer from the given alternatives.

1. Which of the following scientists did not contribute to determining the structure of the atom?
a. Thomson b. Rutherford c. Becquerel d. Dalton
2. What is the frequency in Hz of the gamma radiation from a radioactive cobalt-60 source if its wavelength is 1.0×10^{-9} nm?

- a. 3.3×10^{-27} Hz b. 3.3×10^{-8} Hz c. 3.0×10^{18} Hz d. 3.0×10^{-26} Hz
3. What is the energy of the electronic transition associated with the sodium-D line having a wavelength of 589 nm?
- a. 6.63×10^{-34} J b. 1.13×10^{-27} J c. 3.38×10^{-19} J d. 5.82×10^2 J
4. among the following, which color corresponds to light of the highest frequency?
- a. Green b. Red c. Yellow d. Blue
5. Which of the following orbital designations does not exist?
- a. 1s b. 2d c. 3p d. 4f
6. Which of the following sets of quantum numbers are not allowed in the hydrogen atom?
- a. n= 3, l= 2,m_l=2 b. n= 4, l= 3,m_l=4 c. n=1, l= 0,m_l=0 d. n= 2, l= 1,m_l=-1
7. The species that has the same number of electrons as ³²S is:
- a. ³²Cl b. ³³P⁺ c. ³⁴S⁺ d. ²⁸Si²⁻
8. Which of the following has the lowest electronegativity?
- a. Carbon b. Magnesium c. Beryllium d. Boron
9. How many unpaired electrons are there in the Cr³⁺ion?
- a. 0 b. 1 c. 2 d. 3
10. Which of the following species would require the highest energy for the removal of one electron?
- a. Mg²⁺ b. Na⁺ c. Ne d. F⁻

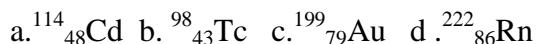
Part II Complete the following Statements

11. The atomic number gives the number of _____ in the nucleus.
12. In an atom, the number of electrons is equal to the number of _____.
13. When n= 2, the values of l could be _____ and _____
14. When l= 1, the values of m_lcould be _____, _____ and _____ as well as the subshell has the letter label _____.

15. When $\ell = 1$, the subshell is called a _____ subshell with _____ total orbitals.
16. When the subshell is labeled p, there are _____ values of $m\ell$ and _____ orbitals occur within the subshell.
17. When the subshell is labeled f, there are _____ values of $m\ell$ and _____ orbitals occur within the subshell.

Part III Short Answer Questions and Problems

18. For the following atoms, determine the number of protons, neutrons, and electrons:



19. Iridium has two naturally occurring isotopes. ^{191}Ir and ^{193}Ir have atomic masses of 190.9609 amu and 192.9633 amu, respectively. The average atomic mass for iridium is 192.22 amu. What is the percent natural abundance for each isotope?

20. The following are representative wavelengths in the IR, UV and x-ray regions of the electromagnetic spectrum, $1.0 \times 10^{-6}\text{m}$, $1.0 \times 10^{-8}\text{m}$ and $1.0 \times 10^{-10}\text{m}$, respectively.

- a. What is the energy of a photon from each transition?
b. Which of them has the highest energy per photon.

21. What is the wavelength of a beam of protons having a velocity of $1.38 \times 10^7\text{ Cm/s}$? The mass of a proton is $1.76 \times 10^{-24}\text{kg}$.

22. The photon emitted by a cyclotron has a velocity of $1.50 \times 10^3\text{ m/s}$. What is the wavelength of this photon? The mass of photon = $1.676 \times 10^{-27}\text{kg}$ and Planck's constant = $6.62 \times 10^{-34}\text{J.s}$

23. Calculate the wavelength of the light emitted when an electron falls from $n=3$ to the $n=1$ state in hydrogen atom.

24. Write the number and the letter for the orbital that corresponds to the following Pairs of n and l quantum numbers:

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

25. What type of orbital (i.e. 3s, 4p ...) is designated by these quantum numbers?

- a. $n=5, l=1, m\ell=0$ b. $n=4, l=2, m\ell=-2$ c. $n=2, l=0, m\ell=0$ d. $n=4, l=3, m\ell=-3$

26. Write the ground-state electron configurations for the following elements:

- a. Br (Z= 35) b. Mo (Z= 42) c. W (Z= 74)

27. Write the period number for each of the following and state if they are metal, non-metal or metalloid:

- a. P b. Ge c. F d. W

Answer to Review Exercise

Part I: Multiple Choice Type Questions

1. d 2.d 3. c 4.d 5. b

6. b 7. d 8. B 9. d 10.a

Part II: Complete the following statements

11. protons 12. Electron 13. 0 and 1 14. -1,0, and 1; p 15. p; three

16. Three, three 17. Seven; seven

Part III: Short answer questions and Problems

18. a. 48 protons, 66 neutrons, 48 electrons

b. 43 protons, 55 neutrons, 43 electrons

c. 79 protons, 120 neutrons, 79 electrons

d. 86 protons, 136 neutrons, 86 electrons.

19. 37.1 % ^{191}Ir and 62.9% ^{193}Ir

20. a. i. $E_{\text{IR}} = 1.98 \times 10^{-19} \text{ J}$ ii. $E_{\text{UV}} = 1.98 \times 10^{-17} \text{ J}$ iii. $E_{\text{x-ray}} = 1.98 \times 10^{-15} \text{ J}$

b. x-ray has the highest energy

21. $2.73 \times 10^{-15} \text{ m}$

22. $2.63 \times 10^{-10} \text{ m}$

23. 102.5 nm

24. a. 3p b. 4s c. 3d d. 5f

25. a. $5p_x$ b. $4d_{xy}$ c. $2s$ d. $4f_{xyz}$

26. a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ or [Ar] $4s^2 3d^{10} 4p^5$
b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^4$ or [Kr] $5s^2 4d^4$
c. W ($Z = 74$) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^4$ or
[Xe] $6s^2 4f^{14} 5d^4$
27. a. Period 3; nonmetal b. Period 4; metalloid c. Period 2; nonmetal
d. Period 6; metal e. Period 6; metal

CHAPTER 2

CHEMICAL BONDING

2.1 INTRODUCTION

- The attractive force which holds atoms, ions, and molecules together is called a chemical bond. Since these forces of attraction are intramolecular forces, they have an effect on the chemical properties as well as the physical properties of the chemical

2.1.1 The Octet Rule

- All noble gases except helium ($1s^2$) have ns^2np^6 electron configurations (where n indicates the highest occupied shell).
- The noble gases are quite unreactive because they have very stable electron configurations, as reflected by their high ionization energies and low electron affinities. Because all the noble gases (except helium) have outer shells with eight electrons, many atoms undergoing reactions also attain eight valence electrons (ns^2np^6). This rule has become known as the octet rule, as follows:
- Atoms tend to gain or lose electrons until they have achieved an outer shell that contains an octet of electrons (eight electrons).

2.1.2 Types of Chemical Bonding

- In general, there is a gradual change from metallic to non-metallic character as you move from left to right across a period and from bottom to top within most groups in the periodic table. Accordingly, atoms can combine to form three types of bond: metal with non-metal (ionic bond), non-metal with non-metal (covalent bond), and metal with metal (metallic bond).

2.2 Ionic Bonds

- An ionic bond is formed by the electrostatic attraction between positive and negative ions.
- The bond forms between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other.
- The atom that loses electrons becomes a cation(positive ion), and the atom that gains electrons becomes an anion(negative ion). Any given ion tends to attract as many neighboring ions of opposite charge as possible.
- When large numbers of ions gather together, they form an ionic solid. The solid normally has a regular, crystalline structure that allows for the maximum attraction of ions, given their particular sizes.
- Example 1, The formation of NaCl from sodium and chlorine can be explained as:
 - $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$
 - [Ne]3s1 [Ne]
 - $\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$
 - [Ne]3s²3p⁵ [Ne]3s²3p⁶ or [Ar]
 - $\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$ or Na^+Cl^-
 - The bond formed, as a result of the electrostatic attraction between the positive and negative ions is called the electrovalent bond or ionic bond.
 - Note: Ionic compounds are usually formed when metal cations bond with non-metal anions. The only common exception is ammonium ion which is not a metal, but it forms ionic compounds

Exercise 2.1

1. Explain the formation of bonds in the following pairs of elements:
 - a. potassium and chlorine c. sodium and oxygen
 - b. magnesium and oxygen
2. Which of the following elements will form an ionic bond with chlorine, why?
 - a. calcium b. carbon c. oxygen d. silicon
3. Identify the species found in the following ionic compounds: CaCl_2 MgO , and Al_2O_3 . From this what can you conclude about the formation of these compounds?

4. Why do elements located on the opposite sides of the periodic table tend to form ionic bonds?

Answer to Exercise 2.1

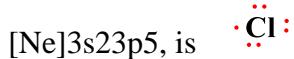
1. a. When the two atoms are in contact, potassium readily transfers its outer electron to chlorine which readily accepts it, resulting in both atoms achieving a state of eight outermost electrons. With this electron transfer, the ionic bond in KCl is formed.
- b. When magnesium reacts with oxygen to form magnesium oxide, the magnesium atom loses two electrons to form the Mg^{2+} cation, which has electronic configuration 2,8. Oxygen atom gain the two electrons to form the O^{2-} anion with configuration 2,8,8. Then, Mg^{2+} cation interact with O^{2-} anion to form ionic bond.
- c. Two sodium atoms losing two electrons; one oxygen atom gaining the two lost electrons to form ionic bond.
2. Only calcium because chlorine is a non-metal, and calcium is a metal. An ionic bond is between a metal and a non-metal. Carbon, oxygen and silicon are nonmetals.
3. The net attractive force that holds positive and negative ions together in a crystalline solid is called an ionic bond. It is formed by transfer of electrons from one atom to another atom. Electrons are not actually gained or lost by the atoms involved in covalent bonding. They pass into a “shared” state. A metallic bond is one in which all of the metal atoms share with each other a cloud of electrons. The electrons that make up that cloud originate from the outermost energy levels of the atoms.
4. Metals, at the left of the periodic table, are elements with small ionization energies and electron affinities. Relatively little energy is needed to remove electrons from them to produce positive ions. Nonmetals, at the upper right of the periodic table, have large ionization energies and generally exothermic electron affinities. It is quite difficult to remove electrons from these elements, but sizable amounts of energy are released when they gain electrons.

2.2.1 Lewis Electron – Dot Formula

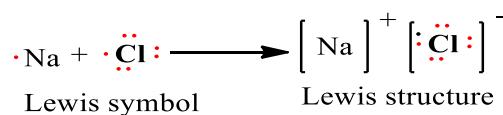
- The American Chemist Gilbert N. Lewis (1875–1946) developed a special set of symbols for his theory. A Lewis symbol consists of a chemical symbol to represent the

nucleus and core (inner-shell) electrons of an atom, together with dots placed around the symbol to represent the valence (outer-shell) electrons.

- For example, the Lewis symbol for chlorine, which has the electron configuration,



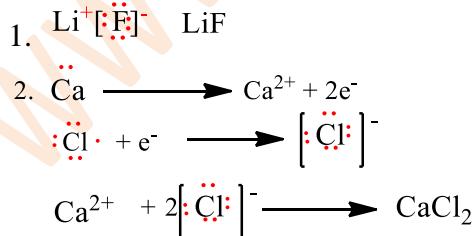
- A Lewis structure is a combination of Lewis symbols that represents either the transfer or the sharing of electrons in a chemical bond.
- For example, the formation of sodium chloride from sodium and chlorine atoms can be represented as:

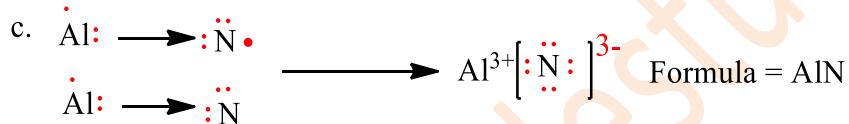
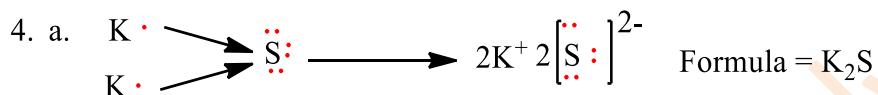
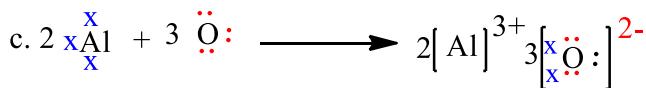
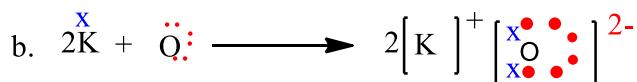
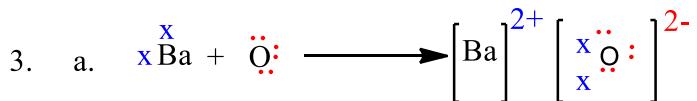


Exercise 2.2

1. Use Lewis electron-dot symbols to depict the formation of lithium and fluoride ions from the atoms and determine the formula of the compound.
2. Apply the Lewis formula to illustrate the formation of calcium chloride from calcium and chlorine atoms.
3. Write Lewis structures for the following compounds:
 - a. BaO b. potassium oxide c. aluminum oxide
4. Use Lewis symbols to show electron transfer between the following atoms to form cations and anions:
 - a. K and S b. Ca and O c. Al and N

Answer to Exercise 2.2





2.2.2 Formation of Ionic Bonds

- The formation of ionic compounds is not merely the result of low ionization energies and high affinities for electrons, although these factors are very important. It is always an exothermic process; the compound is formed because it is more stable (lower in energy) than its elements. Much of the stability of ionic compounds results from the packing of the oppositely charged positive and negative ions together.
- A measure of just how much stabilization results from this packing is given by the lattice energy (U). This quantity is the energy change occurring when gaseous ions come together to form one mole of a solid ionic compound, or the enthalpy change required for one mole of the solid ionic substance to be separated completely into ions far removed from one another.
- The lattice energy is an important indication of the strength of ionic interactions and is a major factor influencing melting points, hardness, and solubility of ionic compounds.

- The lattice energy plays a crucial role in ionic compound formation, but it is difficult to measure it directly. Nevertheless, the lattice energies of many compounds have been determined using Hess's law of heat summation, which states that an overall reaction's enthalpy change is the sum of the enthalpy changes for the individual reactions that make it up:

- $\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$

Lattice Energies from the Born–Haber Cycle

- Lattice energies can be calculated through a Born-Haber cycle, in which a series of steps from elements to ionic compounds for which all the change in enthalpies are known except the lattice energy.
- Consider the Born-Haber cycle for the formation of NaCl. We think that solid sodium chloride can be formed from the elements by two different routes, as shown in Figure 2.1.
- In one route, NaCl(s) is formed directly from Na(s) and $\frac{1}{2}\text{Cl}_2(\text{g})$; $\Delta_f H^\circ = -411 \text{ kJ mol}^{-1}$

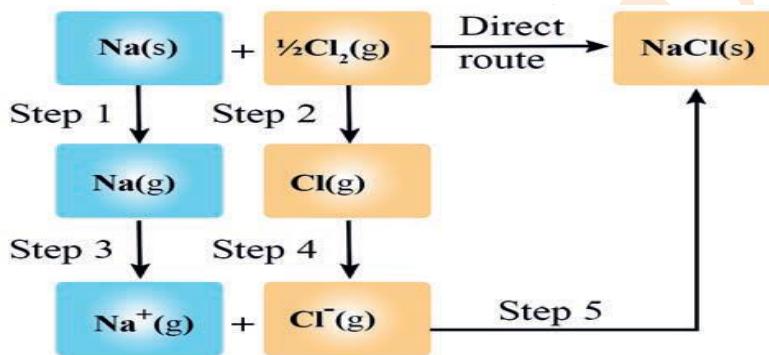
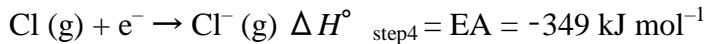


Figure 1: Born–Haber cycle for NaCl

- The second route consists of the following five steps, along with the enthalpy change for each.
- Step 1: Metallic sodium is vaporized to a gas of sodium atom:
 $\text{Na (s)} \rightarrow \text{Na (g)} \quad \Delta H^\circ_{\text{step1}} = + 108 \text{ kJ mol}^{-1}$
- Step 2: Chlorine molecules are dissociated to atoms:
 $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl (g)} \quad \Delta H^\circ_{\text{step2}} = \frac{1}{2} \text{ bond energy of Cl}_2$
 $= \frac{1}{2} (240 \text{ KJ}) = + 120 \text{ kJ mol}^{-1}$
- Step 3: Sodium atoms are ionized to Na+ ions:



➤ Step 4: Formation of chloride ion:



➤ Step 5: Formation of NaCl(s) from ions. The ions Na^+ and Cl^- combine to give solid sodium chloride whose enthalpy changes (the lattice energy) is unknown:



➤ We know the enthalpy formation ($\Delta_f H^\circ$) of NaCl (Direct route) and equals -411 kJ mol^{-1} . Therefore, we can calculate the lattice energy using Hess's law: Solving for U_{NaCl} gives:

$$\text{U}_{\text{NaCl}} = \Delta_f H^\circ - (\Delta H^\circ_{\text{step1}} + \Delta H^\circ_{\text{step2}} + \Delta H^\circ_{\text{step3}} + \Delta H^\circ_{\text{step4}})$$

$$= -411 \text{ kJ mol}^{-1} - [108 \text{ kJ mol}^{-1} + 120 \text{ kJ mol}^{-1} + 496 \text{ kJ mol}^{-1} + (-349 \text{ kJ mol}^{-1})]$$

$$= -786 \text{ kJ mol}^{-1}$$

➤ Note: Ionic solids exist only because the lattice energy exceeds the energy required for the electron transfer.

Exercise 2.3

1. Draw a Lewis electron-dot symbol for each atom:

- a. Rb b. As c. I

2. Give the group number and general electron configuration of an element with each electron-dot symbol:

3. How does the lattice energy of an ionic compound depend on the charges and sizes of the ions?

4. Use condensed electron configurations and Lewis electron dot symbols to depict the monatomic ions formed from each of the following atoms, and predict the formula of the compound the ions produce.

- a. Ba and Cl b. Sr and O c. Al and F d. Rb and O

5. Identify the main group to which X belongs to in each ionic compound formula:

- a. X_2O_3 b. XCO_3 c. Na_2X

6. For each pair, choose the compound with the lower lattice energy, and explain your choice:

- a. CaS or BaS b. NaF or MgO c. LiCl or CsCl d. BaS or CsCl

Answer to Exercise 2.3

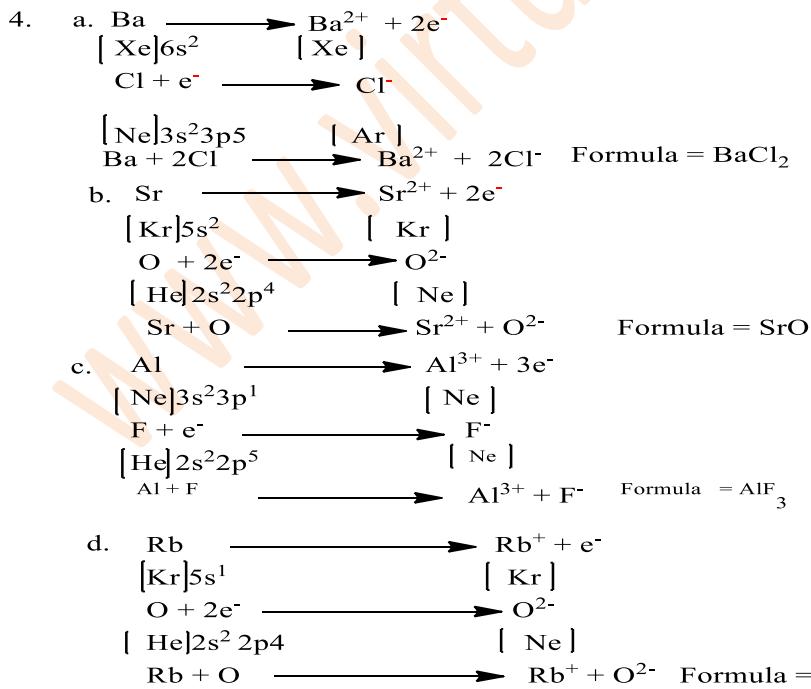


1 a. group 3 b. group 5

2 3. Lattice energy thus is a measure of coulombic attractive force between the combining ions. The lattice energy (U) of an ionic compound depends directly on the product of the ionic charges ($q_1 \times q_2$), and inversely on the distance (r) between them.

$$U \propto \frac{q_1 \times q_2}{r}$$

where q_1 and q_2 are the charges on +ve and -ve ions respectively, and r is the distance between the charges q_1 and q_2 . Thus, small ions having higher ionic charge shall have larger lattice energy.



5. a. Group 3 b. Group 1 c. Group 6
6. a. BaS; Ba^{2+} is larger than Ca^{2+}
- b. NaF; the charge on each ion is less than the charge on Mg and O
- c. CsCl; Cs^+ is larger than Li^+
- d. CsCl; the charge on each ion is less than the charge on Ba and S

Factors Affecting the Formation of Ionic Bonds

- The formation of ionic bonding is influenced by various factors. Some of the major factors are presented below.
- ✓ **Ionization energy (IE):** The lesser the ionization energy, the greater is the ease of the formation of a cation. Thus, low ionization energy of metallic elements such as alkali and alkaline earth metals favors the formation of an ionic bond.
- ✓ **Electron affinity (EA):** A higher electron affinity favors the formation of an anion.

Generally, the elements having higher electron affinity such as halogens favor the formation of an ionic bond.

Thus, low ionization energy of a metal atom and high electron affinity of a non-metal atom facilitate the formation of an ionic bond between them.

- ✓ **Lattice energy:** When a cation and an anion come closer, they get attracted to each other due to the electrostatic (columbic) force of attraction.
- The electrostatic force of attraction between oppositely-charged ions release a certain amount of energy and an ionic bond is formed. If the columbic attraction forces are stronger, then more energy gets released and a more stable or a stronger ionic bond is formed. Larger lattice energy would favor the formation of an ionic bond.
- Lattice energy thus is a measure of columbic attractive force between the combining ions.
- The lattice energy (U) of an ionic compound depends directly on the product of the ionic charges ($q_1 \times q_2$), and inversely on the distance (r) between them:

$$U \propto \frac{q_1 \times q_2}{r}$$

2.2.3 The Exceptions of the Octet Rule in Ionic Compounds

There are certain exceptions to the octet rule.

Less than Octet (Central Atom is Deficient of Electrons)

Ions of some elements which are near to helium in the periodic table do not obey the octet rule. The tendency of these atoms (H, Li, Be and B) is to attain an arrangement of two electrons like the noble gas He, which is also a stable configuration. The hydride ion (H^-), lithium ion (Li^+), beryllium ion (Be^{2+}) and boron ion (B^{3+}) are isoelectronic with He.

Although atoms with less than an octet may be stable, they will usually attempt to form a fourth bond to get eight electrons.

For example BF_3 is stable, but it will form BF_4^- when possible.

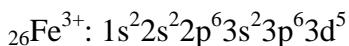
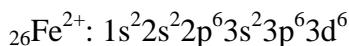
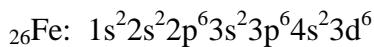
More than Octet (18-Electron Rule)

The ions of some transition and post-transition elements do not usually obey the octet rule.

For transition metals, the 18-electron rule replaces the octet rule, due to the involvement of d orbitals of these atoms.

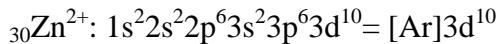
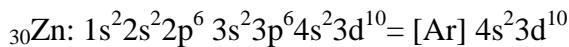
Note that when these atoms form positive ions, electrons are always lost first from the shells with the highest value of the principal quantum number (n). Consider the electron configurations of the ions of the transition elements iron and zinc and the post-transition elements gallium and tin.

Electron Configurations of Iron:



A stable ion of iron with valence shell electron configuration is $3s^23p^63d^5$ which is not isoelectronic with a noble gas. Fe^{2+} is a well-known stable ion with a valence shell electron configuration $3s^23p^63d^6$ which is not isoelectronic with any of the noble gases.

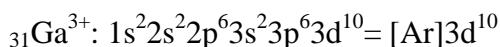
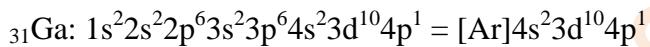
Electron configurations of zinc:



Zn^{2+} is also not isoelectronic with any of the noble gases.

Electron configurations of gallium:

The post-transition element gallium(Ga) loses electrons first from the 4p orbital and then from the 4s orbital to form a Ga^{3+} ion as



From the electron configurations of Zn^{2+} and Ga^{3+} , we will realize that ions have completely-filled outer subshells and a noble gas core. Their valance electron configuration can be generally represented as $ns^2np^6nd^{10}$.

Exercise 2.4

1. From which orbital (s) do the heavier post-transition elements such as Pb and Sn lose electrons?
2. Can you write the electron configurations of Sn, Sn^{2+} , and Sn^{4+} ? Check if any of these tin ions are isoelectronic with any of the noble gases.
3. Which groups of ions of elements, in general, show more than the octet (18-electron rule)?

Answer to Exercise 2.4

1. The heavier post-transition elements like Pb and Sn lose the p electrons or both the p and s electrons from the valence shell.
2. $2.50Sn: [Kr]5s^24d^{10}5p^2$



${}_{50}\text{Sn}^{4+}: [\text{Kr}]4d^{10}$, Neither of these configurations are noble gas configurations.

3. The ions of some transition elements and post-transition elements do not usually obey the octet rule. Generally, these properties are exhibited by ions of elements from
 - i. Group IB and Group IIB (transition elements) and
 - ii. Group IIIA and Group IVA (heavier post-transition elements)

2.2.4 Properties of Ionic compounds

- Ionic compounds are crystalline solids at room temperature.
- The fundamental units of ionic solid are positive and negative ions.
- Crystalline ionic solids are usually brittle and non-conductors of electricity, although molten crystals may be good conductors.
- They usually have high melting and boiling points.
- Ionic compounds are nonvolatile.
- Ionic compounds are usually soluble in inorganic solvents (water is the most common solvent for ionic compounds) but insoluble in organic solvents like benzene, ethanol and carbon tetrachloride.

Note! Ionic compounds are very resistant to heat but many will be easily broken by water.

2.3 Covalent Bonds and Molecular Geometry

Formation of covalent Bonding

- Consider the formation of a hydrogen molecule (H_2). When two isolated hydrogen atoms come close together, electrostatic interactions begin to develop between them.
- The two positively charged nuclei repel each other, and the two negatively charged electrons repel each other, but each nucleus attracts both electrons and each electron is attracted to both nuclei (Figure.2).

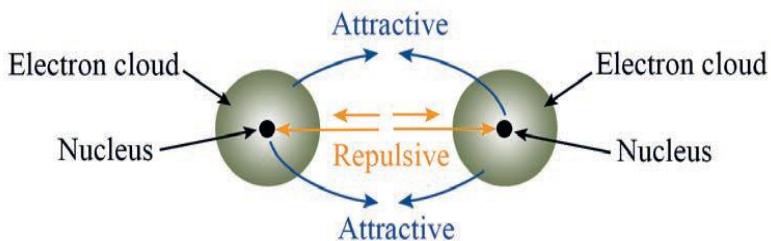


Figure 2: Attractive and repulsive forces in a covalent H–H bond formation

The magnitudes of the various attractive and repulsive forces between nuclei and electrons in a covalent bond depend on how close together the atoms are.

There is an optimum distance between nuclei, called the **bond length**, where net attractive forces are maximized and the H–H molecule is most stable.

In the H₂ molecule, the bond length is 74 pm.

On a graph of energy versus inter-nuclear distance, the bond length is the H–H distance in the minimum energy. This is the most stable arrangement (Figure 2.3).

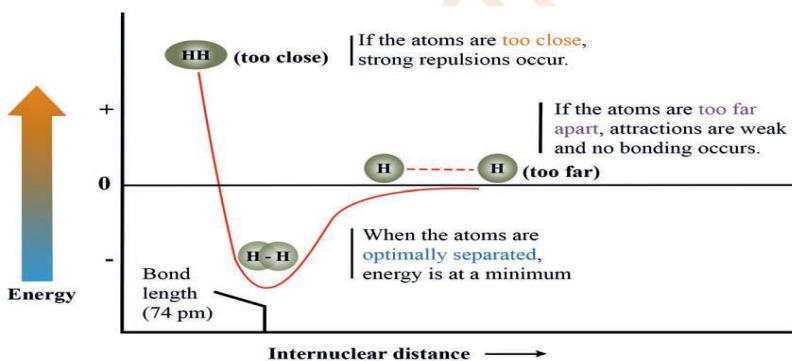


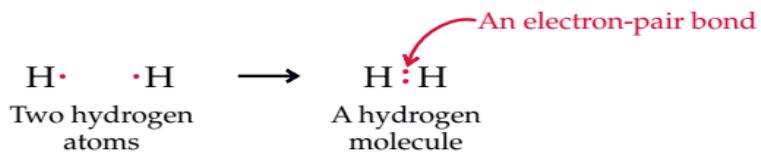
Figure 3: Covalent bond formation in H₂

Therefore, a covalent bond is formed when a pair of electrons is shared between two atoms. Formation of a bond always results in greater electron density between the nuclei. Some examples of covalent molecules are HCl, H₂S, C₂H₄, N₂, CCl₄, BCl₃, H₂O, NH₃, SO₂, PCl₅, O₃, etc. Generally, substances that contain covalent bonds are called molecules.

Representation of Covalent Bonds (Drawing Lewis Structures)

The representation of covalent bonding through Lewis symbols and shared electron pairs is called a **Lewis structure**.

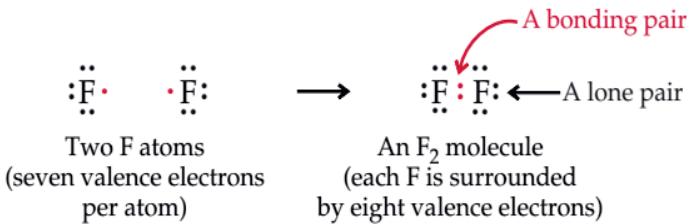
The Lewis structure for a hydrogen molecule formed from hydrogen atoms is:



By sharing two electrons in a covalent bond, each hydrogen effectively has one electron pair and the stable, $1s^2$ electron configuration of helium.



- Similarly, fluorine has seven valence electrons, and an electron-dot structure for the F_2 molecule shows how a covalent bond can form:

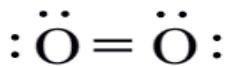


- The shared pairs of electrons in a molecule are called bonding pairs. The other electron pairs that stay with one atom and are not shared are called non-bonding pairs or lone pairs.
- Note that in molecules such as O_2 , N_2 , and many others, the atoms share more than one pair of electrons, leading to the formation of multiple covalent bonds.
- For example, consider the formation of oxygen molecule (O_2) from the oxygen atoms.

- The electronic configuration of oxygen atoms is 2,6 . Now each oxygen atom needs two electrons to complete its octet. The two oxygen atoms share two electrons and complete their octet:



- The 4 electrons (or 2 pairs of electrons) which are shared between the two oxygen atoms. So these two pairs of shared electrons can be represented by two bonds between the oxygen atoms. An oxygen molecule can be shown as follow:



- The two oxygen atoms are said to be bonded together by two covalent bonds. Such a bond consisting of two covalent bonds is also known as a double bond.
- Steps to Writing a Lewis Formula:
 - We can write the Lewis formula for a covalent compound of known geometry by using the following steps.
 - 1. Determine the total number of valence electrons. The total number of electrons for a molecule is the sum of the valence electrons for each atom. For a polyatomic anion, which has one or more extra electrons, add one electron for each unit of negative charge. For a polyatomic cation, which is missing one or more electrons, subtract one electron for each unit of positive charge.
 - 2. Write the skeletal structure. The most electropositive atom usually occupies the central position. Connect bonded atoms with an electron-pair bond (a dash).
 - Hydrogen is an exception; it is always a terminal atom, even when bonded to a more electronegative atom.
 - 3. Place electron pairs around terminal atoms so that each (except hydrogen) has an octet. Assign any remaining electrons as lone pairs around the central atom.
 - 4. If at this stage, a central atom has fewer than eight electrons, a multiple bond(s) is likely. Move one or more lone-pair of electrons from a terminal atom(s) to a region between it and the central atom to form a double or a triple bond.

Example 2; Write the Lewis structure for nitrogen tri-fluoride (NF_3) in which all three F atoms are bonded to the N atom.

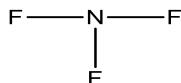
Solution:

We follow the steps for writing Lewis structures.

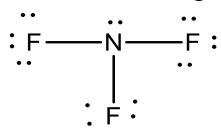
Step 1: The outer-shell electron configurations of N and F are $2s^22p^3$ and

$2s^22p^5$, respectively. Thus, there are $5 + (3 \times 7)$, or 26, valence electrons to account for in NF_3 .

Step 2: The N atom is less electronegative than F, so in the skeletal structure of NF_3 , N goes in the center with the more electronegative F atoms bonded to it.



Step 3: We draw a single covalent bond between N and each F, and complete the octets for the F atoms. We place the remaining two electrons on N:



Because this structure satisfies the octet rule for all the atoms, step 4 is not required.

Example 3: Write the Lewis structure for the carbonate ion (CO_3^{2-}).

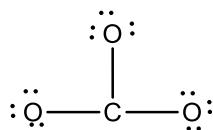
Solution: We follow the steps for writing Lewis structures and note that this is an anion with two negative charges.

Step 1: The outer shell electron configurations of C and O are $2s^22p^2$ and $2s^22p^4$, respectively, and the ion itself has two negative charges. So, the total number of electrons is $4 + (3 \times 6) + 2$, or 24.

Step 2: We can deduce the skeletal structure of the carbonate ion by recognizing that C is less electronegative than O. Therefore, it is most likely to occupy a central position as follows:

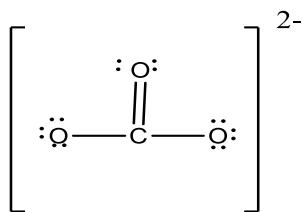


Step 3: We draw a single covalent bond between C and each O and comply with the octet rule for the O atoms:



This structure shows all 24 electrons.

Step 4: Although the octet rule is satisfied for the O atoms, it is not for the C atom. Therefore, we move a lone pair from one of the O atoms to form another bond with C. Now the octet rule is also satisfied for the C atom:

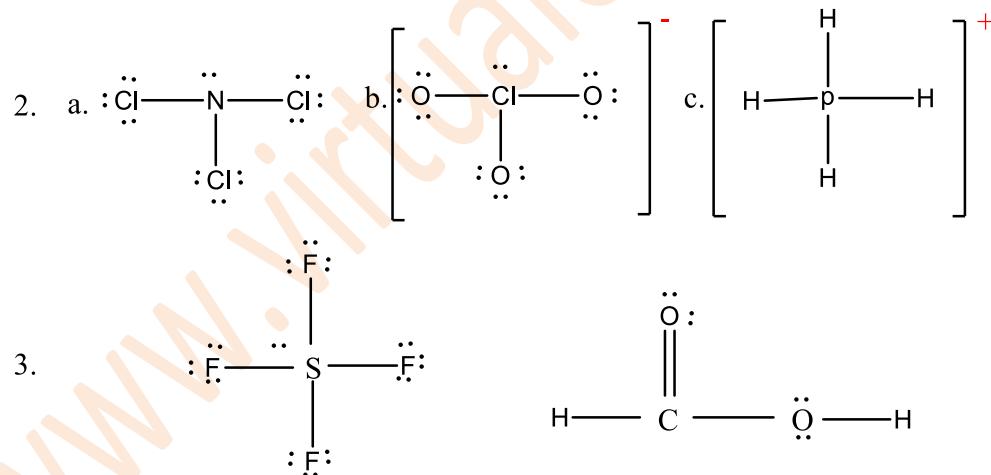


Exercise 2.5;

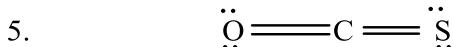
1. Determine the total number of valence electrons for the following:
a. CO_2 b. SO_4^{2-} c. NH_4^+ d. N_2O_4
2. Write a Lewis structure of
a. nitrogen trichloride, NCl_3 b. chlorate ion, ClO_3^-
c. phosphonium ion, PH_4^+
3. Draw a Lewis structure for SF_4 and HCOOH (formic acid).
4. Which of the following atoms O, He, F, H, and P cannot be used as a central atom in a Lewis structure? Explain.
5. Write a Lewis structure for carbonyl sulphide, COS .

Answer to Exercise 2.5

1. a. CO_2 has $(1 \times 4) + (2 \times 6) = 16$ c. NH_4^+ has $(1 \times 5) + (4 \times 1) = 8$
b. SO_4^{2-} has $(1 \times 6) + (4 \times 6) + 2 = 32$ d. N_2O_4 has $(2 \times 5) + (4 \times 6) = 34$



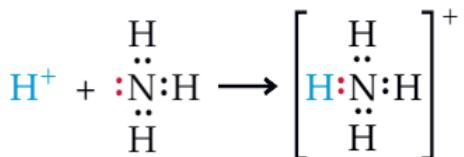
4. H and F because they cannot form more than one covalent bond.



Coordinate-Covalent Bonding

- Most covalent bonds form when two atoms each contribute one electron. However, bonds can also form when one atom donates both electrons (a lone pair) to another atom that has a vacant valence orbital.

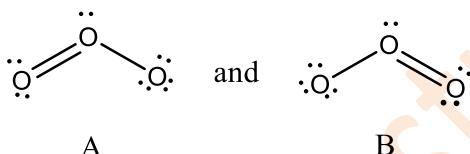
- The ammonium ion (NH_4^+), for example, forms when the lone-pair electrons from the nitrogen atom of ammonia, NH_3 , bond to H^+ .
 - Such kind of bonds is called **coordinate covalent bonds or dative bonds**.



- Some examples of molecules which contain coordinate-covalent bonds include NH_3 , BCl_3 , H_3O^+ and AlCl_4^- .

Resonance Structures

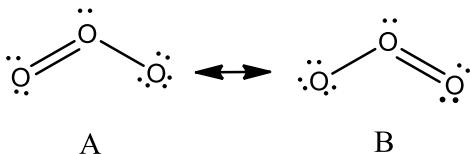
- Sometimes more than one valid Lewis structure is possible for a given molecule. For example, two Lewis structures are possible for ozone (O_3):



- In formula A, the oxygen–oxygen bond on the left is a double bond and the oxygen–oxygen bond on the right is a single bond.
 - In formula B, the situation is just the opposite. These are not two different O_3 molecules, just different Lewis structures for the same molecule. However, neither one of these two Lewis structures accounts for the known bond lengths in O_3 (1.278 Å).



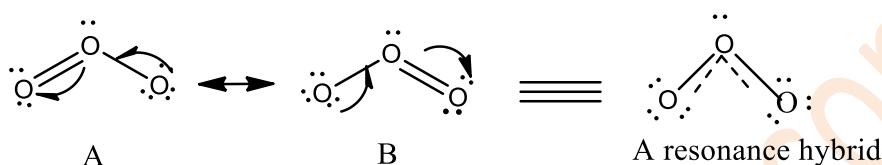
- Since both the bonds are identical, which one is a double bond? Bond length and bond energy measurements indicate that the two oxygen-oxygen bonds in O₃ are identical, with properties that lie between those of an O–O bond and an O=O bond, something like a “one-and-a-half” bond.
 - The molecule is shown more correctly with two Lewis structures, called **resonance structures (or resonance forms)**, and a two headed resonance arrow (\longleftrightarrow) between them.



Resonance structures have the same relative placement of atoms but different locations of bonding and lone electron pairs.

Our need for more than one Lewis structure to depict the ozone molecule is the result of electron-pair delocalization.

You can convert one resonance form to another by moving lone pairs to bonding positions, and vice versa:



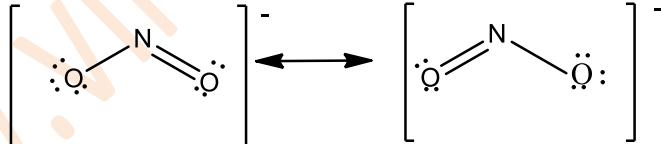
This description of O_3 is called resonance, in which two or more possible Lewis structures can be written and the true structure is a composite or hybrid of them. The different structures used to represent the molecule or ions are called **resonance forms** or **resonance contributors or resonance structures**.

Example 4: Write two equivalent Lewis structures for the nitrite ion, NO_2^- . Describe its resonance hybrid structure.

Solution: In NO_2^- there are $5 + 2(6) + 1 = 18$ valence electrons. Indicating the single bonds gives the structure.



The remaining 14 electrons ($18 - 4$) can be distributed to produce these structures:

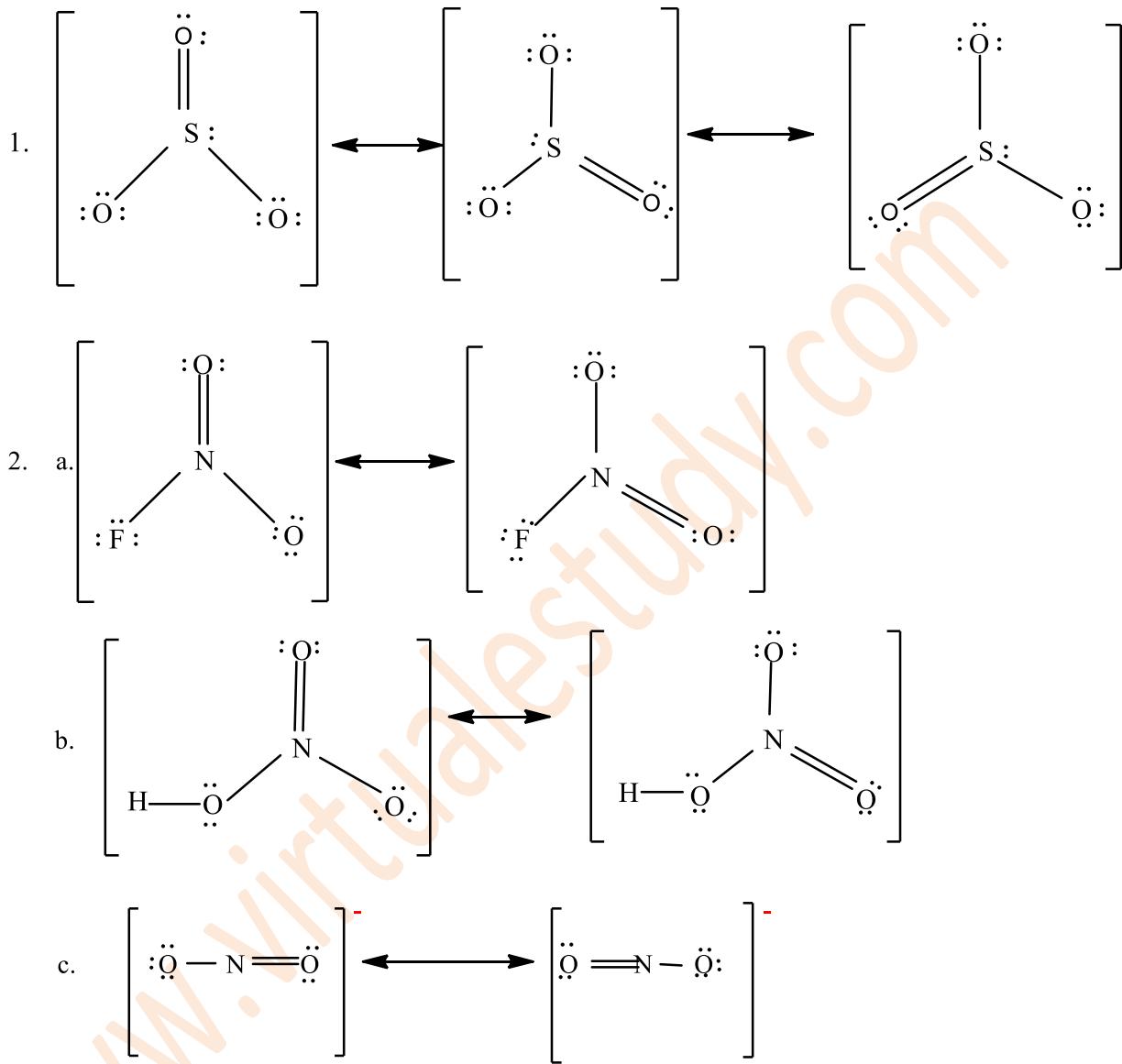


The electronic structure of the molecule is correctly shown by the average of the two. There are two equivalent N---O bonds, each one intermediate between a single and a double bond.

Exercise 2.6

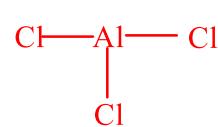
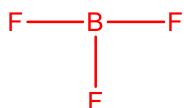
1. Write three equivalent structures for the SO_3 molecule that obey the octet rule.
2. Draw Lewis structures of all the important resonance forms of each of the following:
 - NO_2F (N central)
 - HNO_3
 - NO_2^-

Answer to Exercise 2.6



Exceptions to the Octet rule in Covalent Bonding

- Although many Lewis structures follow the octet rule, there are exceptions. There can be categorized into three groups:
 - i. **Less than octet (central atom is deficient of electrons):**
 - Electron-deficient compounds are compounds in which an element has an incomplete octet. The central atoms of such molecules have fewer than eight electrons (below octet). This group consists of molecules containing central atoms from Group IIA and IIIA.
 - For example, BeCl₂, BF₃ and AlCl₃, whose Lewis formulas are shown:



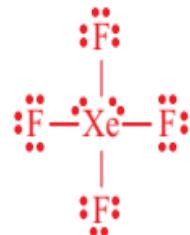
4 electrons around Be

6 electrons around B

6 electrons around Al

ii. More than octet (central atom has excess of electrons):

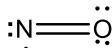
- Elements with an expanded valence (also called an expanded octet) have more than 8 electrons (often 10 or 12) in a Lewis structure.
- Elements in the third period and below, such as phosphorus, sulfur, and bromine, often have an expanded valence because of their larger radii (when compared to the second-row elements) and the availability of empty d orbitals in the valence shell. For example PF_5 , SF_6 and XeF_4 :



10 electrons around P 12 electrons around S 12 electrons around Xe

iii. Molecules containing an odd number of electrons:

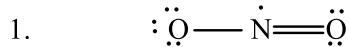
- Even if stable molecules of this kind (free radicals) are rare, they do exist.
- Free radicals can also be electron-deficient compounds. Some examples are ClO_2 , NO and NO_2 having 19, 11 and 17 valence electrons, respectively. For example, the best way to suggest the Lewis-like structure for the NO molecules is:



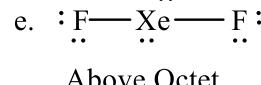
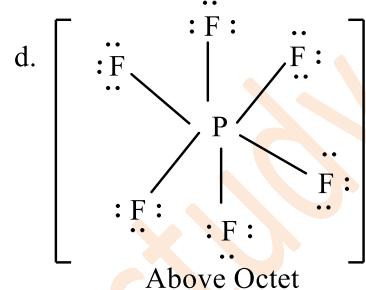
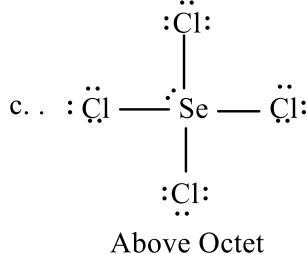
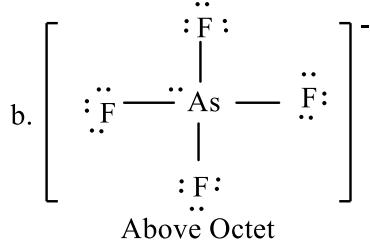
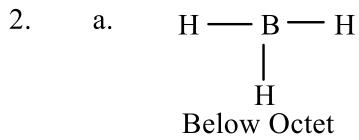
Exercise 2.7

1. Suggest the Lewis-like structure for NO_2 and ClO_2 molecules.
2. The following do not obey the octet rule. Draw a Lewis structure for each one and state the type of octet rule exception:
 - a. BH_3
 - b. AsF_4^-
 - c. SeCl_4
 - d. PF_6

Answer to Exercise 2.7

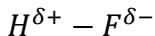


ClO_2 no possible Lewis structure

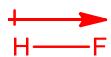


Polar and Non-Polar Covalent Molecules

- When the atoms are alike in a covalent bond, as in the case of the H–H bond of H_2 , the bonding electrons are shared equally.
 - That is, the electrons spend the same amount of time near each nucleus.
 - The bond formed is called **a non-polar covalent bond**.
 - In a covalent bond between atoms of different electronegativities, there is an unequal sharing of an electron pair and the electrons spend more of their time around the more electronegative atom.
 - Such a bond is said to be **polar covalent bond**.
 - The H–F bond is a polar bond because fluorine is more electronegative than the hydrogen atom.
 - The bonding electrons spend more time near the fluorine atom than the hydrogen atom.
- The polar nature of a bond is shown like this:



- In the representation the δ^+ and δ^- (read “delta plus” and “delta minus”) signify that one end (H) is partially positive and the other end (F) is partially negative.
- The term “partial charge” implies something less than the full charges of the ions that would result from complete electron transfer.
- The bond polarity can also be shown by drawing an arrow so that the head points toward the negative end (F) of the bond and the crossed tail indicates the positive end (H).



- For a diatomic molecule having a polar covalent bond, such as HF, we can describe a quantity called the dipole moment, which is a vector sum of the bond moments in a molecule.
- **Bond moment** is a measure of polarity of a diatomic covalent bond.
- **The dipole moment (μ)** is defined as the product of the magnitude of the charge (δ) at either end of the dipole multiplied by the distance (d) that separates the charge.

$$\mu = \delta \times d$$

- The SI-unit of dipole moment is coulomb-metre (C.m). Dipole moments are often expressed in the non-SI unit debye (D), where $1D = 3.33564 \times 10^{-30}$ C.m.
- A very polar molecule is one with a large dipole moment, while a non-polar molecule will have a zero-dipole moment.
- **Note:** For a diatomic molecule, the bond moment is the dipole moment.
- The dipole moment of a polyatomic molecule (three or more atoms) depends on the geometry of the molecule.
- If the bond moments are equal in magnitude but opposite in direction, then they will cancel each other and the resultant dipole moment will be zero, provided that the vector sum of the bond moments is zero.

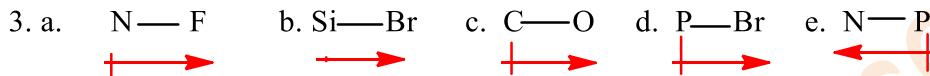
Exercise 2.8

1. Both CO_2 and BCl_3 have zero dipole moments, but the C = O and B – Cl bond moments are not zero. Explain.
2. Compare the dipoles in the covalent molecules HF, HCl, HBr, and HI. Explain your answer.
3. For each of the following bonds, indicate the positive end with δ^+ and the negative end with δ^- . Draw an arrow to show the dipole for each.
 - a. N and F
 - b. Si and Br
 - c. C and O
 - d. P and Br
 - e. N and P

Answer to Exercise 2.8

1. From their electronegativity data, one can predict that there is a bond moment in both CO_2 and BCl_3 . But from the molecular geometry of these molecules (CO_2 linear and BCl_3 trigonal planar), it can be predicted that the bond moments cancel to give a non-polar molecule to produce a zero resultant dipole moment.
2. The dipoles in decreasing order is $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$. This is due to dipole moment ($f\hat{E}$) is defined as the product of the magnitude of the charge ($f\hat{\Delta}$) at either end of the dipole multiplied by the distance (d) that separates the charge. $f\hat{E} = f\hat{\Delta} \bullet \sim d$

Hydrogen fluoride can form hydrogen bonds because fluorine is the most electronegative of all the elements, the fluorine-hydrogen bond is highly polarized. The hydrogen atom carries a high partial positive charge ($f\text{\AA}^+$); the fluorine is fairly negatively charged ($f\text{\AA}^-$). The other hydrogen halides do not form hydrogen bonds because the larger halogens are not as electronegative as fluorine; therefore, the bonds are less polar. That is, the other halogens do not carry such an intensely concentrated negative charge; therefore, other hydrogen atoms are not attracted as strongly. For the other hydrogen halides, the distance is more important than the charge developed.



Properties of Covalent Compounds

- Unlike any ionic compound, many of the covalent compounds are found in gaseous state at room temperature. Consider methane (CH_4), is gas at room temperature.
- Unlike melted ionic compounds, liquid covalent compounds do not conduct electricity. Therefore, liquid methane does not conduct electricity.
- Covalent compounds are molecular substances.
- They have low melting and boiling points.
- Most covalent compounds are soluble in non-polar solvents.
- Generally:
 - Covalent compounds exist as separate molecules because electrically neutral atoms form them and the forces of attraction between these molecules are relatively weak.
 - Due to weak intermolecular forces, many covalent molecules or covalent compounds are liquids or gases at room temperature. However, some covalent molecules like iodine are solids at room temperature.
 - Liquid: H_2O , Br_2
 - Gas: CO_2 , H_2 , Cl_2 , NH_3
 - Covalent compounds are volatile.
 - Generally, they have low melting points and boiling points.
 - Covalent compounds are generally insoluble in water.
 - Most covalent compounds are soluble in non-polar solvents.
 - Non-polar covalent compounds are non-electrolytes because they do not conduct electricity.

2.3.1 Molecular Geometry

- **Molecular geometry** is the three-dimensional arrangement of atoms in a molecule.

There is a simple procedure that enables us to predict the geometry of a molecule or ion if we know the number of electrons surrounding a central atom in its Lewis structure.

The basis of this approach is the assumption that electron pairs in the valence shell of an atom repel one another.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

In a covalent bond, a pair of electrons, often called the bonding pair, is responsible for holding two atoms together.

However, in a polyatomic molecule, where there are two or more bonds between the central atom and the surrounding atoms, the repulsion between electrons in different bonding pairs causes them to remain as far apart as possible.

The geometry that the molecule ultimately assumes (as defined by the positions of all the atoms) minimizes the repulsion. This approach to the study of molecular geometry is called the **valence-shell electron-pair repulsion (VSEPR)** model.

The basic principle of VSEPR theory is that the pair of valence-shell electron pairs around the central atom arrange as far away from one another as possible to minimize electron-pair repulsions.

The arrangements that best minimize repulsions naturally depend on the number of **electron sets**.

An electron set is defined as any number of electron pairs that occupies a localized region around a central atom.

This set may consist of a single bond (–), a double bond (=), a triple bond (≡), lone-pair(s) or in some cases even a lone (single) electron.

Once we have counted the number of electron groups surrounding the central atom, we can determine its specific shape from the number of atoms bonded to the central atom.

Electron Pair Arrangement and Molecular Shape

The electron pair arrangement is defined by the orientation or distribution of pairs of electrons, both bonding and non-bonding (lone pair), around the central atom.

On the other hand, the molecular shape is defined by the relative positions of the atomic nuclei.

Molecular shapes that occur when all the surrounding electrons are bonding differ from molecular shapes when some of the electrons are non-bonding.

Thus, the same electron set arrangement can give rise to different molecular shapes.

For the prediction of **geometrical shapes** of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as molecules in which the central atom has no lone pair and molecules in which the central atom has one or more lone pairs.

i. molecules in which the central atom has no lone pair

Consider molecules that contain atoms of only two elements, A and B, of which A is the central atom.

These molecules have the general formula AB_x , where x is an integer 2, 3, (If x = 1, we have the diatomic molecule AB, which is linear by definition.)

In the vast majority of cases, x is between 2 and 6. In the compounds of AB_2 , AB_3 , AB_4 , AB_5 and AB_6 , the arrangements of electron pairs and the B atoms around the central atom A are: linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral, respectively.

Such arrangements can be seen in molecules such as $BeCl_2$ (AB_2), BF_3 (AB_3), CH_4 (AB_4) and PCl_5 (AB_5) as shown below (Figure 2.4) by their ball and stick models.

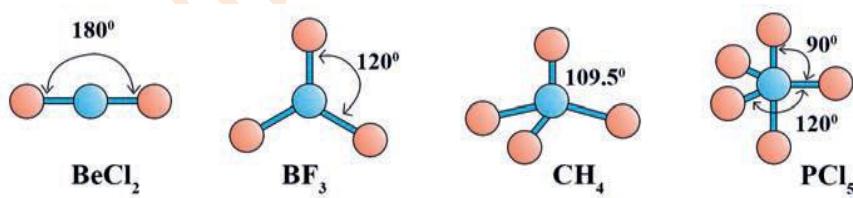


Figure 4: The shapes of molecules in which the central atom has no lone pair

In the case of multiple (double or triple) bonds the counting is not different, because a double bond is considered as one set and a triple bond as another set of electrons.

For example, in the case of CO_2 , $O=C=O$, there are two sets of electrons around the central atom, acetylene, C_2H_2 , $H-C\equiv C-H$, two sets of electrons around each of the central atoms.

Molecules in which the central atom has one or more lone pairs

In such molecules there are three types of repulsive forces—those between bonding pairs, those between lone pairs, and those between a bonding pair and a lone pair.

In general, according to the VSEPR model, the repulsive forces decrease in the following order:

Lone pair vs lone pair > lone pair vs bonding pair > bonding pair vs bonding pair

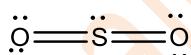
To keep track of the total number of bonding pairs and lone pairs, we show molecules with lone pairs as AB_xE_y , where A is the central atom, B is a surrounding atom, and E is a lone pair on A. Both x and y are integers; $x = 2, 3, \dots$ And $y = 1, 2, \dots$

Thus, the values of x and y indicate the number of surrounding atoms and number of lone pairs on the central atom, respectively.

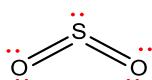
The simplest such molecule would be a triatomic molecule with one lone pair on the central atom and the formula is AB_2E .

AB_2E : Sulfur Dioxide (SO_2)

The Lewis structure of sulfur dioxide is:



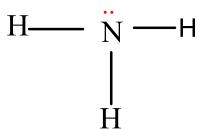
Because VSEPR treats double bonds as though they were single, the SO_2 molecule can be viewed as consisting of three electron pairs on the central S atom. Of these, two are bonding pairs and one is a lone pair. Thus, the overall arrangement of **three electron pairs** is **trigonal planar**. But because one of the electron pairs is a lone pair, the SO_2 molecule has a “bent” shape.



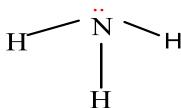
Because the lone-pair versus bonding-pair repulsion is greater than the bonding-pair versus bonding-pair repulsion, the two sulfur-to-oxygen bonds are pushed together slightly and the OSO angle is less than 120° .

AB_3E : Ammonia (NH_3)

The ammonia molecule contains of three bonding pairs and one lone pair:

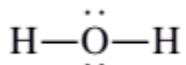


The overall arrangement of four electron pairs is **tetrahedral**. But in NH_3 one of the electron pairs is a lone pair, so the geometry of NH_3 is **trigonal pyramidal**. Because the lone pair repels the bonding pairs more strongly, the three NH bonding pairs are pushed closer together:



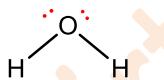
AB₂E₂: Water (H_2O)

A water molecule contains two bonding pairs and two lone pairs:



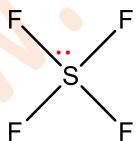
The overall arrangement of the four electron pairs in water is tetrahedral, the same as in ammonia.

However, unlike ammonia, the HOH angle is 104.5° . The geometry of H_2O is bent.



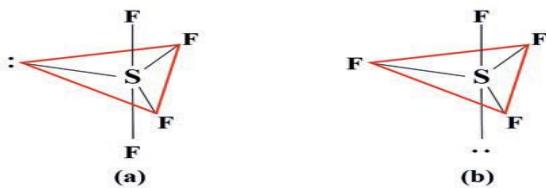
AB₄E: Sulfur Tetra fluoride (SF_4)

The Lewis structure of SF_4 is:



The central sulfur atom has five electron pairs whose arrangement is **trigonal bipyramidal**.

In the SF_4 molecule, however, one of the electron pairs is a lone pair, so the molecule must have one of the following geometries:



In (a) the lone pair occupies an equatorial position, and in (b) it occupies an axial position.

The axial position has three neighboring pairs at 90° and one at 180° , while

the equatorial position has two neighboring pairs at 90° and two more at 120° .

The repulsion is smaller for (a), and indeed (a) is the structure observed experimentally.

Guidelines for Applying VSEPR Model

Here are some guidelines for applying the VSEPR model:

Molecular Shape and Molecular Polarity

Bond Polarity and Dipole Moment

For a molecule made up of three or more atoms, both the polarity of the bonds and the molecular geometry determine whether there is a dipole moment.

Polar bonds do not necessarily lead to polar molecules.

For example, the large electronegativity difference between carbon and oxygen makes each C–O bond quite polar. However, because carbon dioxide(CO_2) has a linear shape, and its bonds are directed 180° from each other, there is no net dipole moment (μ); $\mu = 0 \text{ D}$.

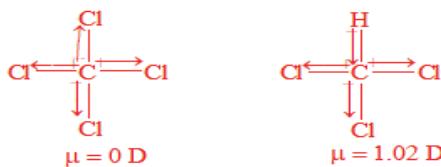


Equal dipole moments with opposite direction
cancel each other.

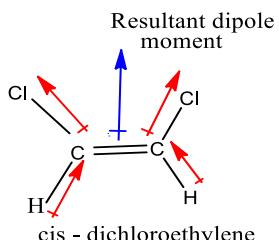
- Another molecule with identical atoms bonded to the central atom is water. Unlike carbon dioxide, water has a significant dipole moment ($\mu = 1.87 \text{ D}$). In each O–H bond, electron density is pulled toward the more electronegative O atom, but the bond polarities do not counter-balance each other, because the water molecule is V-shaped.
- Instead, the bond polarities partially reinforce each other, and the oxygen end of the molecule is considerably more negative than the other end.



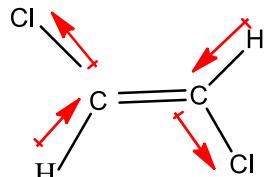
- Carbon dioxide and water demonstrate how molecular shape influences polarity.
- When two or more different molecules have the **same shape**, the nature of the atoms surrounding the central atom can have a **major effect** on the **polarity** of a molecule.
- Consider tetra-chloromethane (CCl_4) and tri-chloromethane (CHCl_3), two AB_4 type molecules: tetrahedral shape with different polarities.
- In CCl_4 , the surrounding atoms are all Cl atoms. Although each C–Cl bond is polar, the molecule is non-polar because the individual bond polarities counter-balance each other. In CHCl_3 , an H atom substitutes for one of the Cl atoms, disturbing the balance and giving chloroform a significant dipole moment.



- If you consider the two constitutional isomers of dichloroethene ($\text{C}_2\text{H}_2\text{Cl}_2$), they have the same molecular formula. However, they have different physical and chemical properties.
- VSEPR theory predicts that all the nuclei lie in the same plane with a trigonal planar molecular shape around each carbon atom.



$$\mu = 1.89\text{D}$$



$$\mu = 0\text{D}$$

- The trans- isomer has no dipole moment ($\mu = 0 \text{ D}$) because the C – Cl bond polarities balance each other. In contrast, the cis-isomer is polar ($\mu = 1.89 \text{ D}$) because the bond dipoles partially reinforce each other, with the molecular dipole pointing between the Cl atoms.

Exercise 2.9

1. Determine the molecular shape and ideal bond angles in:
a. COCl_2 b. PCl_3 c. SF_2 d. SO_4^{2-} e. CS_2
2. When is the molecular shape and the electron-set arrangement the same?
3. Arrange the following AF_n species in order of increasing F–A–F bond angles. BF_3 , BeF_2 , CF_4 , NF_3 , OF_2
4. In the gas phase, phosphorus pent chloride exists as separate molecules. In the solid phase, however, the compound is composed of alternating PCl_4^+ and PCl_6^- ions. How does the molecular shape change as PCl_5 solidifies? How does the angle change?
4. For molecules of general formula AB_n (where $n > 2$), how do you determine if a molecule is polar?

Answer to Exercise 2.9

1. a. trigonal planar, 120° b. trigonal pyramidal, 109.5° c. bent, 98.3°
d. Tetrahedral, 109.5° e. Linear, 180°
2. When there is no lone pair of electron(s) on the central atom.
3. $\text{OF}_2 < \text{NF}_3 < \text{CF}_4 < \text{BF}_3 < \text{BeF}_2$
4. $\text{PCl}_5(\text{g})$ (AX_5 type) has a trigonal bipyramidal molecular shape. In the solid phase, PCl_4^+ (AX_4 type) is tetrahedral, and PCl_6^- (AX_6 type) is seesaw in shape.
5. By the vector sum of bond moments.

2.3.2 Intermolecular Forces in Covalent Compounds

- There are two types of force that hold matter together.
- These are intra-molecular and intermolecular forces.
- Intra-molecular force is a chemical bond (ionic, covalent or metallic) that exists within a particle (molecule or polyatomic ion) and affects the chemical property of the species.
- Intermolecular forces are those bonds that hold particles (ions or molecules) together.

Intermolecular forces are relatively weak as compared to intra-molecular forces, because they typically involve lower charges that are farther apart.

However, the strength of the intermolecular forces is important because they affect physical properties of the species such as melting point and boiling point.

A glass of water for example, contains many molecules of water. These molecules are held together by intermolecular forces, whereas the intra-molecular forces hold the two hydrogen atoms to the oxygen atom in each molecule of water.

Three types of attractive force are known to exist between neutral molecules: dipole–dipole forces, London (or dispersion) forces, and hydrogen bonding forces.

The term van der Waals forces are a general term for those intermolecular forces that include dipole–dipole and London forces.

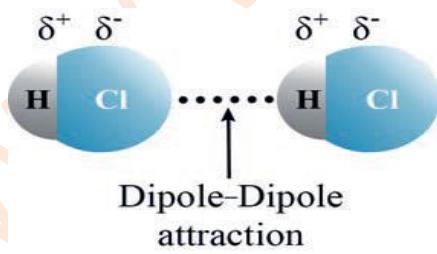
Van der Waals forces are the weak attractive forces in a large number of substances, including Cl_2 , and Br_2 .

Dipole-Dipole forces

Dipole-dipole forces act between the molecules possessing permanent dipole.

When polar molecules are brought near one another, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces; the partially positive end of one molecule attracts the partially negative end of another.

Ends of the dipoles possess “partial charges” and these charges are shown by Greek letter delta (δ).



This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.

The attractive force decreases with the increase of distance between the dipoles.

Hydrogen Bonding

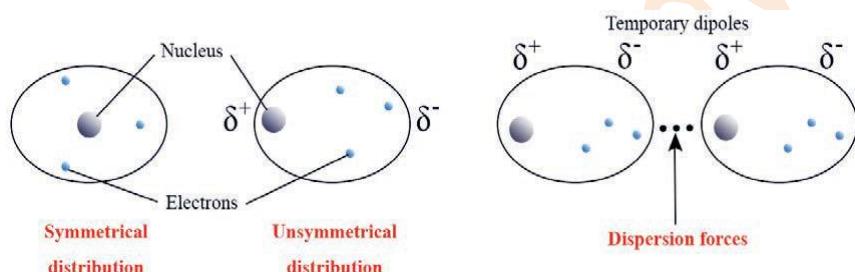
Polar molecules containing hydrogen atoms bonded to highly electronegative atoms of nitrogen, oxygen, or fluorine form especially strong dipole-dipole attractions.

This type of attraction, called a hydrogen bond, occurs between the partially positive hydrogen atom in one molecule and the partially negative nitrogen, oxygen, or fluorine atom in another molecule.

Hydrogen bonds are the strongest type of attractive forces between polar covalent molecules.

Dispersion or London Forces

- Usually, the electrons in a non-polar covalent molecule are distributed symmetrically. However, the movement of the electrons may place more of them in one part of the molecule than another, which forms a temporary dipole.



These weak attractive forces between molecules resulting from the small, instantaneous dipoles that occur because of the varying positions of the electrons during their motion about nuclei are called London forces or dispersion forces.

They are present between all particles (atoms, ions, and molecules).

Although dispersion forces are very weak, they make it possible for non-polar molecules like CO_2 , Cl_2 , noble gases, etc., to form liquids and solids.

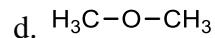
London forces tend to increase with molecular weight increase.

For molecules of about the same molecular weight, the strength of the dispersion forces is affected by molecular geometry (shape). Shapes that allow more points of contact have more area over which electron clouds can be distorted, so stronger attractions result.

This is probably the reason why n-pentane has a higher boiling point(36°C) than its isomers 2-methylbutane (28°C), and 2, 2-dimethylpropane (9.5°C).

Exercise 2.10

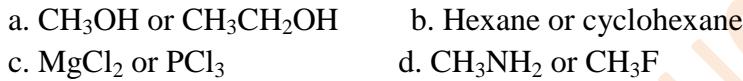
In which of the following substances do hydrogen bonds occur? Explain by using diagrams.



2. What kinds of intermolecular forces (London, dipole–dipole, hydrogen bonding) would you expect in the following substances?



3. Identify the dominant intermolecular force that is present in each of the following substance and select the substance with the higher boiling point in each pair:



4. Compare intermolecular forces with intra-molecular bonding.

5. Compare the strength and polarity of intermolecular forces.

Answer to Exercise 2.10

1. a. In b and c because hydrogen is bonded to highly electronegative atoms oxygen and nitrogen.

2. a. Note that London forces are always present. Tri-chloromethane is an unsymmetrical molecule with polar bonds. Thus, we expect dipole-dipole forces, in addition to London forces.

b. Water has two hydrogen atoms attached to an oxygen atom. Therefore, you expect hydrogen bonding. Because the molecule is polar (from the OH bond), you also expect dipole-dipole forces. London forces exist too, because such forces exist between all molecules.

c. Fluorine (F_2) is a nonpolar molecule. Hence, the only intermolecular attractions are London forces.

d. Hydrogen bromide molecule is polar (from the H–Br bond), you also expect dipole-dipole forces. London forces exist too, because such forces exist between all molecules.

3. a. ethanol (hydrogen bonding) b. hexane (Dispersion forces)

b. magnesium chloride (ionic) d. methyl amine (hydrogen bonding)

4. Intermolecular forces act between molecules or between molecules and ions. Whereas, intramolecular forces are chemical bonds that hold atoms together in a molecule. Generally, intermolecular forces are much weaker than bonding forces.

5. Dipole-dipole forces and ion-dipole forces attract molecules with dipole moments to other polar molecules or ions. Dispersion forces are the result of temporary dipole moments induced in ordinarily nonpolar molecules. The extent to which a dipole moment can be induced in a molecule is determined by its polarizability. The term “van der Waals forces” refers to dipole-dipole, dipole-induced dipole, and dispersion forces. Hydrogen bonding is a relatively strong dipole-dipole force that acts between a polar bond containing a hydrogen atom and the bonded electronegative atoms, N, O, or F. Hydrogen bonds between water molecules are particularly strong.

2.4 Metallic Bonding

2.4.1 Formation of Metallic Bonding

- Metallic bonds are the chemical bonds that hold atoms together in solid metals such as copper, iron, and aluminum.
- In these metals, each metal atom is bonded to several neighboring atoms.
- Metallic bonding is the sharing of free electrons (delocalized electrons) among a lattice of positively charged metal ions.
- The bonding electrons are relatively free to move throughout the three-dimensional structure.
- The strength of the metallic bond depends on:
 1. The number of electrons in the delocalized “sea” of electrons.
- More delocalized electrons result in a stronger bond and a higher melting point.
 1. The packing arrangement of the metal atoms. The more closely packed the atoms are the stronger the bond is and the higher the melting point.

2.4.2 Electron sea- Model

- The electron-sea model is a very simple model, which pictures the metal as an array of metal cations in a “sea” of electrons, as illustrated in Figure 2.5.
- It proposes that all the metal atoms in a sample pool their valence electrons to form an electron “sea” that is delocalized throughout the piece.
- The metal ions (nuclei plus core electrons) are submerged within this electron sea in an orderly array.

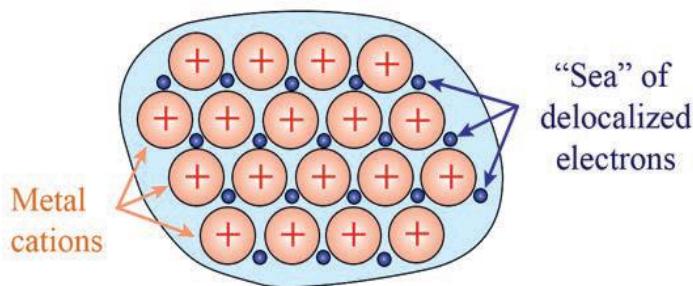


Figure 5: The electron-sea model for the electronic structure of metals

- The metal ions are not held in place as rigidly as the ions in an ionic solid, and no two metal atoms are bonded through a localized pair of electrons as in a covalent bond.
- Rather, the valence electrons are shared among all the atoms in the sample, and the piece of metal is held together by the mutual attraction of the metal cations for the mobile, highly delocalized valence electrons.
- The mobile electrons, known as conduction electrons, can transfer thermal vibration from one part of the structure to another i.e., metals can conduct heat. They are good conductors of electricity also.

2.4.3 Properties of Metallic Bonding

- The general properties of metals include malleability and ductility and most are strong and durable.
- They are good conductors of heat and electricity. Their strength indicates that the atoms are difficult to separate.
- The delocalized electrons are not attached to atoms, so they can move through the metal easily.
- This makes metals good conductors of electricity and heat, even when they are solid.
- The electrostatic bonds between the metal ions and the delocalized electrons are hard to break, so metals are strong.
- Many metals can be flattened into sheets (malleable) and pulled into wires (ductile).
- The combination of strength and malleability means that metals are easy to bend but hard to break.
- Metals have moderate to high melting points because the attractions between the cations and the delocalized electrons are not broken during melting, but boiling points are very high because each cation and its electron(s) must break away from the others.
- Gallium provides a striking example: it melts in your hand ($mp\ 29.8\ ^\circ C$) but doesn't boil until $2403\ ^\circ C$.
- The alkaline earth metals [Group IIA(2)] have higher melting points than the alkali metals [Group IA(1)] because of greater attraction between their $2+$ cations and twice the number of valence electrons.

2.5 Chemical Bonding Theories

- The Lewis model, one of the earliest models of covalent bond formation, represents chemical bonds by an electron dot formula.
- However, it fails to explain the formation of chemical bonds.
- It gives no idea about the shapes of polyatomic molecules. Similarly, the VSEPR theory gives the geometry of simple molecules but, theoretically, it does not explain them and it has limited applications.
- Covalent bonds are more accurately explained using modern bonding theories:
- The valence bond theory and the molecular orbital theory.
- The valence bond (VB) theory assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms.
- It give us a picture of individual atoms taking part in the bond formation.
- The molecular orbital (MO) theory, assumes the formation of molecular orbitals from the atomic orbitals.

2.5.1 The Valence Bond (VB) Theory

- The valence-bond approach is the most useful approach to answer questions such as: what is a covalent bond, and what characteristic gives it strength? How can we explain molecular shapes based on the interactions of atomic orbitals?
- The basic principle of valence bond theory is that a covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons.
- By overlap, we mean that the two orbitals share a common region in space.
- For example, consider the formation of the H₂ molecule from two hydrogen atoms.
- Each atom has the electron configuration 1s¹. As the H atoms approach each other, their 1s orbitals begin to overlap and a covalent bond forms (Figure 2.6).
- Electron density is higher in the overlap region than anywhere else, and the build-up of negative electron charge between the positive nuclei provides the electrostatic attraction that holds the atoms together.

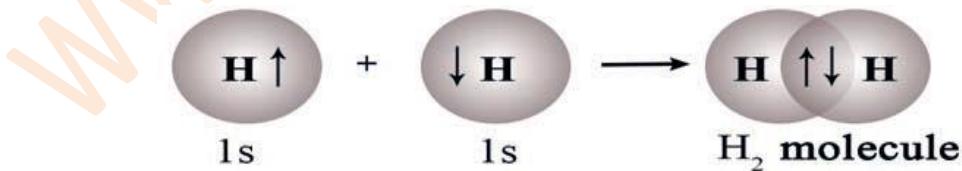


Figure 6: Atomic orbital overlap and bonding in H₂

- When two atoms are brought closely together, the repulsion of the atomic nuclei becomes more important than the electron-nucleus attraction and the bond becomes unstable.

- There is a condition of optimal orbital overlap that leads to maximum bond strength (bond energy) at a particular inter-nuclear distance (bond length).
- The bond strength depends on the attraction of the nuclei for the shared electrons, so the greater the orbital overlap, the stronger (more stable) the bond.
- The extent of overlap depends on the shapes and directions of the orbitals.
- An s orbital is spherical, but p and d orbitals have more electron density in one direction than in another.
- In the HF bond, for example, the 1s orbital of H overlaps the half-filled 2p orbital of F along the long axis of that orbital (Figure 2.7).

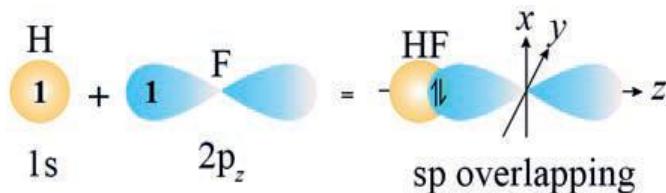


Figure 2.7: Orbital and spin pairing in the formation of a HF molecule

- Similarly, in the F–F bond of F_2 , the two 2p orbitals interact end-to-end, that is along the orbital axes, to attain maximum overlap (Figure 2.8).

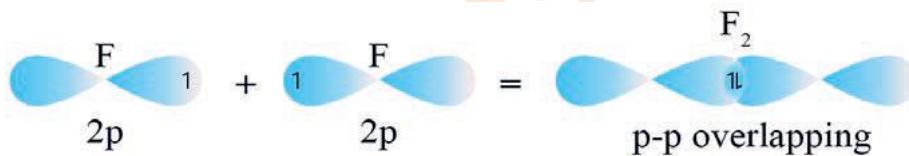


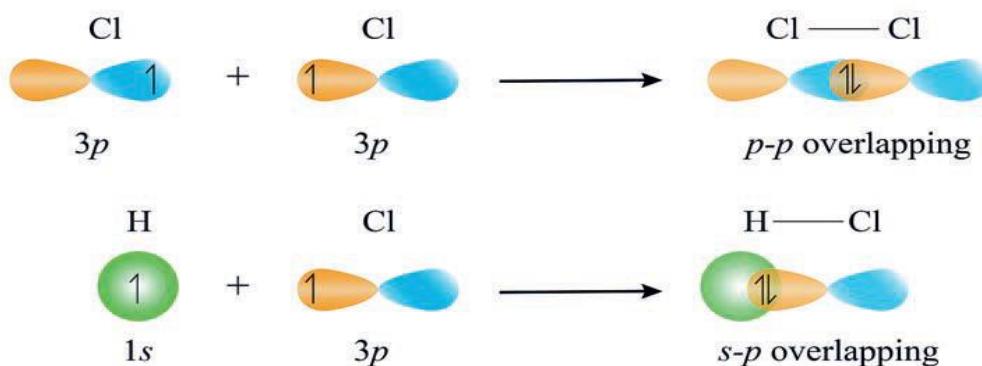
Figure 2.8: Orbital and spin pairing in the formation of a F_2 molecule

- When two atomic orbitals overlap to build up electron density along the two axis between the two nuclei, the resulting localized bond is called a sigma bond (σ).
- Such an overlap is sometimes referred to as a head on, end-to-end, end on or linear overlap.
- In Figures 2.6, 2.7 and 2.8, head-to-head overlap resulted in sigma bonds.

Exercise 2.11

1. Sketch the sigma bonds in Cl_2 and HCl molecules.
2. Identify the overlapping orbitals that form the single bond in a BrCl molecule.

Answer to Exercise 11



2. $4p$ of Br overlaps with $3p$ of chlorine.

- Bonds in which the highest electron density lies along the bond axis (an imaginary line joining the nuclei) in between the bonded nuclei.
- The shape of p atomic orbitals allows them to overlap not only in a head-to-head fashion.
- If they are oriented in a parallel position, they can overlap sideways or laterally as shown in Figure 2.9.
- A bond formed in this way is called *pi-bond (π)*.

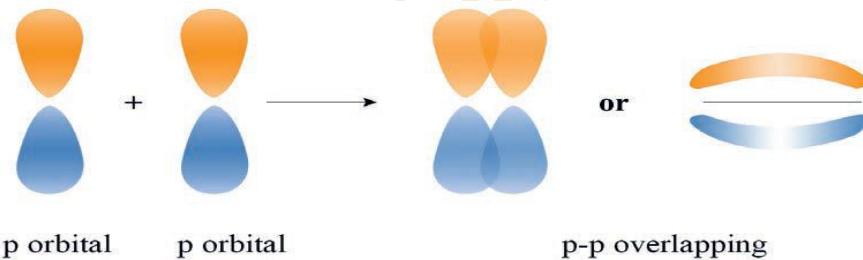


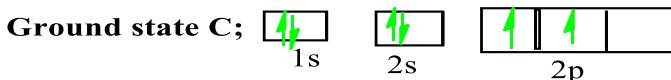
Figure 2.9: Formation of a pi bond (π bond) by the overlap of two half-filled p orbitals that are perpendicular to the inter-nuclear axis.

- Note that the directional nature of p orbital allows to overlap in two ways: end-to-end or sideways.
- These two modes give rise to the two types of covalent bond: sigma (σ) and pi (π) bond, respectively.
- However, s-s and s-p will always overlap along the nuclear axis, resulting only in sigma bonds. Pi bonds are present in molecules containing multiple bonds.
- All of the electron density in a π bond is found in lobes above and below the line connecting the atomic centers: one above and one below the sigma bond axis.
- One π bond holds two electrons that occupy both regions of the bond.

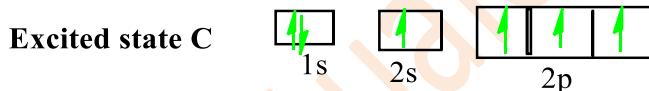
- A double bond always consists of one σ and one π bond.
- The double bond increases electron density between the nuclei.
- A triple bond consists of one σ and two π bonds.

Hybridization of Orbitals

- Hybridization is an imaginary mixing process in which the orbitals of an atom rearrange themselves to form new orbitals called hybrid orbitals.
- Consider covalent bond formation of carbon atom.
- From its ground state configuration, two unpaired electrons in the 2p subshell are observed.



- The simplest stable hydrocarbon is methane, CH_4 .
- To account for this, you need an orbital diagram that shows four unpaired electrons in the valence shell of carbon, requiring four bonds (and therefore four atoms of hydrogen).
- To get such a diagram imagine that one of the 2s electrons is promoted to the empty 2p orbital.
- To excite the 2s electron to a higher energy sublevel, energy must be absorbed.
- The resulting electron configuration is that of an excited state having energy greater than the configuration in the ground state.



- Valence bond theory proposes that the one 2s and all three 2p orbitals of the carbon atom mix to produce four new orbitals (sp^3) that are equivalent to each other in energy and in shape and pointing in different directions with equal $\text{H}-\text{C}-\text{H}$ bond angles.
- This blending is called hybridization and the resultant orbital as hybrid orbitals.
- The symbols used for hybrid orbitals identify the kinds and numbers of atomic orbitals used to form the hybrids.
- The number of new hybrid orbitals is equal to the total number of atomic orbitals that are combined.
- Hybridization provides a useful and convenient method of predicting the shapes of molecules. Note that it does not explain the reason for the shape.

Exercise 2.12

Which of the following statements are false? Give a reason for your answer.

1. Two σ bonds comprise a double bond.
2. A triple bond consists of one π bond and two σ bonds.
3. Bonds formed from atomic s orbitals are always σ bonds.
4. A π bond consists of two pairs of electrons.

5. End-to-end overlap results in a bond with electron density above and below the bond axis.

Answer to Exercise 2.12

1. False 2. False 3. True 4. False 5. False

sp hybrid orbital

- sp type of hybridization involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.
- Each sp hybrid orbitals has 50% s-character and 50% p-character.
- Such a molecule in which the central atom is sp hybridized and linked directly to two other central atoms possesses linear geometry.
- This type of hybridization is also known as diagonal hybridization.
- For example, Be in BeCl_2 molecule has an sp hybridization.
- BeCl_2 : The ground state electronic configuration of Be is $1s^22s^2$.
- In the excited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its bivalence Figure 2.10.
- One 2s and one 2p-orbital gets hybridized to form two sp hybridized orbitals as shown in Figure 2.11.

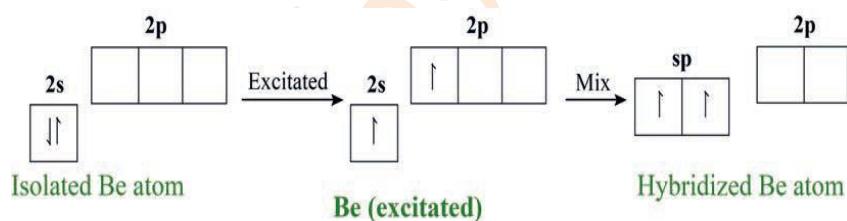


Figure 2.10: Excitation of Be 2s electrons and sp hybrid orbitals formation

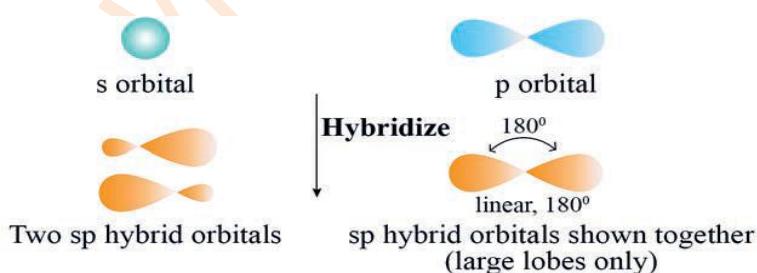


Figure 2.11: The formation of two equivalent *sp* hybrid orbitals in Be.

- These two sp hybrid orbitals face opposite directions, forming an angle of 180° .
- Each of the sp hybridized orbitals overlaps with the 2p-orbital of chlorine axially and forms two BeCl sigma bonds. This is shown in Figure 2.12.

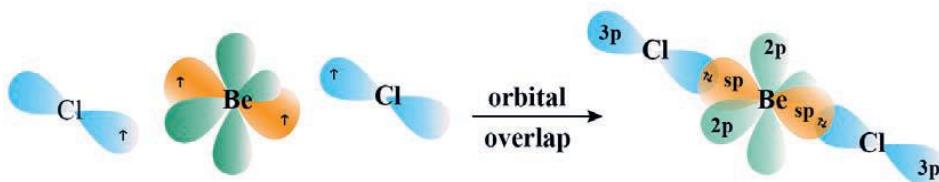


Figure 2.12: The sp hybrid orbitals in gaseous BeCl_2 sp² hybrid orbitals sp^2 hybridization

- In this hybridization there is involvement of one s and two p-orbitals in order to form three equivalent sp² hybridized orbitals.
- For example, in BCl_3 molecule, the ground state electronic configuration of central boron atom is $1\text{s}^2 2\text{s}^2 2\text{p}^1$.
- In the excited state, one of the 2s electrons is promoted to vacant 2p orbital (Figure 2.13) as a result boron has three unpaired electrons.
- These three orbitals (one 2s and two 2p) hybridize to form three sp² hybrid orbitals as shown in Figure 2.13.

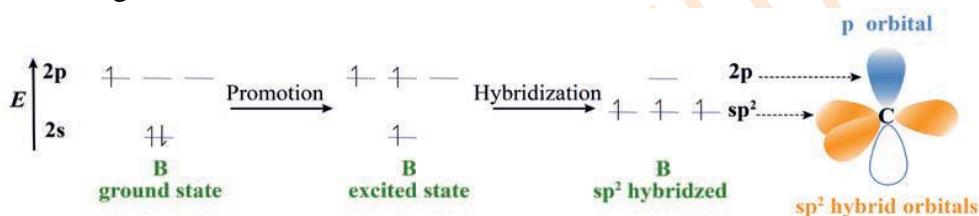


Figure 2.13: Excitation of boron 2s electrons and sp² hybrid orbitals formation

- The three equivalent hybrid orbitals formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B-Cl bonds.
- Therefore, in BCl_3 (Figure 2.14), the geometry is trigonal planar with $\text{Cl}-\text{B}-\text{Cl}$ bond angle of 120° .

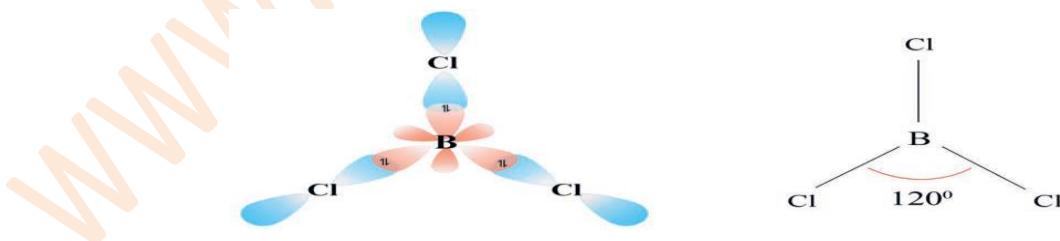


Figure 2.14: sp² hybrid orbitals and bonding in BCl_3

sp³ hybridization

- sp³ type of hybridization is mixing of one s-orbital and three p-orbitals (Figure 2.15) of the valence shell to form four sp³ hybrid orbital of equivalent energies and shape in CH₄ molecule.
- The four sp³ hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp³ hybrid orbital is 109.5° as shown in Figure 2.16.

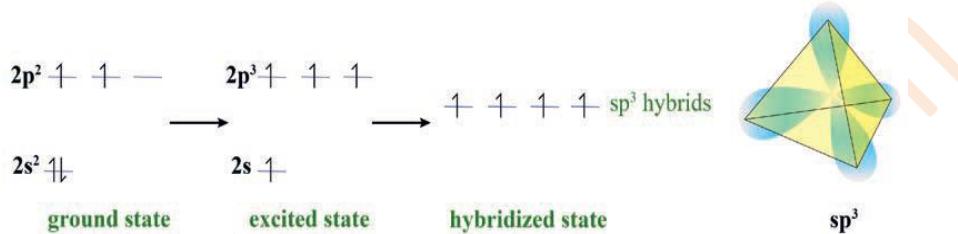


Figure 2.15: Excitation of carbon 2s electrons and sp³ hybrid orbitals formation

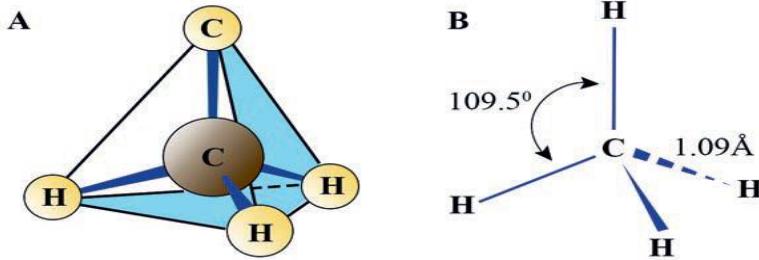


Figure 2.16: sp³ hybrid orbitals and bonding in methane

- The structure of NH₃ and H₂O molecules can also be explained with the help of sp³ hybridization.
- In NH₃, the valence shell (outer) electronic configuration of nitrogen in the ground state is 2s²2p_x¹2p_y¹2p_z¹.
- In the formation of NH₃, one 2s orbital and three 2p orbitals of nitrogen are mix up forming four hybrid orbitals (sp³) of equivalent energy.
- One of the sp³ hybrid orbitals has a lone pair of electrons and the other three sp³ orbitals are half-filled.
- These three half-filled hybrid orbitals overlap with 1s orbitals of hydrogen atoms to form three N–H sigma (δ) bonds.
- We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons.
- So the molecule gets distorted and the bond angle is reduced to 107° from 109.5°.
- The geometry of such a molecule will be pyramidal as shown in Figure 2.17.

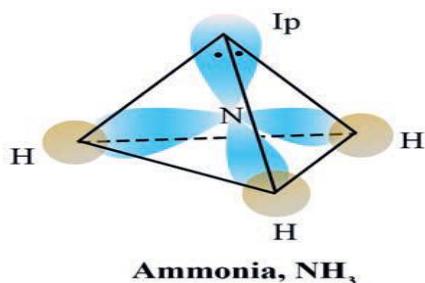


Figure 2.17: sp^3 hybrid orbitals and bonding in NH_3

- In the case of H_2O molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp^3 hybridization forming four sp^3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons.
- These four sp^3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° (Figure 2.18) and the molecule thus acquires a V-shape or angular geometry.

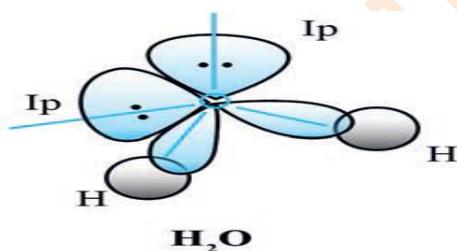


Figure 2.18: sp^3 hybrid orbitals and bonding in H_2O

Hybridization of elements involving d orbitals

- The elements present in the third period contain d orbitals in addition to s and p orbitals.
 - The energy of the 3d orbitals is comparable to the energy of the 3s and 3p orbitals.
 - The energy of 3d orbitals is also comparable to those of 4s and 4p orbitals.
- As a consequence, the hybridization involving either 3s, 3p and 3d or 3d, 4s and 4p is possible.

i. Formation of PCl_5 (sp^3d hybridization):

- The ground state and the excited state outer electronic configurations of phosphorus ($Z=15$) are represented below in Figure 2.19a.

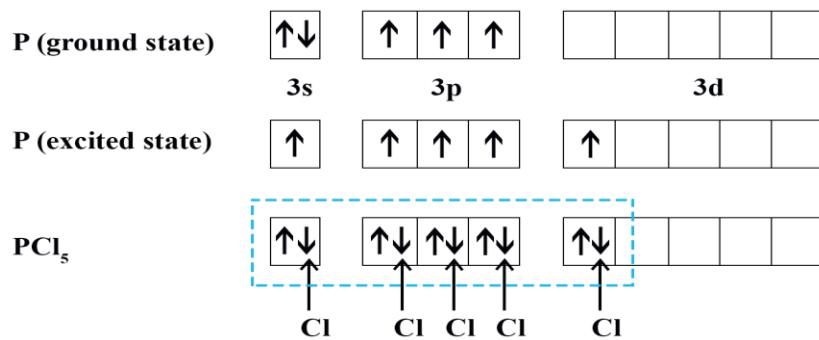


Figure 2.19 (a): sp³d hybrid orbitals filled by electron pairs donated by five Cl atoms

- Now the five orbitals (i.e., one s, three p and one d orbitals) are available for hybridization to yield a set of five sp³d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as in Figure 2.19b.

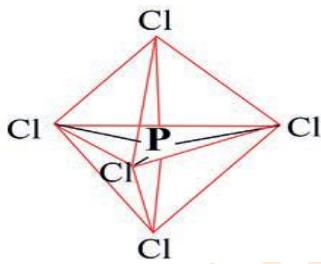


Figure 2.19 (b): Trigonal bipyramidal geometry of PCl₅ molecule

- Note that all the bond angles in trigonal bipyramidal geometry are not equivalent.
- In PCl₅ the five sp³d orbitals of phosphorus overlap with the singly occupied p orbitals of chlorine atoms to form five P-Cl sigma bonds.
- Three P-Cl bonds lie in one plane and make an angle of 120° with each other; these bonds are termed as **equatorial bonds**.
- The remaining two P-Cl bonds—one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called **axial bonds**.
- As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl₅ molecule more reactive.
- ii. Formation of SF₆ (sp³d² hybridization):
 - In SF₆ the central sulphur atom has the ground state outer electronic configuration 3s²3p⁴.
 - In the excited state the available six orbitals i.e., one s, three p and two d orbitals are singly occupied by electrons (Figure 2.20a).

- These orbitals hybridize to form six new sp^3d^2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF_6 .
- These six sp^3d^2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds.
- Thus, SF_6 molecule has a regular octahedral geometry as shown in Figure 2.20b.

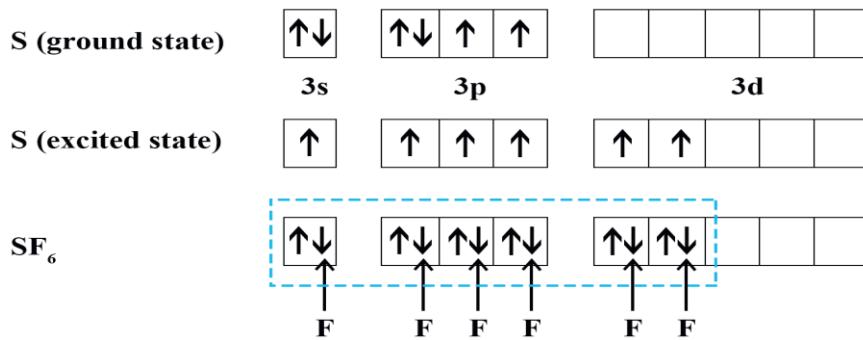


Figure 2.20 (a): sp^3d^2 hybridization

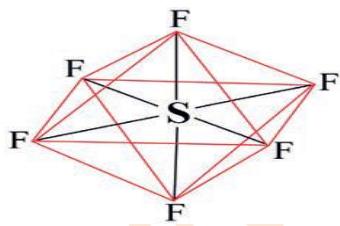


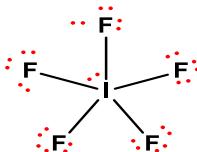
Figure 2.20 (b): Octahedral geometry of SF_6 molecule

- In hybridization schemes, one hybrid orbital is produced for every single atomic orbital involved.
- In a molecule, each of the hybrid orbitals of the central atom acquires an electron pair, either a bond-pair or a lone-pair. And the hybrid orbitals have the same orientation as the electron-set arrangement predicted by VSEPR theory.
- When describing the probable hybridization scheme for a structure, follow the following four steps:
 1. Write a reasonable Lewis structure for the chemical.
 2. Use VSEPR theory to predict the electron-set arrangement of the central atom.
 3. Select the hybridization scheme that corresponds to the VSEPR prediction.
 4. Describe the orbital overlap.

Example 5; Describe a hybridization scheme for the central atom of iodine pentafluoride, IF_5 .

Solution:

- a. The reasonable Lewis structure for IF_5 is



b. VSEPR predicts an octahedral electron-set arrangement for six electron pairs (AB_5E type)

- c. The hybridization scheme corresponding to octahedral electron arrangement is sp^3d^2
 d. The six sp^3d^2 hybrid orbitals are directed to the corners of an octahedron, but one of the orbitals is occupied by a lone pair of electrons.

The resulting molecular shape is that of a square pyramid with bond angles of approximately 90°.

Exercise 2.13

- List the three types of hybrid orbital that may be formed by an atom with only s and p orbitals in its valence shell. Draw the shapes of the hybrid orbitals produced.
- Describe a hybridization scheme for the central atom and molecular geometry of the triiodide ion, I_3^-

Answer to Exercise 2.13

- sp , sp^2 , sp^3 ; linear, trigonal planar, and tetrahedral shapes, respectively.

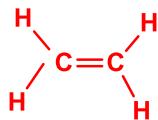


- sp , linear geometry.

Multiple bonds and hybridization

- The hybrid orbital model accounts well for the geometry of molecules involving single covalent bonds.
- Is it also capable of describing molecules containing double and triple bonds?

- We will discuss here the ethene, C_2H_4 , and acetylene, C_2H_2 molecules.
- The Lewis structure of ethene, C_2H_4 , shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



- The three bonding regions form a *trigonal planar* electron-pair geometry.
- Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the $2p$ orbitals and the $2s$ orbital (Figure 2.21).
- These orbitals form the C–H single bonds and the σ bond in the $\text{C} = \text{C}$ double bond (Figure 2.22).
- The π bond in the $\text{C} = \text{C}$ double bond results from the overlap of the third (remaining) $2p$ orbital on each carbon atom that is not involved in hybridization.
- This un-hybridized p orbital (lobes shown in red and blue in Figure 2.22) is perpendicular to the plane of the sp^2 hybrid orbitals.
- Thus, the hybridized $2p$ orbitals overlap in a side-by-side fashion, above and below the inter-nuclear axis and form a π bond.

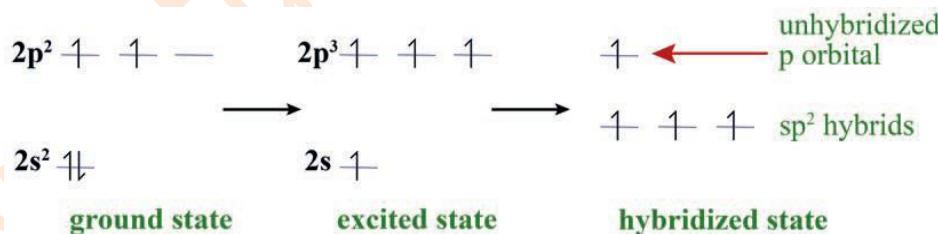


Figure 2.21: sp^2 hybridization of each carbon atom in ethane.

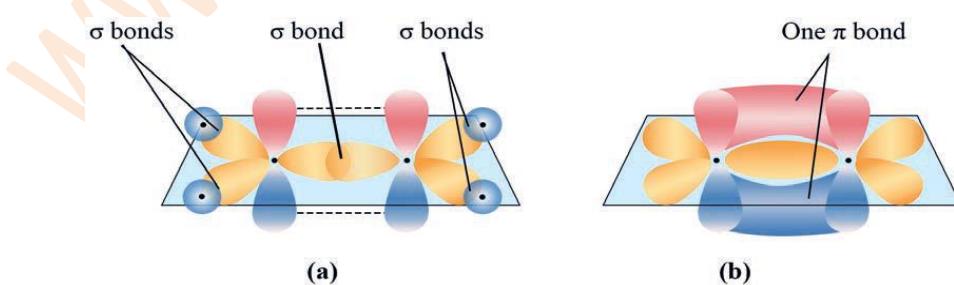


Figure 2.22: Bond formation in the ethene molecule, C_2H_4 : (a) five σ bonds and (b) one π bond

- In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane.
- If the two planes of sp^2 hybrid orbitals tilted relative to each other, the p orbitals would not overlap enough to create the π bond.
- In molecules with sp hybrid orbitals, two un-hybridized p orbitals remain on the atom (Figure 2.23). We find this situation in acetylene, $H-C\equiv C-H$, which is a linear molecule.
- The two linear sp hybrid orbitals of a carbon atom which lie in a straight line, and the two un-hybridized p orbitals at perpendicular angles (Figure 2.23).
- The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms (Figure 2.24).
- The remaining sp orbitals form σ bonds with two hydrogen atoms.
- The two un-hybridized p orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds.
- The two carbon atoms of acetylene are bound together by one σ bond and two π bonds, giving a triple bond.

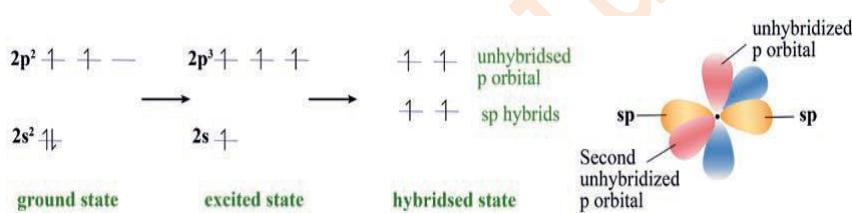


Figure 2.23: sp hybridization of each carbon atom and the two linear sp hybrid orbitals of a carbon atom in acetylene

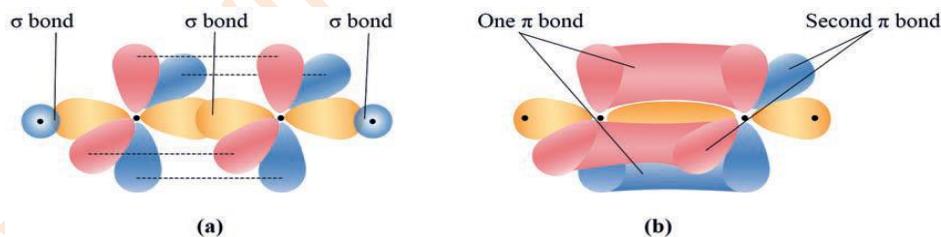


Figure 2.24: (a) The formation of δ bonds in an acetylene molecule, C_2H_2 , and (b) π bonds.

Exercise 2.14

1. Describe the hybridization of the central atoms N and S in molecules and the molecular geometry of:

- a. NO_2 b. SO_3

2. Discuss the bonding in ammonium and sulphate ions: predict the ideal bond angles, bond length, shape of the ions, and the number of σ and π bonds.

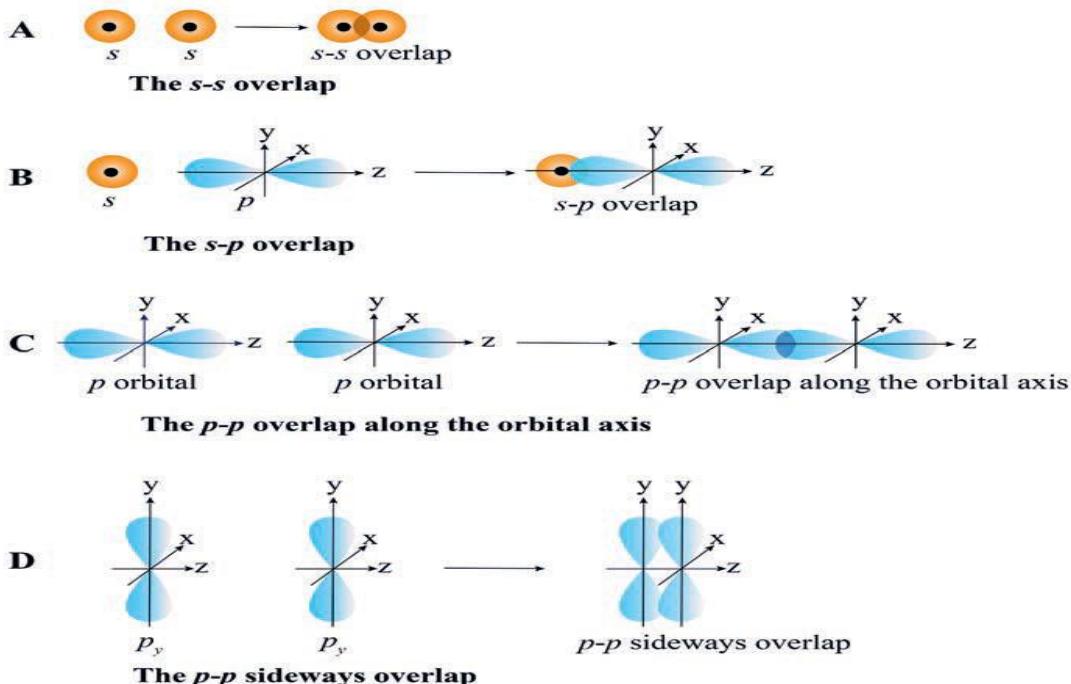
3. Prepare sketches of the overlaps of the following atomic orbitals:

- a. s with s;
- b. s with p along the bond axis;
- c. p with p along the bond axis (head-on overlap);
- d. p with p perpendicular to the bond axis (side-on overlap).

Answer to Exercise 2.14

1. For NO_2 ; sp^2 , bent and for SO_3 sp^2 , trigonal planar

2. Ammonium ion is formed by coordinate covalent interaction between ammonia and hydrogen ion. The bond angle in $\text{H}-\text{N}-\text{H}$ is 109.5° , bond length is about 1.031 \AA , tetrahedral in geometry, four sigma bonds and zero pi bond. In sulphate ion, the bond angle is also 109.5° , bond length is about 149 pm , tetrahedral in geometry, four sigma bonds and zero pi bond.



3.

2.5.2 Molecular Orbital Theory

- The molecular orbital theory assumes that when atoms come together, their orbitals not only overlap, but are also simultaneously transformed into new orbitals.
- These new orbitals, called molecular orbitals (MOs), play the same role for molecules that atomic orbitals play for atoms.

Note that atomic orbitals are the allowed states for an electron moving in the field of one nucleus, whereas molecular orbitals are the allowed states for an electron moving in the field of several nuclei (atoms present in the molecules).

Bonding and Anti-Bonding Molecular Orbitals

In contrast to VB theory, in which one bonding orbital is formed as a result of the interaction of two atomic orbitals, in MO theory two molecular orbitals result from the combination of two atomic orbitals.

In mathematical terms, the two molecular orbitals result from the addition of the atomic orbitals that overlap.

The molecular orbitals that results from the addition of the atomic orbitals that overlap is called a bonding orbital.

In a bonding molecular orbital, because the electron density is concentrated between the two nuclei, the energy of the system is lowered compared with that of isolated atomic orbitals.

The molecular orbital that results from the subtraction of atomic orbitals that overlap is called an anti-bonding molecular orbital.

In anti-bonding molecular orbitals, the electron density is concentrated away from the region between the two nuclei.

That is, anti-bonding molecular orbitals have a region of zero electron density (a node) between the nuclei.

The net effect of having a low electron density between the nuclei is that the two nuclei repel each other.

Therefore, energy of an anti-bonding orbital is increased compared with that of the two isolated atomic orbitals.

When two atomic orbitals overlap end-to-end, they form two σ MOs.

Consider the H_2 molecule, which has two H atoms and therefore two 1s AOs.

The two 1s atomic orbitals combine (Figure 2.25) to produce two σ MOs, which differ in energy and location.

One of the σ MOs is a bonding orbital, denoted $\sigma 1s$, the other is an anti-bonding orbital denoted σ^*1s .

The relative energy levels of these two MOs are different.

The $\sigma 1s$ MO has a lower energy than the original 1s AOs, while the σ^*1s MO has a higher energy.

Electron Configuration of Diatomic Molecules

Electrons occupy molecular orbitals following the same rules that apply to the filling of atomic orbitals: the *aufbau principle* and the *Pauli Exclusion Principle* and *Hund's rule* are obeyed.

The electronic structure of the molecule is obtained by feeding the appropriate number of electrons into the new molecular orbitals.

For example, both electrons in H_2 will go into the lower energy orbital denoted by $(\sigma 1s)^2$.

There are no more electrons in H_2 so the σ^*1s orbital remains empty in the ground state.

A molecular orbital diagram shows the relative energy and number of electrons in each MO, as well as the atomic orbitals from which they form.

Figure 2.25 is the molecular orbital diagram for H_2 .

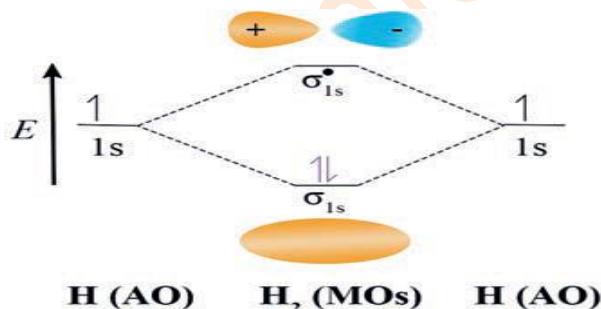


Figure 2.25: Molecular orbital diagram and bonding in the H_2 molecule

- Note: The number of molecular orbitals formed must equal the number of atomic orbitals available for combination.
- Unfilled molecular orbitals are considered to be there, even when there are no electrons in them.
- MO theory uses the term “bond order” to indicate whether a covalent bond is single (bond order = 1), double (bond order = 2) or triple (bond order = 3).
- Bond order is defined as the number of electrons in bonding MOs minus the number in anti-bonding.
- MOs, divided by two:

Bond order = $\frac{1}{2}$ [(number of e- in bonding MOs – number of e- in anti-bonding MOs)]

- Thus, for H₂, the bond order is $\frac{1}{2}$ ($2 - 0$) = 1.
- A bond order greater than zero indicates that the molecule is stable relative to the separate atoms.
- Whereas a bond order of zero implies no net stability.
- In general, the higher the bond order, the stronger the bond.

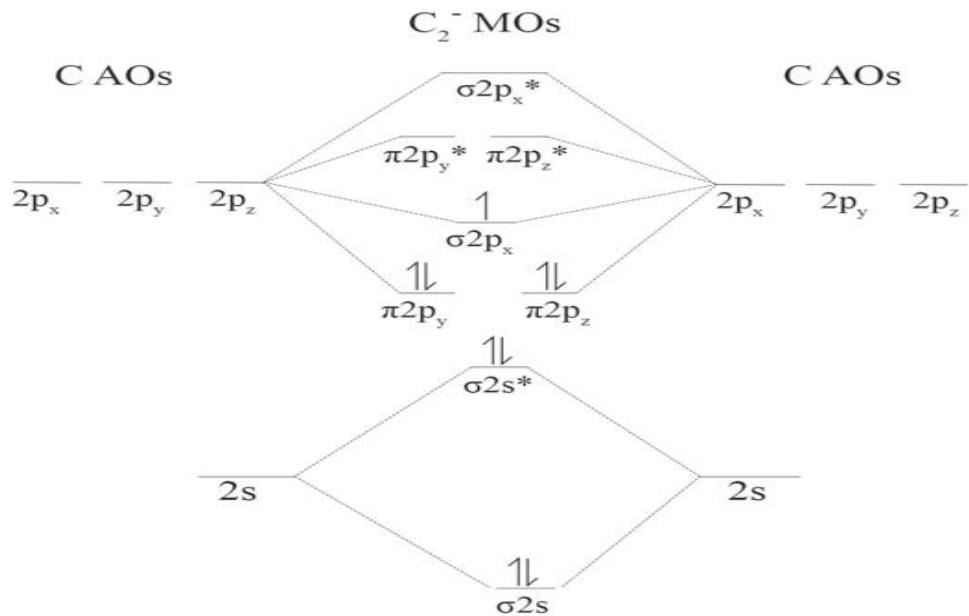
Exercise 2.15

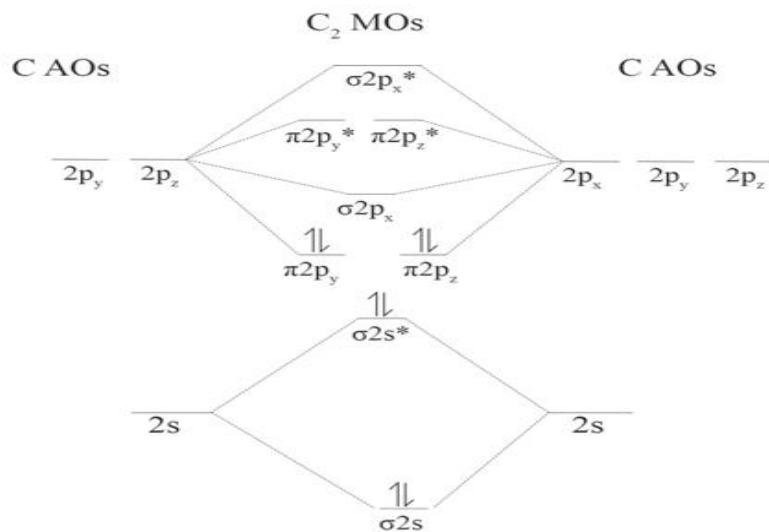
1. Draw molecular orbital energy diagrams for:

- a. C₂⁻ b. C₂ c. C₂⁺

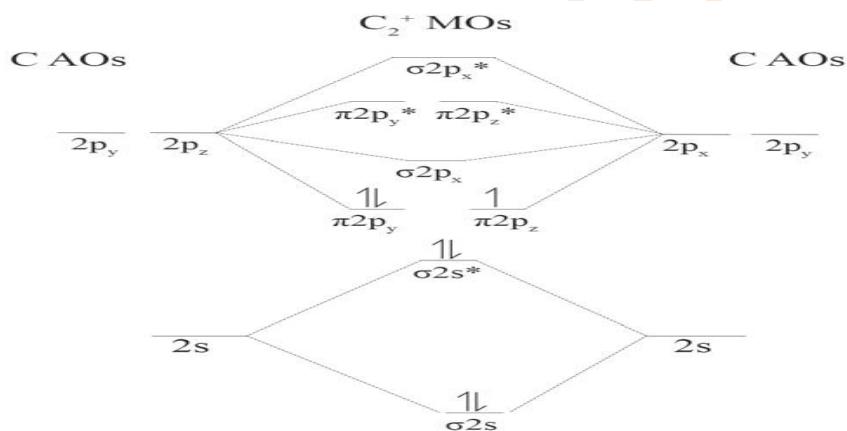
Answer to Exercise 2.15

1. a.





b.



c.

The order of energy of molecular orbitals has been determined mainly from spectroscopic data.

- a. In simple homo-nuclear diatomic molecules (total electrons = 14 or less) the order is:
 $\sigma_{1s} \sigma_{1s}^* \sigma_{2s} \sigma_{2s}^* (\pi_{2py} = \pi_{2pz}) \sigma_{2px} (\pi_{2py}^* = \pi_{2pz}^*) \sigma_{2px}^*$
- b. For simple homo-nuclear diatomic molecules (total electrons greater than 14) the $\pi_{2py} = \pi_{2pz}$ comes after σ_{2px} and the order is:
 $\sigma_{1s} \sigma_{1s}^* \sigma_{2s} \sigma_{2s}^* \sigma_{2px} (\pi_{2py} = \pi_{2pz}) (\pi_{2py}^* = \pi_{2pz}^*) \sigma_{2px}^*$
- Note that the 2py atomic orbital give π bonding and π anti-bonding (π^*) MOs of the same energy as those produced from 2pz orbitals.
- The π_{2py} and π_{2pz} orbitals are said to be double degenerate, and similarly π_{2py}^* and π_{2pz}^* are double degenerate.

- A similar arrangement of MOs exists from σ_{3s} to σ_{3px}^* , but energies are known with less certainty

- **Example 6;** Use the molecular orbital theory to derive the electron configuration of:

a. H_2^+ b. Li_2 c. He_2^+ d. O_2

Which of these molecules or molecular ions exist?

Solution:

a. H_2^+ molecular ion. This may be considered as a combination of H atom and a H^+ ion, giving one electron to be accommodated in a MO.

The bond order is $\frac{1}{2}(1-0) = \frac{1}{2}$, so we predict that H_2^+ does exist. The electron configuration is σ_{1s}^1 .

d. Li_2 molecule. Each Li atom has two electrons in its inner shell, and one in its outer shell, making a total of six electrons arranged: $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2$. We ignore the inner electrons here because, in general, only outer (valence) orbitals interact enough to form molecular orbitals.

The bond order is $\frac{1}{2}(2-0) = 1$, so we predict that Li_2 does exist.

e. He_2^+ Molecular ion. The electron configuration is $(\sigma_{1s})^2 (\sigma_{1s}^*)^1$.

The filled bonding orbital gives stabilization whilst the half-filled gives destabilization.

The bond order is $\frac{1}{2}(2-1) = \frac{1}{2}$, there is some stabilization, so the He_2^+ should exist, and it has been observed spectroscopic ally.

f. O_2 molecule. Each oxygen has eight electrons, making a total of sixteen for the molecule. These are arranged:

$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}^2 = \pi_{2pz}^2) (\pi_{2py}^* \pi_{2pz}^* = 1) \sigma_{2px}^*$$

The anti-bonding orbitals π_{2py}^* and π_{2pz}^* are singly occupied in accordance with Hund's rule.

the inner shell does not participate in bonding and the π_{2py} and π_{2pz} bonding and anti-bonding 2s orbitals cancel each other.

A σ bond results from the filling of $(\sigma_{2px})^2$.

Two half π bonds arise from bonding and anti-bonding.

Therefore, $1\delta + \frac{1}{2\pi} + \frac{1}{2\pi} = 2$ bonds are formed

Exercise 2.16

1. Use the molecular orbital theory and derive the electron configuration of the following molecules. Identify those which exist and those which do not exist.
 - a. He_2 b. Be_2 c. B_2 d. C_2 e. N_2

2. Use the MO theory to predict the bond order and the number of unpaired electrons in O_2^{2-} , O_2^- , O_2^+ , NO and CO.

Answer to Exercise 2.16

1. a. $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$; Does not exist b. $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2$; does not exist
 c. $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 \{ (\pi_{2py})^1 = (\pi_{2pz})^1 \}$; Exist
 d. $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 \{ (\pi_{2py})^2 = (\pi_{2pz})^2 \}$; Exist
 e. $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 \{ (\pi_{2py})^2 = (\pi_{2pz})^2 \}$; Exist

2. Bond order = $\frac{1}{2}$ (number of e^- in bonding MOs – number of e^- in anti-bonding MOs)

a. Number of electrons in O_2^{2-} ion = 18

$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}^2 = \pi_{2pz}^2) (\pi_{2py}^{*2} = \pi_{2pz}^{*2})$$

Nb=10, Na=8

$$B.O = \frac{1}{2}(Nb - Na)$$

$$B.O = \frac{1}{2}(10-8)$$

$$B.O = 1$$

Unpaired electrons = 0 \Rightarrow Diamagnetic

b. Number of electrons in O_2^- ion = 17

$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}^2 = \pi_{2pz}^2) (\pi_{2py}^{*2} = \pi_{2pz}^{*1})$$

Nb=10, Na=7

$$B.O = \frac{1}{2}(Nb - Na)$$

$$B.O = \frac{1}{2}(10-7)$$

$$B.O = 1.5$$

Unpaired electrons = 1 \Rightarrow Paramagnetic

c. Number of electrons in O_2^+ ion = 15

$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}^2 = \pi_{2pz}^2) (\pi_{2py}^{*2} = \pi_{2pz}^{*0})$$

Nb=10, Na=5

$$B.O = \frac{1}{2}(Nb - Na)$$

$$B.O = \frac{1}{2}(10-5)$$

$$B.O = 2.5$$

Unpaired electrons = 1 \Rightarrow Paramagnetic

d. Number of electrons in NO molecule = 15

$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2px})^2 (\pi_{2py}^2 = \pi_{2pz}^2) (\pi_{2py}^{*2} = \pi_{2pz}^{*0})$$

Nb=10, Na=5

$$B.O = \frac{1}{2}(Nb - Na)$$

$$B.O = \frac{1}{2}(10-5)$$

$$B.O = 2.5$$

Unpaired electrons = 1 => Paramagnetic
 e. Number of electrons in CO molecule = 14
 $(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 \{ (\pi_{2p_y})^2 = (\pi_{2p_z})^2 \} (\sigma_{2p_x})^2$

Nb=10, Na=4
 $B.O = \frac{1}{2} (Nb - Na)$
 $B.O = \frac{1}{2} (10-4)$
 $B.O = 3$
 Unpaired electrons = 0 => Diamagnetic

Magnetic Properties

Molecules with unpaired electrons exhibit paramagnetic properties. The species is attracted by an external magnetic field.

When all the electrons are paired, there is diamagnetism. Such species are not attracted (and, in fact, are slightly repelled) by a magnetic field.

The anti-bonding π_{2p_y} and π_{2p_z} orbitals for O₂ are singly occupied in accordance with Hund's rule.

Unpaired electrons give rise to Para magnetism. Since there are two unpaired electrons with parallel spins, this explains why oxygen is paramagnetic.

The MO theory successfully predicts the Para magnetism of O₂, a fact not even thought of with the VB representation of the oxygen molecule (O = O).

Exercise 2.17

What is the bond order for CN⁻, CN and CN⁺?

Which homo-nuclear diatomic molecules from the second period elements, besides O₂, should be paramagnetic?

Answer to Exercise 2.17

1. Bond order = 3 (CN⁻) = 2.5 (CN) = 2 (CN⁺)
2. None is paramagnetic.

2.6 Types of Crystal

Solids can be crystalline or amorphous.

A crystalline solid is composed of one or more crystals. Each crystal has a well-defined, ordered structure in three dimensions.

Sodium chloride (table salt) and sucrose (table sugar) are examples of crystalline substances.

An amorphous solid has a disordered structure; it lacks the well-defined arrangement of basic units (atoms, molecules, or ions) found in a crystal.

A glass is an amorphous solid obtained by cooling a liquid rapidly enough that its basic units are “frozen” in random positions before they can assume an ordered crystalline arrangement.

A structural unit of a crystalline solid has a characteristic repetitive pattern.

The crystalline solids can be classified as ionic, molecular, covalent network or metallic.

Ionic Crystals

Ionic crystals consist of ions held together by ionic bonds.

The structure of an ionic crystal depends on the charges on the cation, anion and on their radii. The properties of ionic solids are direct consequences of the strong interionic forces, which create high lattice energy.

Ionic solids have high melting points, an indication of the strong attraction force holding the ions together.

Molecular Crystals

Molecular solids are made up of discrete molecules that interact via intermolecular forces.

Various combinations of *dipole-dipole*, *dispersion* and *hydrogen-bonding forces* are operative in molecular solids, which accounts for their wide range of physical properties.

Dispersion forces are the principal forces acting in non-polar substances, so melting points generally increase with molar mass.

Among polar molecules, dipole-dipole forces and where ever possible, hydrogen-bonding dominates.

The fundamental unit of a molecular solid is molecules or monatomic elements. Such solids are common among organic compounds and simple inorganic compounds.

Molecular crystals are usually transparent, brittle, and break easily when stressed.

They are usually non-conductors of heat and electricity and usually have low melting points.

Covalent Network Crystals

In this type of crystalline solids, separate particles are not present.

Instead, strong covalent bonds link the atoms together throughout the network of covalent solid.

As a consequence of the strong bonding, all these substances have extremely high melting and boiling points, but their conductivity and hardness depend on the nature of their bonding.

The two common crystalline forms of elemental carbon (graphite and diamond) are examples of network covalent solids.

The most important network covalent solids are the silicates.

In a covalent network solid, the whole crystal is one giant molecule.

The fundamental units are atoms covalently bonded to their neighbors. These crystals are usually hard, non-conductor of heat and electricity, and have high melting points.

Metallic Crystals

The strong metallic bonding forces hold individual atoms together in metallic solids.

Bonding in metals can be explained as a network of positive ions immersed in a sea of electrons. That is, the electrons in the valence shell of the metal atoms are highly delocalized. For this reason, metals are very good conductors of electricity.

Metallic bonding forces are stronger than those arising from intermolecular forces, so metallic solids have higher melting points than molecular solids.

Metals have a wide range of melting points and hardness, which are related to the packing efficiency of the crystal structure and the number of valence electrons available for bonding.

For example, Group IIA metals are harder and higher melting than Group

IA metals, because the IIA metals have closer packed structures and twice as many delocalized valence electrons.

The fundamental units of pure metallic solids are identical metal atoms.

Metallic crystals are opaque with reflective surfaces.

They are ductile and malleable, good conductors of heat and electricity, and they usually have high melting points.

Copper, silver, gold, iron and aluminum are familiar examples of metals.

Exercise 2.18

1. Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:
 - a. SiO₂
 - b. KCl
 - c. Cu
 - d. CO₂
 - e. C (diamond)
2. Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting point	Electrical conductivity	Solubility in water
x	brittle, white	800 °C	only if melted/dissolved	soluble
y	shiny, malleable	1100 °C	high	insoluble
z	hard, colorless	3550 °C	none	insoluble

Answers to Exercise 2.18

1. a. network covalent b. ionic C. metallic d. molecular e. network covalent
2. X = Ionic; Y = metallic; Z = Covalent network

UNIT SUMMARY

- Lewis electron-dot formulas are simple representations of the valence-shell electrons of atoms in molecules and ions.
- An ionic bond is a strong attractive force holding ions together. An ionic bond can form between two atoms by the transfer of electrons from the valence shell of one atom to the valence shell of the other.
- A covalent bond is a strong attractive force that holds two atoms together by their sharing of electrons. These bonding electrons are attracted simultaneously to both atomic nuclei, and they spend part of the time near one atom and part of the time near the other.
- In some cases of covalent bonding, one atom appears to provide both electrons in the bonding pair; the bond is known as coordinate-covalent bond or dative bond.
- Molecular geometry refers to the spatial arrangement of atoms in a molecule.
- The valence-shell electron-pair repulsion (VSEPR) model is a simple model for predicting molecular geometries.
- In the valence bond method (VB) a covalent bond is viewed as the overlap of atomic orbitals of the bonded atoms in a region between the atomic nuclei.
- In the VB theory, hybridized atomic orbitals are formed by the combination and rearrangement of orbitals of the same atom.

- Hybridized orbitals are all of equal energy and electron density, and the number of hybridized orbitals is equal to the number of pure atomic orbitals that combine.
- Molecular orbital theory describes bonding in terms of the combination and rearrangement of atomic orbitals to form orbitals that are associated with the molecule as a whole.
- Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than individual atomic orbitals. Anti-bonding molecular orbitals have a region of zero electron density between the nuclei, and an energy level higher than that of the individual atomic orbitals.

REVIEW EXERCISE

Part I: Multiple Choice Questions:

- I. Choose the correct answer from the given alternatives
 1. Which of the following is not a property of ionic bonds?
 - a. loss of electrons
 - b. gain of electrons
 - c. sharing of electrons
 - d. transferring of electrons
 2. Which one of the following does not comply with the octet rule?
 - a. PCl₃
 - b. CBr₄
 - c. NF₃
 - d. AsF₅
 3. A π (pi) bond is the result of the:
 - a. overlap of two s orbitals
 - b. overlap of an s and a p orbital
 - c. overlap of two p orbitals along their axes
 - d. sidewise overlap of two parallel p orbitals
 4. The maximum number of hydrogen bonds that a molecule of water can have is:
 - a. 1
 - b. 2
 - c. 3
 - d. 4
 5. Which of the following is planar?
 - a. NO₃⁻
 - b. H₃O⁺
 - c. SO₃²⁻
 - d. PF₃
 6. Among the following mixtures dipole-dipole as the major interaction is present in:
 - a. benzene and ethanol
 - b. acetonitrile and acetone
 - c. KCl and water
 - d. benzene and carbon tetrachloride
 7. The main axis of a diatomic molecule is Z. Atomic orbitals px and py overlap to form which of the following orbital?
 - a. π -molecular orbital
 - b. σ -molecular orbital
 - c. δ -molecular orbital

- d. no bond will form
8. The structure of IF_7 is:
- pentagonal bipyramidal
 - square pyramid
 - trigonal bipyramidal
 - octahedral
9. In which of the following molecule is a co-ordinate covalent bond present?
- F_2
 - O_3
 - NH_3
 - CCl_4
10. In which of the following compounds are 8 valence electrons present in every atom?
- IF_7
 - C_2H_4
 - SiF_4
 - KH
11. Molecules are held together in a crystal by:
- hydrogen bonds
 - electrostatic attraction
 - Van der Waal's attraction
 - dipole-dipole attraction
12. Find the molecule with the maximum dipole moment:
- CH_4
 - NH_3
 - CO_2
 - NF_3
13. Which of the molecules does not have a permanent dipole moment?
- SO_3
 - SO_2
 - H_2S
 - CS_2
14. The F-S-F bond angles in SF_6 are _____.
- $109^\circ 28'$
 - 120° only
 - 90° and 120°
 - 90° and 180°
15. A neutral molecule having the general formula AB_3 has two unshared pair of electrons on A. What is the hybridization of A?
- sp
 - sp²
 - sp³
 - sp^{3d}

Part II: Answer the following questions

16. Write Lewis dot symbols for the following atoms and ions: Mg, Na, B, N, Br, Be, Li^+ , Cl^- , O^{2-} , Mg^{2+} and N^{3-}
17. List four major difference between sigma (σ) and pi (π) bonds.
18. Which one is stronger: σ -bond or π -bond? Why?
19. Explain why a BeH_2 molecule has a zero dipole moment although the Be-H bonds are polar?
20. How can one non-polar molecule induce a dipole in a nearby non polar molecule?
21. Describe the change in hybridization of an aluminum atom (if any) during the reaction:
- $$\text{AlCl}_3 + \text{Cl}^- \rightarrow \text{AlCl}_4^-$$
22. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H atoms at the corners of the square and C atom at its center. Explain why CH_4 is not square planar?

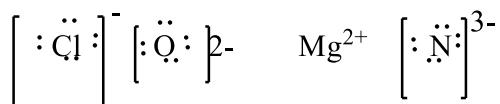
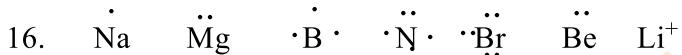
23. Sketch the bond moments and resultant dipole moments in the following molecules: H₂O, PCl₃, NH₃, NF₃
24. Write the resonance structures for SO₂, NO₂ and NO₃⁻. S

Answer to Review Exercise

Part I: Multiple choice item

1. C 2. D 3. D 4. D 5. A 6. B 7. D 8. A
 9. B 10. C 11. C 12. B 13. D 14. D 15. D

Part II: Short answer item



17. Basic difference Between Pi and Sigma Bonds

S. No	Sigma Bond	Pi Bond
1	Covalent bond which is formed by the head on overlapping of the half-filled atomic orbitals.	Covalent bond which is formed by lateral overlapping of the half-filled atomic orbitals.
2	It is a strong covalent bond.	It is a weak covalent bond.
3	It is less reactive.	It is highly reactive.
4	In sigma bonds, overlapping orbitals can be pure orbitals, hybrid orbitals and one hybrid and one pure orbital.	In pi bond, overlapping orbitals are always pure orbitals only. Pure orbitals are un-hybridized orbitals.
5	It can exist independently. Example-alkane.	It can exist with a sigma bond only.Example- alkene and alkyne
6	The electron cloud is symmetrical to the line joining the nuclei of the two atoms.	The electron cloud lies above and below the plane of the line joining the two atoms.

- | | | |
|---|--|---|
| 7 | It allows free rotation of atoms. | It restricts free rotation of atoms. |
| 8 | It is also called localized bond. | |
| 9 | It determines the shape of the molecule. | It doesn't determine the shape of the molecule. |

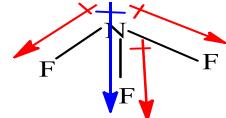
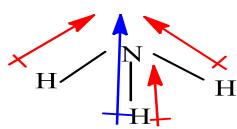
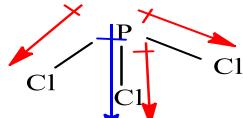
18. In a sigma bond, the electrons are in orbitals between the nuclei of the bonding atoms (in the plane of electron density), where electron density is greatest. The end-to-end axial overlap of electrons attracts the nuclei to form a strong bond. In a pi bond, the p -orbitals overlap side-to-side above and below the nuclei (equatorial plane), so this attraction is more of a “sideways” pull as opposed to a direct line of pulling. Additionally, the electron density is spread out over a greater area. Thus, sigma bonds are stronger than pi bonds.

19. Although the Be–H bonds are polar having the same dipole moment, but due to the linear structure of BeH_2 , the bond dipoles of the two Be–H bonds cancel each other. Therefore, the resultant dipole moment of BeH_2 molecule is zero.

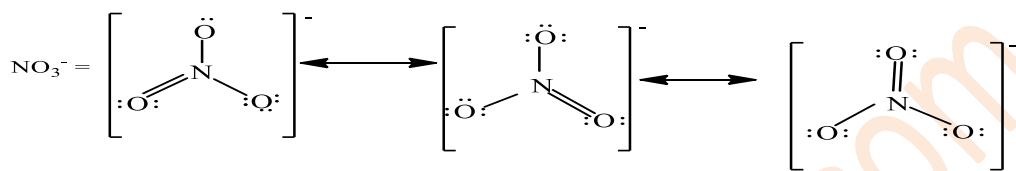
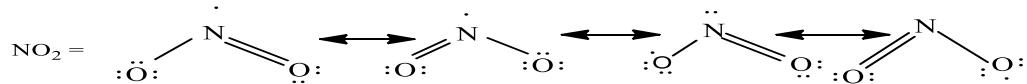
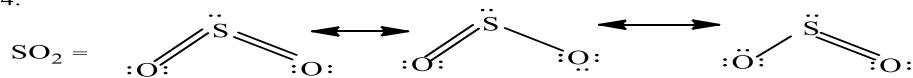
20. It arises from temporary variations in electron density in atoms and molecules. At any instant, the electron distribution may be unsymmetrical and hence produce an instantaneous dipole. This can cause an induced transient dipole in the neighboring molecule and cause the molecules to be attracted.

21. The hybridization of aluminum atom in AlCl_3 is sp^2 whereas in AlCl_4^- , the hybridization of aluminum is sp^3 .

22. According to VESPR theory, if CH_4 were square planar, the bond angle would be 90° . For tetrahedral structure, the bond angle is 109.5° . Therefore, in square planar structure, repulsion between bond pairs would be more and thus the stability will be less.



24.



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UNIT 3

PHYSICAL STATES OF MATTER

3.1 INTRODUCTION

- Matter is defined as anything occupying space and having mass, which is the material of the Universe. It exists in three common states: gas, liquid and solid. For example, the water that we use in our daily life can exist in three physical states of matter.
- The three physical states of water are:
 - Steam (water vapor): gaseous state of water
 - Water: liquid state of water
 - Ice: solid state of water.
- Most solids change to liquids and most liquids change to gases as they are heated.
- Liquids and gases are known as fluids because they flow freely.
- Solids and liquids are referred to as condensed states because they have much higher densities than gases.
- In our everyday life, we experience changes in the state of matter. That is, ice melts and water freezes; water boils and steam condenses.
- Generally, the physical states of matter can be changed to solids, liquids, gases, or plasma by varying temperature and/or pressure.

Solid

- A solid is rigid; it has a fixed volume and a fixed shape. Solids cannot be compressed.
- Solids have higher densities than liquids because their particles are usually packed closer than those in liquids.
- The tightly packed particles of solids are also highly organized.
- The particles of a solid, whether they are atoms, ions or molecules, only vibrate at a fixed point with respect to the neighboring particles. As a result, its particles stay in a fixed position.
- Metals, chalk, sand, soil, and stone are examples of solids.

Liquid

- A liquid has a definite volume, but does not have a definite shape. It takes the shape of its container.
- It is very slightly compressible and has the ability to flow.
- In a liquid, particles vibrate about a point, and constantly shift their positions.
- Water, ethanol, mercury, bromine, and oil are examples of liquids.

Gas

- A gas has neither definite volume nor definite shape; it takes on the shape and volume of its container.
- Gas is highly compressible because most of the volume of a gas is composed of the large amounts of empty space between the gas particles.
- For example, air, hydrogen, oxygen, carbon dioxide, and nitrogen are gases.

Plasma

- Plasma is the fourth physical state of matter that exists at a high temperature (million degrees Celsius).
- At such high temperatures molecules cannot exist.
- Most or all of the atoms are stripped of their electrons and thus, exist in their ionized form.
- This state of matter, a gaseous mixture of positive ions and electrons, is called plasma.
- In another word, plasma is an ionized gas. Because of the extreme temperatures needed for fusion, no material can exist in the plasma state. Like gases, plasmas have no fixed shape and a fixed volume.
- They are also less dense than solids or liquids.
- A particle diagram of a solid, liquid, gas and plasma is given in figure 3.1

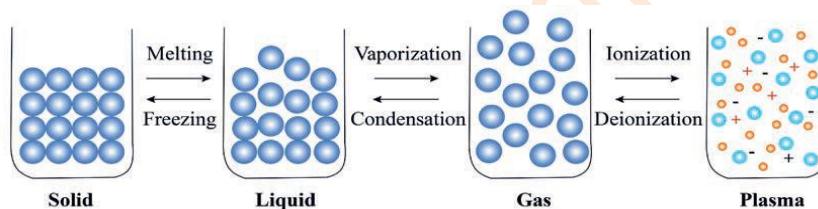


Figure 3.1 A particle diagram of a solid, liquid, gas and plasma

Exercise 3.1

1. Can nitrogen and oxygen exist as liquids and solids?
2. Compare and contrast the three states of matter: gas, liquid and solid.
3. How is plasma different from gas?

Answer to Exercise 3.1

1. Nitrogen and oxygen can exist as liquid and solid at very low temperatures and high pressures.

2. Let students hold discussions in groups about the three states of matter in terms of space between their particles, distance between them, volume and shape, and compressibility and density.
3. Plasma is different from gas, because it is made up of groups of positively and negatively charged particles. For example, in neon gas, its electrons are all bound to the nucleus. But in a neon plasma, its electrons are free to move around the system.

3.2 Kinetic theory and properties of matter

3.2.1 The kinetic theory of matter

- The three states of matter in which substances are chemically the same but physically different are explained by the kinetic theory of matter.
- The kinetic theory of matter gives an explanation on the nature of the motion and the heat energy.
- According to the kinetic theory of matter, every substance consists of a very large number of very small particles called ions, atoms and molecules.
- The particles are in a state of continuous and random motion with all possible velocities.
- The motion of the particles increases with a rise in temperature.
- Generally, the kinetic theory of matter is based on the following assumptions:
 1. All matter is composed of particles that are constantly moving.
 2. All particles have kinetic energy (movement energy) and potential energy.Molecules in the solid phase have the least amount of energy, while gas particles have the greatest amount of energy.
- 3. The difference between the three states of matter is the energy contents they have and the motion of the particles. A change in phase may occur when the energy of the particles is changed.
- 4. The temperature of a substance is a measure of the average kinetic energy of the particles.
- 5. There are spaces between particles of matter. The average amount of empty space between molecules gets progressively larger as a sample of matter moves from the solid to the liquid and gas phases.
- 6. There are attractive forces between atoms/molecules, and these become stronger as the particles move closer together. These attractive forces are called intermolecular forces.

3.2.2 Properties of matter

- The properties of solid, liquid, and gas three states of matter are explained in terms of the kinetic theory as follows:

Properties of Gases

- From the kinetic molecular theory of gases, the following general properties of gases can be summarized.
1. Gases have no fixed shape and fixed volume. They assume the volume and shape of their containers.
 2. Gases can be easily compressed. By applying pressure to the walls of a flexible container, gases can be compressed; the compression results in a decrease of its volume. This happens due to the large spaces between the particles of gases.
 3. Gases have low densities compared to liquids and solids. Because the particles of a gas are very far apart each other and the number of molecules per unit volume is very small. A small mass of a gas occupies a large volume and hence results in a very low density.
 4. Gases exert pressure in all directions. Gases that are confined in a container exert pressure on the walls of their container. This pressure is due to collisions between gas molecules and the walls of the container.
 5. Gases easily flow and diffuse through one another. A gas moves freely and randomly throughout a given space.

Properties of Liquids

- Liquids have the following properties:
1. Liquids have a definite volume, but have no definite shape. They assume the shapes of their container. Lack of a definite shape for liquid substances arises from low intermolecular forces of attraction between their particles as compared to that of solids.
 2. Liquids have higher densities than gases. Their density is a result of the close arrangement of liquid particles. Thus, the particles are closer in liquid than in their gaseous state. This accounts for the higher densities of liquids as compared to gases.
 3. Liquids are slightly compressible. The available free space between particles in liquids is very little as a result; liquids resist an applied external force.
 4. Liquids are fluids. A fluid is a substance that can easily flow. Most liquids naturally flow downwards due to gravitational force. But, the fluidity of liquids is much slower than gases.

Properties of Solids

Solids have the following properties:

1. Solids have a definite shape and definite volume, due to the presence of the strong force of attraction between the particles in a solid.
2. Solids generally have higher densities than gases and liquids. The particles of solids are very close to each other, and thus, there is almost no free space between the particles of solids. This closeness of particles makes solids to have more particles (mass) per unit volume.

3. Solids are extremely difficult to compress because the high inter-particle forces of attraction between the particles of solids are very strong due to a very short distance between them.
4. Solids are not fluids. Solids normally do not flow because particles of solids are rigidly held in position by strong forces that restrict them.

Exercise 3.2

Arrange the three states of matter in terms of their increasing:

- a. intermolecular force c. compressibility
- b. density d. kinetic energy.

Answer to Exercise 3.2

- a. Gas < Liquid < Solid.
- b. Gas < Liquid < Solid.
- c. Solid < Liquid < Gas.
- d. Solid < Liquid < Gas.

3.3 The Gaseous state

3.3.1 The Kinetic Molecular Theory of Gases

- The kinetic molecular theory is a simple model for understanding the behavior of gases. This model predicts the correct behavior for most gases under many conditions. Like other models, the kinetic molecular theory is not perfect.
- Assumptions of the kinetic molecular theory of gases:

1. A gas is a collection of particles (molecules) in constant, straight-line motion.
2. Gas particles do not attract or repel each other, they do not interact. The particles collide with each other and with the surfaces around them, but they bounce back from these collisions like pool balls.
3. There is a lot of space between gas particles compared with the size of the particles themselves. In other word, the volume of the particles is negligible compared to the total volume of the gas. The molecules are so far apart, the total volume of the molecules is extremely small compared with the total volume of the gas. This assumption explains why gases are so easily compressed and why they can mix so readily.

experiments, Robert Boyle concluded that, at constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.

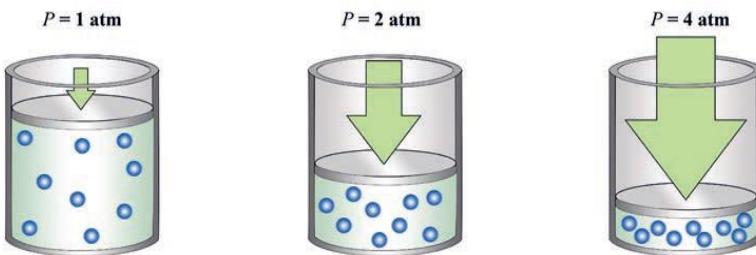


Figure 3.2 the relation between Pressure and Volume

- Boyle studied the relationship between the pressure of the trapped gas and its volume.
- He discovered that at constant temperature doubling the pressure on a sample of gas reduces its volume by one-half, and tripling the gas pressure reduces its volume to one-third of the original. Generally, the volume of a gas decreases, as the pressure on the gas increases.

Table 3.1: Pressure and volume data for a gas at constant mass and temperature

Pressure atm	Volume mL	PV
0.5	1200	600
1.0	600	600
2.0	300	600
3.0	200	600
4.0	150	600
5.0	120	600
6.0	100	600

Generally, Boyle's law states that the volume of a fixed mass of gas is inversely proportional to the pressure at a constant temperature.

Mathematically this is written as:

$$V \propto \frac{1}{P}$$

$$v = k \left(\frac{1}{P} \right) \text{ or } PV = K \dots \dots \dots \dots \dots \dots 3.5$$

Where, k is constant at a specific temperature for a given sample of gas.

- This relationship is true because if the pressure increases, the volume decreases, but the product PV is always equal to the same constant.
- Thus for two different sets of conditions, we can say:
- $P_1 V_1 = k = P_2 V_2 \dots \dots \dots \dots \dots \dots \quad (3.6)$
- $P_1 V_1 = P_2 V_2 \dots \dots \dots \dots \dots \dots \quad (3.7)$
- Where P_1 and V_1 are the initial pressure and volume of the gas, and P_2 and V_2 are the final volume and pressure.
- **Example 1,** Sulfur dioxide (SO_2), that forms acid rain, is found in the exhaust of petrol and diesel vehicles, and power plants. Consider a 1.5 L sample of gaseous SO_2 at a pressure of 5.6 kPa. If the pressure is changed to 15.0 kPa at a constant temperature, what will be the new volume of the gas?

Solution:

We are given: Initial conditions: $P_1 = 5.6 \text{ kPa atm}$ and $V_1 = 1.5 \text{ L}$

Final conditions: $P_2 = 150.0 \text{ kPa}$ and $V_2 = ?$

Use Boyle's law equation: $P_1 V_1 = P_2 V_2$

$$\begin{aligned}\text{Thus, } v_2 &= \frac{P_1 V_1}{P_2} \\ &= \frac{5.6 \text{ kPa} \times 1.5 \text{ L}}{150 \text{ kPa}} = 0.56 \text{ L}\end{aligned}$$

Exercise 3.4

1. A certain gas occupies a volume of 10.0 m^3 at a pressure of 100.0 kPa.

If its volume is increased to 20 m^3 , what would be the new pressure of the gas assuming temperature remains constant?

2. A cylinder equipped with a moveable piston has an applied pressure of 4.0 atm and a volume of 6.0 L. What is the volume of the cylinder if the applied pressure is decreased to 1.0 atm?

Answer to Exercise 3.4

1. 200 kpa

2. $0.75 \text{ L} = 750 \text{ mL}$

ii. Charles' Law

- Jacques Charles (a French physicist), who was the first person to fill a balloon with hydrogen gas and who made the first balloon flight.

- Mathematically:

$$V \propto T$$

- $K = \frac{P}{T}$ 3.10

- The ratio P to T for any set of volume-temperature values always equals the same k .

- $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ 3.11

- **Example 3,** At a temperature of 25°C, the pressure of the gas in a deodorant can is 3 atm. Calculate the pressure of the gas when it is heated to 845°C

- **Solution:**

Given: Initial conditions: $T_1 = 25^\circ\text{C} = 25 + 273 = 298 \text{ K}$, $P_1 = 3.0 \text{ L}$

Final conditions: $T_2 = 845^\circ\text{C} = 1,118 \text{ K}$, $P_2 = ?$

By rearranging, Equation 3.11, P_2 can be calculated:

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{3.0 \text{ atm} \times 1118 \text{ K}}{298 \text{ K}} = 11.23 \text{ atm}$$

Exercise 3.6

1. The pressure of a gas in a cylinder when heated to a temperature of 250 K is 1.5 atm. What is the initial temperature of the gas if its initial pressure was 1.0 atm?
2. List some examples of items that we use in our everyday life that obey Gay-Lussac's Law.

Answer to Exercise 3.6

1. Initial conditions: $T_1 = ?$, $P_1 = 1 \text{ atm}$

Final conditions: $T_2 = 250 \text{ K}$, $p_2 = 1.5 \text{ atm}$

$$T_1 = \frac{T_2 P_1}{P_2} = \frac{250 \text{ K} \cdot 1 \text{ atm}}{1.5 \text{ atm}} = 166.67 \text{ K}$$

a. Tire pressure: Automobile tire pressure drops on a cold day and rises on a hot day. If you put too much air in your tires when they are cold, they could over-pressurize when they heat up. Similarly, if your tires read the proper pressure when they are hot, they will be underinflated when it's cold.

b. Pressure cooker: Applying heat to a pressure cooker increases the pressure inside the device. Increasing pressure raises the boiling point of water, shortening cooking times. Because the container is sealed, flavors aren't lost to the air with steam.

c. Aerosol can: The reason you shouldn't store aerosol cans under hot conditions or dispose of them by burning is because heating the can increases the pressure of its contents, potentially causing the can to burst.

d. Water heater: An electric water heater is a lot like a pressure cooker.

A pressure-relief valve prevents steam from accumulating. If the valve malfunctions, heat drives up the steam pressure inside the heater, eventually bursting it.

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

In this case we have

$$n_1 = 0.5 \text{ mol} \quad n_2 = 0.33 \text{ mol} \quad V_1 = 12.2 \text{ L} \quad V_2 = ?$$

$$\text{Thus, } V_2 = \frac{V_1 n_2}{n_1} = \frac{12.2 \text{ L} \times 0.33 \text{ mol}}{0.5 \text{ mol}} = 8.052 \text{ L} = 8.0 \text{ L}$$

Exercise 3.8

One mole of a gas occupies 27.0 L, and its density is 1.41 g/L at a particular temperature and pressure. What is its molecular weight? What is the density of the gas at STP?

Answer to Exercise 3.8

i. Molecular weight of a gas = density (g/L) $\times \frac{\text{Volume(L)}}{\text{mole}}$
 $= 1.41 \text{ g/L} \times \frac{27 \text{ L}}{\text{mole}} = 38.07 \text{ g/mol}$

ii. At STP, 1 mol of the gas, 38.07 g, would occupy 22.4 L, and its density would be
Density (d) of the gas at STP = $\frac{38.07 \text{ g}}{22.4 \text{ L}} = 1.70 \frac{\text{g}}{\text{L}}$

vi. The Ideal Gas Equation

- An ideal gas is a hypothetical gas that obeys the gas laws.
- Real gases only obey the ideal gas laws closely at high temperature and low pressure.
- Under these conditions, their particles are very far apart. The ideal gas law is a combination of Boyle's law, Charles' law and Avogadro's law.
- We have considered the gas laws that describe the behavior of gases as revealed by experimental observations:
- Boyle's law: $V \propto P$ (at constant T and n)
- Charles' law: $V \propto T$ (at constant P and n)
- Avogadro's law: $V \propto n$ (at constant P and T)
- This relationship indicates how the volume of gas depends on pressure, temperature and number of moles.
- $V \propto n \frac{T}{P}$
- $V = Rn \frac{T}{P}$ 3.16
- Where R, is proportionality constant called the gas constant. By rearranging Equation 3.16, we obtain the ideal gas equation:
- $VP = nRT$ (3.17)
- Thus, the ideal gas equation describes the relationship of the four variables P, V, T and n.
- An ideal gas is a gas whose pressure, volume and temperature behavior can be completely explained by the ideal gas equation.

- At STP ($n = 1 \text{ mol}$, $V = 22.4 \text{ L}$, $T = 273 \text{ K}$ (0°C) and $P = 1 \text{ atm}$), the values of R can be calculated from the ideal gas equation:
- $R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}} = 0.082 \text{ atm.L/mol.K}$

Example 6, What pressure, in atm, is exerted by 54.0 g of Xe in a 1.00 L flask at 20.0°C ? (Molar mass of Xe = 131.3 g/mol)

Solution: By rearranging Equation 3.16

$$V = Rn \frac{T}{P}$$

But $n = m/M$, Where m is given mass and M is molar mass of a substance Thus,

$$P = R \frac{mT}{MV}$$

$$P = 0.082 \text{ atm.L/mol.K} \times \frac{54 \text{ g} \times 193 \text{ K}}{131.3 \text{ g/mol} \times 1 \text{ L}} = 9.88 \text{ atm}$$

Exercise 3.9

1. The density of a gas at a pressure of 1.34 atm and a temperature of 303 is found to be 1.77 g/L. What is the molar mass of this gas?
2. A helium-filled weather balloon has a volume of 7240 ft³. How many grams of helium would be required to inflate this balloon to a pressure of 745 torr at 21°C ? (1 ft³ = 28.3 L)

Answer to Exercise 3.9

1. Given: $P = 1.34 \text{ atm}$, $T = 303 \text{ K}$, $d = 1.77 \text{ g/L}$, $R = 0.082 \text{ atm.L/mol.K}$, M ?

$$M = R \frac{mT}{VP} \text{ but, } \frac{m}{V} = d \\ = 0.082 \text{ atm.L/mol.K} \times \frac{1.77 \text{ g} \times 303 \text{ K}}{1.34 \text{ atm}} = 32.82 \text{ g/mol}$$

2. Given: $P = 745 \text{ torr} = 0.98 \text{ atm}$, $T = 21^\circ\text{C} = 294 \text{ K}$, $V = 7240 \text{ ft}^3 = 204,892 \text{ L}$

$R = 0.082 \text{ atm.L/mol.K}$, Molar mass of He = 4 g/mol, m ?

$$n = \frac{PV}{RT} = \frac{0.98 \text{ atm} \times 204,892 \text{ L}}{0.082 \text{ atm.L/mol.K} \times 294 \text{ K}} = 8,328.9 \text{ mol} = 8.33 \times 10^3 \text{ mol}$$

$$\text{Mass (m) of He} = 8.33 \times 10^3 \text{ mol} \times 4 \text{ g/mol} = 33.32 \times 10^3 \text{ g} = 3.33 \times 10^3 \text{ g}$$

vii. Graham's Law of Diffusion

- Gas molecules are in constant, rapid, random motion and occupy quickly throughout any container. This spreading of gas molecules throughout the container is called **diffusion**.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

This means, rate of diffusion of O₂ is 1.17 times that of CO₂.

Exercise 3.10

1. A sample of ethane, C₂H₆, diffuses at a rate of 3.6×10^{-6} mol/h. An unknown gas, under the same conditions, diffuses at a rate of 1.3×10^{-6} mol/hr. Calculate the molar mass of the unknown gas.
2. Which gas in each of the following pairs diffuses more rapidly, and what are the relative rates of diffusion?
 - a. Kr and O₂
 - b. N₂ and acetylene (C₂H₂)

Answer to Exercise 3.10

1. Given: $r_{C_2H_6} = 3.6 \times 10^{-6}$ mol/hr, $M_{C_2H_6} = 30$ g/mol, $r_{un} = 1.3 \times 10^{-6}$ mol/hr, $M_{un} = ?$
 $\frac{r_{C_2H_6}}{r_{un}} = \sqrt{\frac{M_{un}}{M_{C_2H_6}}}$ By rearranging this equation, M_{un} will be
 $M_{un} = \left(\frac{r_{C_2H_6}}{r_{un}}\right) \times M_{C_2H_6} = \frac{3.6 \times 10^{-6} \text{ mol/hr}}{1.3 \times 10^{-6} \text{ mol/hr}} \times 30 \text{ g/mol} = 230.1 \text{ g/mol}$

2. a. Kr (M = 84 g/mol) & O₂ (M = 32 g/mol): oxygen diffuses faster than Kr. The rate of diffusion of O₂ is 1.62 times rate of diffusion of Kr (i.e., $r_{O_2} = 1.62 r_{Kr}$)

- b. N₂ (M = 28 g/mol) and C₂H₂ (26 g/mol): Both of them have almost equal rate of diffusion since they have nearly equal molecular mass.

3.4 The Liquid State

- As in a gas, particles in a liquid are in constant motion. However, the particles in a liquid are closer together than those in a gas.
- The attractive forces between particles in a liquid are stronger than between particles of a gas. This attraction between liquid particles is caused by the intermolecular forces of attraction such as dipole-dipole forces, London dispersion forces, and hydrogen bonding.
- Liquids are more ordered than gases because of the stronger intermolecular forces and the lower mobility of liquid particles.

3.4.1 Energy Changes in Liquids

- The process by which a liquid changes to a gas is known as vaporization or evaporation.
- **Evaporation** is the process by which molecules on the surface of a liquid break away and go into the gas phase (figure 3.4).
- Molecules on the surface of a liquid are held less tightly than those in the interior, so the most energetic molecule can break away into the gas.

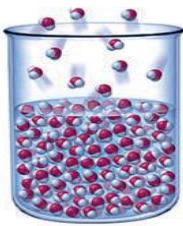


Figure 3.4 Evaporation of Liquid

- Evaporation is explained in terms of the energy that the molecules on the surface of the liquid have.
- **In an open container**, evaporation continues until all of the liquid enters the gas (vapor) phase (Figure 3.4).
- Most of the molecules that escape into the vapor phase do *not* collide with the surface of the liquid and return to the liquid phase.
- Instead, they will diffuse through the gas phase away from the container and equilibrium cannot be established. Under these conditions, the liquid will continue to evaporate until it has disappeared.
- However, **liquids in a closed container** behave differently. The volume of the liquid decreases for some time, and then, remains unchanged. This is because in closed containers, the vapor cannot escape.
- As more molecules leave the liquid, more gaseous molecules collide with the container walls, with each other, and with the liquid surface and return to the original liquid state.
- The process of when a vapor returns to the liquid state is called **condensation**.
- Evaporation and condensation are opposing processes.
- Evaporation is a liquid turning into a gas, and condensation is a gas turning into a liquid.
- For instance, when liquid water is initially put into a closed container, more evaporation happens than condensation because there are so few gaseous water molecules in the space above the water (Figure 3.4a). However, as the number of gaseous water molecules increases, the rate of condensation also increases (Figure 3.4b). At the point where the

rates of condensation and evaporation become equal (Figure 3.4c), dynamic equilibrium is reached and the number of gaseous water molecules above the liquid remains constant.

- **The vapor pressure** of a liquid is the partial pressure of its vapor in dynamic equilibrium with its liquid.

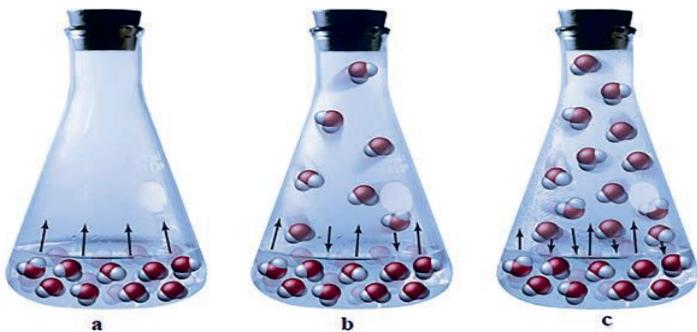


Figure 3.4 Evaporation and condensation (a) when water first put in to a closed container , water molecules begin to evaporate (b) Evaporation continues, but condensation also begins to occur ; and (c) Dynamic equilibrium : the rate of evaporation equals the rate of condensation



The rate of evaporation of a liquid can be affected by these factors:

- Temperature
- intermolecular forces and
- Surface area of the liquid.

Temperature

- An increase in temperature increases the average kinetic energy of the molecules and thus increases the tendency to change into the gaseous state.
- Some liquids evaporate readily at room temperature. Such liquids are said to be **volatile**.
- Volatile liquids have relatively weak forces of attraction between particles. Liquids such as formaldehyde, ethyl alcohol, mercury, and benzene are volatile liquids.
- Liquids that do not vaporize easily at a given temperature are said to be **nonvolatile**. They have relatively stronger attractive forces between their

molecules. Liquids such as motor oil, edible oil, glycerin, water, and molten ionic compounds are nonvolatile.

Vapor pressure

- The partial pressure of the vapor above a liquid is called **vapor pressure**.
- The vapor pressure of a liquid depends up on the temperature. At a given temperature, vapor pressure is constant. The vapor pressures of liquids always increase as temperature increases because the rate of evaporation increases with increasing temperature.

Intermolecular forces

- Vapor pressure depends also on the intermolecular forces between the molecules of the liquid.
- The stronger the intermolecular forces, the lower will be the vapor pressure of the liquid because fewer molecules will have enough kinetic energy to overcome the attractive force at a given temperature. For example, water and ethanol have relatively low vapor pressure because the very strong hydrogen bonding in these liquids account for their unusually low vapor pressures.
- However, liquids with low intermolecular forces have high vapor pressures at room temperature. For example, diethyl ether, a non-polar molecule with relatively weak dispersion forces, has a relatively higher vapor pressure.

Surface area of the liquid

- Evaporation occurs at the liquids surface, where it interfaces with the air surrounding it.
- Liquid surface area is the amount of liquid that is exposed to the atmosphere (air).
- The number of liquid molecules present at the surface increases as the surface area of the container (or the surface area occupied by the liquid) increases. This, in turn, increases the number of molecules that separate from the liquid surface and change into gases at a specific moment, increasing the rate of evaporation.
- However, for liquids having the same surface area, the rate of evaporation depends on the two factors: **temperature** and the **strengths of intermolecular attractions**.

Boiling and Boiling Point

- When heat energy is added to a liquid, it increases the kinetic energy of the molecules and the temperature of the liquid increases.
- Heating a liquid always increases its vapor pressure.
- When a liquid is heated to a sufficiently high temperature under a given applied (usually atmospheric) pressure, bubbles of vapor begin to form below the surface.
- If the vapor pressure inside the bubbles is less than the applied pressure on the surface of the liquid, the bubbles collapse as soon as they form.

On the other hand, if the temperature is raised sufficiently, the vapor pressure is high enough that the bubbles can persist and rise to the surface, and burst, releasing the vapor into the air. This process is called **boiling**.

In short, boiling is the change of a liquid to bubbles of vapor that appear throughout the liquids.

It is the conversion of liquid to vapor within the liquid as well as at its surface.

During evaporation, only molecules at the surface escape into the vapor phase. It is the formation of vapor bubbles within the liquid itself that characterizes boiling and distinguishes it from evaporation.

If the temperature of the liquid is increased, the equilibrium vapor pressure also increases. Finally, the boiling point is reached.

The **boiling point** of a liquid is the temperature at which its vapor pressure equals the external atmospheric pressure.

The **normal boiling point** is the temperature at which the vapor pressure of a liquid is equal to exactly one atmosphere.

For instance, water boils at 100 °C at 1.0 atmospheric pressure and thus, its normal boiling point of water is 100 °C.

Nevertheless, the boiling point of water at 0.83 atm is 95 °C.

Generally, when the pressure exerted on a liquid is varied, the boiling point of a liquid also varies.

Note that as heat energy is added to vaporize a pure liquid at its boiling point, the temperature remains constant until the liquid is completely changed to vapor. Then, the temperature begins to rise after the liquid is completely changed to vapor.

Boiling of a liquid requires a certain amount of heat energy to break the forces of attraction between the molecules.

The amount of heat energy necessary to bring about the vaporization of a fixed amount of a liquid at a fixed temperature to the gaseous state is called **the heat of vaporization**.

For example, the heat of vaporization per mole of water at 298 K and 1 atmosphere is 44.0 kJ. This is called the **molar heat of vaporization (ΔH_{vap})** of water.

The molar heat of vaporization is the amount of heat needed to convert 1 mole of a liquid at its boiling point to a gas.

It is equal to the amount of energy that is released when 1 mole of vapor condenses to liquid at the condensing point of a vapor.

Condensation is the change of a gas to a liquid at the boiling point of the liquid. During condensation heat is released.

Thus, the amount of heat released when 1 mole of a gas is converted to a liquid at its condensation point is called **the molar heat of condensation (ΔH_{cond})**.

Molar heat of vaporization (ΔH_{vap}) and molar heat of condensation (ΔH_{cond}) are equal in magnitude but opposite in sign:

$$-\Delta H_{\text{vap}} = \Delta H_{\text{cond}}$$

Note that vaporization is an endothermic process whereas condensation is an exothermic process.

Exercise 3.11

Discuss the following questions:

1. What is the difference between evaporation and boiling?
2. What are the effects of impurities on the boiling point of liquids?
3. Why does the boiling point of liquid decrease as altitude increases?

Answer to Exercise 3.11

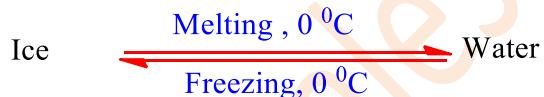
1.

Evaporation is slow process.	Boiling is a fast process.
Evaporation takes place from the surface of the liquid.	Boiling takes place from all the parts of the liquid
Evaporation takes place at all temperatures.	Boiling takes place at a fixed temperature on heating.

2. The boiling point of a liquid is raised when impurities are present; the phenomenon is called boiling point elevation.
3. At higher altitudes, air pressure is lower. Thus, at high altitude, it takes less energy to bring a liquid to the boiling point. Less energy means less heat, which means a liquid will boil at a lower temperature at a higher altitude.

3.5 The Solid State

- The temperature, at which a pure liquid changes to a crystalline solid, or freezes, is called the **freezing point**; it is identical to the melting point.
- The melting or freezing occurs at the temperature where the liquid and solid are in dynamic equilibrium.
- When a solid is continuously heated the ordered crystalline structure of solids will be disturbed. As a result, particles gradually get freedom of motion and melting (or fusion) takes place.
- **Melting** is the process of converting solid into the liquid.
- The temperature at which a crystalline solid changes to a liquid or melts is called the **melting point**.
- On the other hand, when a liquid is cooled, its molecules come closer to one another and thus, the intermolecular forces of attraction between them get stronger.
- As a result, its particles arrange themselves into a regular pattern and then converted to a solid. This process is called **freezing or solidification**. For instance, ice melts at 0 °C and water freezes at 0 °C.
- Ice and water coexist in equilibrium at 0 °C as follows:



- Unlike boiling points, melting points are affected only by large pressure changes.
- Note that both the melting point and the boiling point are characteristics of physical properties of a substance and can be used to help identify it.
- The amount of heat needed to convert one gram of solid to liquid at the melting point is called **heat of fusion**.
- The **molar heat of fusion or molar enthalpy of fusion (ΔH_{fus})** is the quantity of heat needed to convert one mole of a solid at its melting point to the liquid state.
- For example, the molar heat of fusion of ice is 6.01 kJ at 0°C. This is the amount of energy needed to break the attractive forces in the solid, ice, at its **melting point**.
- Melting requires the supply of energy; therefore, it is **an endothermic process**.
- During the process of solidification, the amount of heat liberated is exactly equal to the heat of fusion. The heat liberated is called **the heat of solidification or heat of crystallization**.
- **The molar heat of crystallization (ΔH_{cryst})** is the quantity of energy that is removed from one mole of a liquid to convert it to the solid state at its freezing point.

$$-\Delta H_{\text{cryst}} = \Delta H_{\text{fus}}$$

- Some solids have significant vapor pressure and thus, evaporate directly from the solid to the vapor state without passing through the liquid state. This process is called **sublimation**, i.e., the change of solid to vapor.
- The opposite of sublimation is **deposition** that is the change of vapor to solid. The process can be expressed as follows



- Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions.
- The **enthalpy of sublimation**, ΔH_{sub} , is the energy required to convert one mole of a substance from the solid to the gaseous state.
- Sublimation is an endothermic process.
- The reverse of sublimation is called deposition, a process in which gaseous substances directly change into the solid state, by passing the liquid state.
- Whereas, during deposition heat energy (ΔH_{dep}) is released.
- The enthalpy change during deposition is equal in magnitude but opposite in sign to sublimation.
- The enthalpy of deposition, (ΔH_{dep}), is the energy released when one mole of a substance from the gaseous state change to solid.
- The heat (enthalpy) of sublimation is related to the enthalpies of fusion and vaporization by:

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

$$\Delta H_{\text{sub}} = -\Delta H_{\text{dep}}$$

Exercise 3.12

1. What is the difference between melting and solidification?
2. What could happen to temperature during a phase change?

Answer to Exercise 3.12

1. Melting is the process of converting solid into the liquid.
When a liquid is cooled, its molecules come closer to one another and thus, the intermolecular forces of attraction between them get stronger, the process is solidification.
2. The temperature varies or changes during phase changes

Heating curve

- A **heating Curve** is a plot of the temperature versus the amount of heat added

(Figure 3.5). It is commonly used to show the relationship between phase changes and enthalpy for a given substance. There are two main observations that we can learn from the heating curve: regions where the temperature increases as heat is added and plateaus where the temperature stays constant. It is at plateaus that a phase change occurs.

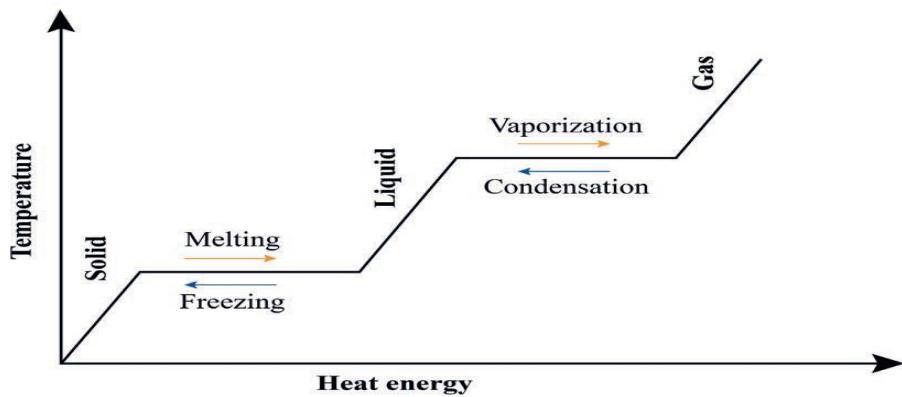


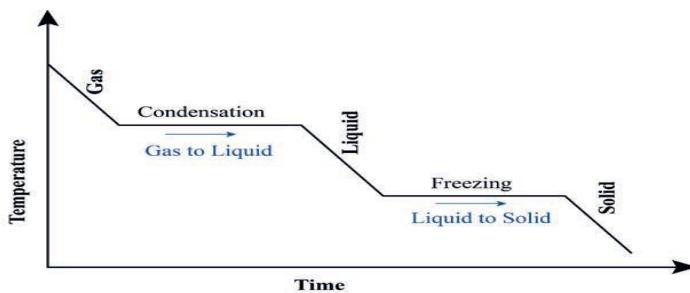
Figure 3.5 A heating curve

Exercise 3.13

1. Draw a cooling curve.
2. What is the relationship and difference between a heating curve and a Cooling curve?

Answer to Exercise 3.13

1. Cooling curve



2. Heating curves show how the temperature changes as a substance is heated up. However, cooling curves are the opposite. They show how the temperature change as a substance is cooled down. Just like heating curves, cooling curves have horizontal flat parts where the state changes from gas to liquid, or from liquid to solid.

UNIT SUMMARY

Matter is anything that has mass and occupies space.

Matter exists in one of the three states: a solid, a liquid or a gas.

Solids have a definite volume and a definite shape.

A liquid has a definite mass but doesn't have a definite shape.

A gas has neither a definite volume nor a definite shape.

Plasma is a gaseous mixture of positive ions and electrons.

Gases and liquids are fluids whereas solids are not.

According to Boyle's law at fixed temperature the volume of a fixed mass of gas is inversely proportional to the pressure.

Charles' law states that at constant pressure the volume of a fixed mass of gas is directly proportional to the temperature.

According to Gay-Lussac's law the pressure of a fixed amount of a gas varies directly with the temperature.

Combined gas law states that the ratio PV to T for any set of pressure, volume and temperature values always equals the same k.

Avogadro's stated that at the same temperature and pressure, equal volumes of gases contain equal numbers of moles.

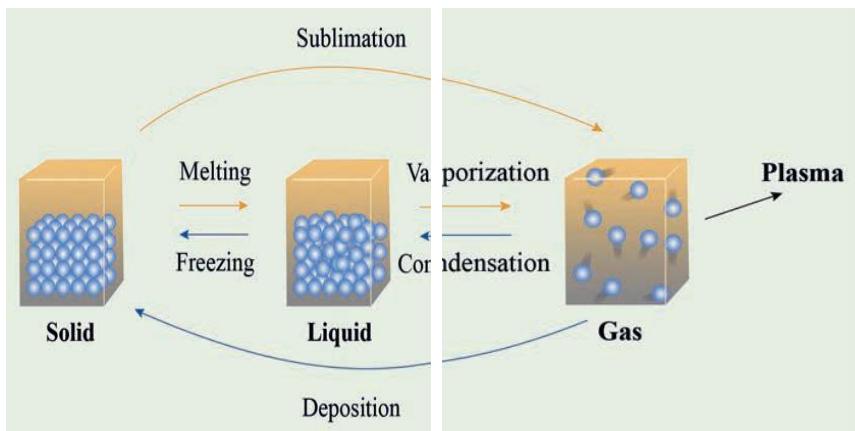
The ideal gas law is a combination of Boyle's law, Charles' law and Avogadro's law.

At constant temperature and pressure, the rate of diffusion of a gas, r, is inversely proportional to the square root of its density, d, or molar mass, M.

When energy is supplied to a solid, it melts and changes to a liquid, the particles move faster. Application of additional energy will make the liquid to boil and changes to a gas.

Gaseous particles are much more widely spaced and move much faster than in a liquid and a solid.

Phase changes can be illustrated as here:



- Energy is released when a less ordered phase is converted to a more ordered phase, as indicated in the follows

Phase Change	Physical Process	Energy Change
Fusion (melting)	Solid → Liquid	Energy is absorbed.
Vaporization	Liquid → Gas	Energy is absorbed.
Sublimation	Solid → Gas	Energy is absorbed.
Freezing	Liquid → Solid	Energy is released.
Condensation	Gas → Liquid	Energy is released.
Deposition	Gas → Solid	Energy is released

REVIEW EXERCISE

Part I: Write what each of these refers to:

1. They have a definite shape and a definite volume.
2. Their molecules are highly disordered.
3. The motion of their molecules is highly restricted.

4. They can be easily compressed.
5. They have a tendency to flow.
6. They can take the shape of their container.
7. They can move in all direction at high speed.
8. They can easily diffuse through each other.
9. They can sublime.
10. They have less density relative to the other states.

Part II: Complete the following statements:

11. Liquids and gases have no definite _____.
12. The freezing point of a liquid is the same as _____.
13. The temperature at which a crystalline solid is directly converted to a gas is called _____.
14. The lowest attainable temperature is _____.
15. “At the fixed temperature and pressure, equal volumes of different gases have equal numbers of molecules.” This statement is postulated by _____.

Part III: Multiple Choice Questions:

Choose the correct answer from the given alternatives.

16. Which of the following would take up the entire shape of the container it is enclosed within?
 - a. Gas
 - b. Liquid
 - c. Solid
 - d. both a and b
17. If a gas expands at constant temperature, it indicates that:
 - a. Number of the molecules of gas increases
 - b. Kinetic energy of molecules decreases
 - c. Pressure of the gas increases

d. Kinetic energy of molecules remains the same

18. A sample of oxygen occupies 47.2 L under a pressure of 1240 torr at 25 °C. What volume would it occupy at 25°C if the pressure were decreased to 730 torr?

- a. 27.8 L b. 32.3 L c. 29.3 L d. 80.2 L

19. A sample of nitrogen occupies 5.50 liters under a pressure of 900.0 torr at 25.0°C. At what temperature will it occupy 10.0 liters at the same pressure?

- a. 542 °C b. c. 269 °C c. 45.5°C d. d. 144°C

20. A quantity of gas has a volume of 25 L at 17°C and 3 atm of pressure. To what volume must the gas be increased for a gas to be under STP conditions?

- a. 79.7 L b. 26.6 L c. 70.6.0 L d. 75.0 L

21. What is the molecular weight of a pure gaseous compound having a density of 4.95 g/L at -35°C and 1020 torr?

- a. 24 g/mol b. 72 g/mol c. 120 g/mol d. 85 g/mol

22. If helium (He) diffuses through a porous barrier at a rate of 4.0 moles per minute, at what rate (in moles per minute) would oxygen (O₂) gas diffuse?

- a. 1.4 b. 2.0 c. 0.7 d. 0.5

23. What will happen water when freezes?

- a. Water changes from a gas to a liquid state
b. Water changes from a liquid to a solid state
c. Water changes from a solid to a gas state
d. Water changes from a gas to a plasma state

24. What is sublimation?

- a. When a solid turns into a gas b. When a gas turns into a liquid
c. When a gas turns into a solid d. When a solid turns into plasma

25. What eventually happens if energy is continually removed from a liquid?

- a. It boils b. It freezes c. It evaporates d. It condenses

Part IV: Solve the following problems

26. What will be the minimum pressure required to compress 500 dm³ of air at 1 bar to 200 dm³ at 30°C ?
27. A vessel of 120 mL capacity contains a certain amount of gas at 35°C and 1.2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C . What would be its pressure?
28. Using the ideal gas equation (i.e., $pV = nRT$), show that at a given temperature density of a gas is proportional to gas pressure p .
29. 34.05 mL of phosphorus vapor weighs 0.0625 g at 546 °C and 0.1 bar pressure. What is the molar mass of phosphorus?
30. If 0.500 mole of nitrogen gas occupies a volume of 11.2 L at 0°C ; what volume will 2.00 mole of nitrogen gas occupy at the same temperature and pressure?
31. What mass of helium in grams is required to fill 15.0 L balloon to a pressure of 1.1 atm at 25 °C?
32. A sample of a certain gas has a volume of 1.25 L at -125 °C and 5.0 atm. The gas is compressed at 50.0 atm to a volume of 325 mL. What is the final temperature of the helium gas in °C ?
33. If 140 cm³ of methane diffuse into air in 72 seconds, how long will it take 210 cm³ of sulphur dioxide to diffuse under the same conditions?
34. The temperature of 2.5 L of a gas initially at STP is raised to 250°C at constant volume; calculate the final pressure of the gas in atmosphere.
35. What total gas volume at 520°C and 880 torr would result from the decomposition of 33 g of potassium bicarbonate according to the equation:



Answers to Review Questions

Part I

1. Solid 2. Gas 3. Solid 4. Gas 5. Gas and Liquid 6. Liquid
7. Gas 8. Gas 9. Solid 10. Gas

Part II

11. Shape 12. Melting point 13. Sublimation point 14. 0 K or -273 ° C
15. Avogadro

Part III

16. A 17. D 18. D 19. C 20. A 21. B 22. A 23. B 24. A 25. B

Part IV

26. 2.5 bar 27. 0.8 bar 28. Since, n, T and R are constant, $d \propto P$
29. 1, 232.7 g/mol 30. 44.8 L 31. 2.7 g 32. $884.8 \text{ K} = 111.8^\circ\text{C}$
33. 144 seconds 34. 1.92 atm 35. 35. 9.27 L

UNIT 4

CHEMICAL KINETICS

4.1 INTRODUCTION

- Every chemical reaction proceeds at a different rate or speed.
- Some reactions proceed very slowly and may take a number of days to complete; while others are very rapid, requiring only a few seconds.
- For example, rusting of iron could start quickly, while ripening of fruits may be completed in a few days.
- On the other hand, weathering of stone may take more than a decade and the breakdown of plastics in the environment takes more than hundred years.
- However, other reactions, like the combustion of gasoline or the explosion of gunpowder occur in a few seconds.
- The area of chemistry that is concerned with reaction rates is called **chemical kinetics**.
- The word “**kinetic**” suggests **movement or change**.
- Chemical kinetics refers to the rate of reaction, which is the changeover time in the concentration of a reactant or a product.

4.2 The Rate of a Reaction

- The **rate of a chemical reaction** measures the change in concentration of a reactant or a product per unit time. This means that the rate of a reaction determines how fast the concentration of a reactant or product changes with time.
- For example, for a general reaction:
$$\text{Reactants} \rightarrow \text{Products}$$
- This equation tells us that, during the course of a reaction, reactant molecules are consumed while product molecules are formed
- As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.
- Consider the progress of a simple reaction in which A molecules are converted to B molecules:
$$A \rightarrow B$$
- The decrease in the number of A molecules and the increase in the number of B molecules with time are shown in figure 4.1
- In general, it is more convenient to express the rate in terms of change in concentration with time.

$$\text{Rate of reaction} = \frac{\text{change in concentration of substance}}{\text{change in time}} = \frac{\Delta C}{\Delta t}$$

- Note that Δ denotes the difference between the final and initial state
- Thus, for the preceding reaction we can express the rate as:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t} \quad \text{or rate} = \frac{\Delta [B]}{\Delta t}$$

in which, $\Delta[A]$ and $\Delta[B]$ are the changes in concentration (mol L^{-1}) over period Δt .

- Because the concentration of A decreases during the time interval, $\Delta [A]$ is a negative quantity.
- The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive.
- On the other hand, the rate of product formation does not require a minus sign because $\Delta [B]$ is a positive quantity (the concentration of B increases with time).

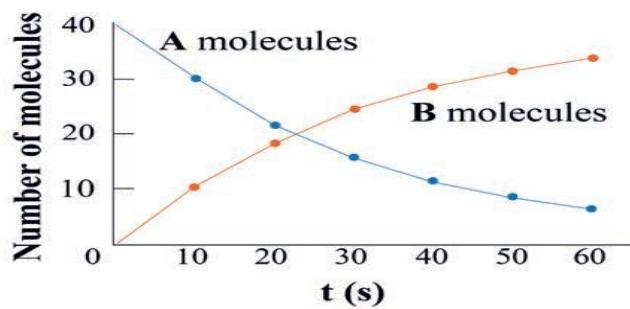


Figure 4.1 The rate of a reaction $A \rightarrow B$ represented as the decrease of A molecules with time and increase of B molecules with time.

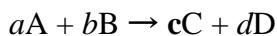
- For more complex reactions, we must be careful in writing the rate expression.
- Consider, for example, the reaction:



- Two moles of A disappear for each mole of B that forms, that is, the rate at which B forms is one half the rate at which A disappears. We write the rate as either:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t} \quad \text{or rate} = \frac{\Delta [B]}{\Delta t}$$

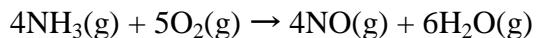
Similarly, for the reaction:



$$\text{the rate is given by Rate} = -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \frac{\Delta [D]}{\Delta t}$$

Example 4.1 ,

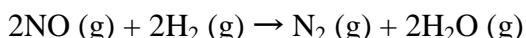
1. Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:



Solution; In this reaction

$$\text{Rate} = -\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

2. In the reaction of nitric oxide with hydrogen,



If the rate of disappearance of NO is $5.0 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$, what is the rate of reaction for the formation of N₂?

Solution:

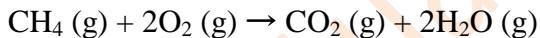
The rate of reaction for the formation of N₂

$$\text{Rate} = \frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = -\frac{1}{2} \times (-5.0 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1})$$

$$\text{Rate} = 2.5 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

Exercise 4.1

1. Write the rate expression for the following reaction:



- a. the formation of CO₂ and H₂O
- b. the disappearance of CH₄ and O₂

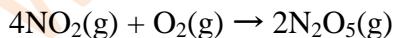
2. The reaction for the formation of ammonia is given as



Write the rate reaction for:

- a. the formation of NH₃
- b. the disappearance of N₂ and H₂

3. Consider the reaction of:



Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of $0.037 \text{ mol L}^{-1}\text{s}^{-1}$.

- a. At what rate is N₂O₅ being formed?
 - b. At what rate is NO₂ reacting?
4. Consider the reaction of:



Suppose that, at a particular moment during the reaction, molecular

hydrogen is being formed at the rate of $0.078 \text{ mol L}^{-1}\text{s}^{-1}$.

- At what rate is P_4 being formed?
- At what rate is PH_3 reacting?

Answer to Exercise 4.1

- | | |
|---|---|
| 1. a. Rate = $\frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$ | b. Rate = $-\frac{\Delta[\text{CH}_4]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t}$ |
| 2. a. Rate = $\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t}$ | b. Rate = $-\frac{\Delta[\text{N}_3]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$ |
| 3. a. $0.074 \text{ mol L}^{-1}\text{s}^{-1}$ | |
| b. $0.15 \text{ mol L}^{-1}\text{s}^{-1}$ | |
| 4. a. $0.013 \text{ mol L}^{-1}\text{s}^{-1}$ | |
| b. $0.052 \text{ mol L}^{-1}\text{s}^{-1}$ | |

Determination of Rate of Reaction

Reaction rate is change in an observable property over time.

The observable property should be selected based upon what can be measured in the laboratory. This could be a color change, a temperature change, a pressure change, a mass change, or the appearance of a new substance (for example, amount of precipitate formed).

The observable (measurable) properties can be used to determine the change in concentration over time.

Consider, for example, the thermal decomposition of gaseous di-nitrogen pentoxide, N_2O_5 , to give the brown gas nitrogen dioxide:



Colorless Brown Colorless

Changes in concentration as a function of time can be determined by measuring the increase in pressure as 2 gas molecules are converted to 5 gas molecules. Alternatively, concentration changes can be monitored by measuring the intensity of the brown color due to NO_2 formation. Reactant and product concentrations as a function of time at 55°C are listed in table 4.1 Using this data, we can calculate the rate:

Table 4.1: Concentrations ($\text{mol L}^{-1}\text{s}^{-1}$) as a function of time at 55°C for the thermal decomposition of gaseous di-nitrogen pent-oxide (N_2O_5)

Time (s)	N ₂ O ₅	NO ₂	O ₂
0	0.0200	0	0
100	0.0169	0.0063	0.0016
200	0.0142	0.0115	0.0029
300	0.0120	0.0160	0.0040
400	0.0101	0.0197	0.0049
500	0.0086	0.0229	0.0057
600	0.0072	0.0256	0.0064
700	0.0061	0.0278	0.0070

Note: The concentrations of NO₂ and O₂ increase as the concentration of N₂O₅ decreases. In the decomposition of N₂O₅, the rate of formation of O₂ is given by the equation:

$$\text{Rate of formation of O}_2 = \frac{\Delta[O_2]}{\Delta t} = \frac{\text{con.of O}_2 \text{ at time } t_2 - \text{con.of O}_2 \text{ at time } t_1}{t_2 - t_1}$$

- During the time period 300 to 400 s, for example, the average rate of formation of O₂ is $9 \times 10^{-6} \text{ mol L}^{-1} \text{s}^{-1}$:
 - Rate of formation of O₂ = $\frac{\Delta[O_2]}{\Delta t} = \frac{0.0049M - 0.0040M}{400s - 300s} = 9 \times 10^{-6} \text{ molL}^{-1} \text{S}^{-1}$
- The average rate of formation of NO₂ during the time period 300s -400 s is

$3.7 \times 10^{-5} \text{ molL}^{-1} \text{s}^{-1}$, which is four times the rate of formation of O₂, as with the 4:1 ratio of the coefficients of NO₂ and O₂ in the chemical equation for the decomposition of N₂O₅.

$$\text{Rate of formation of NO}_2 = \frac{\Delta[NO_2]}{\Delta t} = \frac{0.0197M - 0.0160M}{400s - 300s} = 3.7 \times 10^{-5} \text{ molL}^{-1} \text{s}^{-1}$$

Similarly, during the time period 300–400 s, the average rate of decomposition of

N₂O₅ is $1.9 \times 10^{-5} \text{ molL}^{-1} \text{s}^{-1}$;

$$\text{Rate of formation of N}_2\text{O}_5 = \frac{\Delta[N_2O_5]}{\Delta t} = \frac{0.0101M - 0.0120M}{400s - 300s} = 1.9 \times 10^{-5} \text{ molL}^{-1} \text{s}^{-1}$$

- In general, the rate of reaction at the beginning is fast and it decreases as the reaction proceeds.
- Plotting the data of Table 4.1 gives the three curves in figure 4.2. Looking at the time period 300 – 400 s on the O₂ curve, Δ[O₂] and Δt is represented, respectively, by the vertical and horizontal sides of a right triangle.
- The slope of the third side, the hypotenuse of the triangle, is Δ[O₂]/Δt, the average rate of O₂ formation during that period. The steeper the slope of the hypotenuse, the faster the rate. For example, compare the hypotenuse of the triangle defined by Δ[NO₂] and Δt during the time period 300 – 400 s and 600 – 700 s.

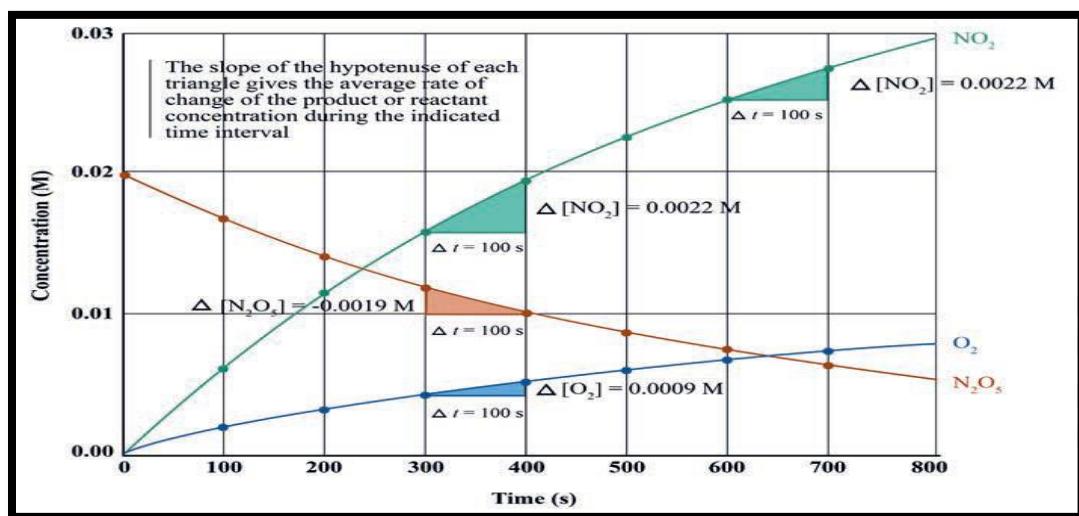


Figure 4.2 concentration as a function of time when gaseous N_2O_5 decompose to gaseous NO_2 and O_2 at 55°C

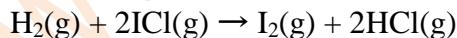
Chemists want to know the rate of a reaction at a specific time t rather than the rate averaged over a time interval Δt . For example, what is the rate of formation of NO_2 at time $t = 350 \text{ s}$? Such **instantaneous rate** is calculated from the slope of a tangent drawn at any points on the graph of concentrations versus time (figure 4.2)

The slope of tangent taken at the initial point of the graph is assumed to be equal to its **initial rate**

. In **the initial rate** the change in concentration of a reactant or product as a function of time is measured within minutes (or seconds) the reaction starts.

Example 4.2

Consider the gas-phase reaction that occurs when we mix 1.000 moles of hydrogen and 2.000 moles of iodine chloride at 230°C in a closed 1.000-liter container.



From the experimental data given in the table below, determine the instantaneous rate of reaction at time, $t = 2 \text{ s}$.

Time (s)	0	1	2	3	4	5	6	7	8
[ICl]molL ⁻¹	2.000	1.348	1.052	0.872	0.748	0.656	0.586	0.530	0.484
[H ₂] molL ⁻¹	1.000	0.674	0.526	0.436	0.374	0.328	0.293	0.265	0.242

Solution: First, plot H₂ concentration versus time for the reaction of 1.000 M H₂ with 2.000 M ICl. Then, draw a tangent line to the curve. The instantaneous rate of reaction at any time, *t*, equals the negative of the slope of the tangent to this curve at time *t*. figure 4.3 ,shows how to find the instantaneous rate at *t* = 2 seconds .

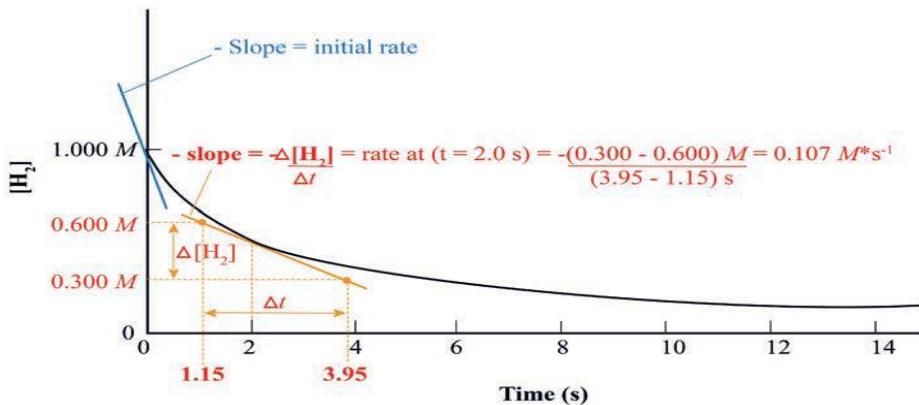
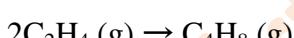


Figure 4.3 A plot of the hydrogen concentration versus time , using data of the above table

Exercise 4.2

- Using the initial concentrations and the fact that $[O_2] = 0.64 \times 10^{-2} \text{ mol.L}^{-1}$ at $t = 600 \text{ s}$ in Table 4.1, calculate $[N_2O_5]$ and $[NO_2]$ at $t = 600 \text{ s}$.

- Consider the reaction:



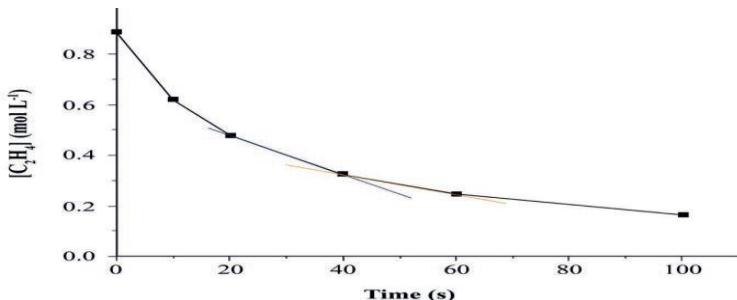
From the experimental data given in the table below, plot a graph for the consumption of ethylene, C₂H₄, versus time.

- Calculate the rate of reaction between the time intervals 10s to 30s.
- Calculate the rate of reaction at 45 s.

Time (s)	0	10	20	40	60	100
[C ₂ H ₄] (mol.L ⁻¹)	0.884	0.621	0.479	0.328	0.250	0.169

Answer to Exercise 4.2

- $NO_2 = 0.0256$ $N_2O_5 = 0.0072$
- Graph of [C₂H₄] (mol L⁻¹) vs Time (s) with tangent lines



- a. $0.011 \text{ mol L}^{-1}\text{s}^{-1}$
- b. $0.305 \text{ mol L}^{-1}\text{s}^{-1}$

Conditions needed for a chemical reaction

- Chemical reactions are usually explained by the **collision theory**.
- The assumption of the collision theory is that chemical reactions take place due to collisions between molecules.

Collisions between reactants

- The collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact).
- The rate of reaction is directly proportional to the number of collisions per second (the frequency of collision).

$$\text{Rate} \propto \frac{\text{number of collisions}}{\text{Second}}$$

1. Proper Orientation

- According to collision theory, the more collisions there are the faster the rate of reaction would be. However, not all collisions between reacting species result in a reaction. This is because collisions between reactants can be either effective or ineffective.
- **Effective collisions** are collisions that result in a reaction to form the desired products.
- **Ineffective collisions** are collisions that do not result in a reaction to form the desired products. Thus, the collision between molecules should have the proper orientation figure 4.4

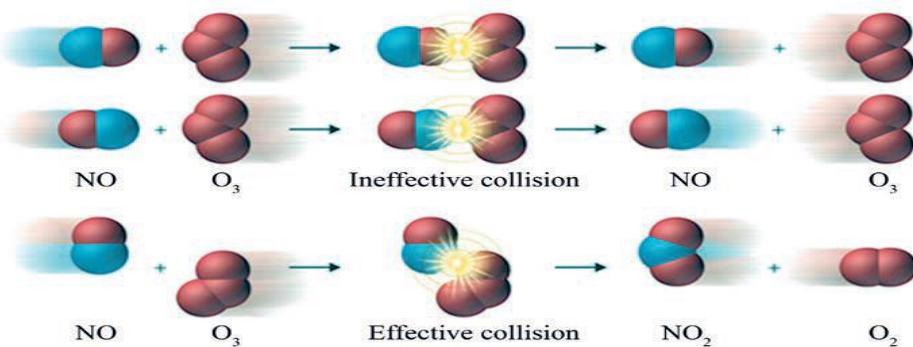


Figure 4.4, The effect of molecular orientation on the reaction of NO and O₃

2. Activation energy

- If the collisions between the reactant molecules do not have sufficient energy, then no reaction will occur. Therefore, for the reaction to take place collision must always occur with sufficient energy to break the bonds in the reactants and form new bonds in the product. Thus, minimum amount of energy needed for the reaction is known as **activation energy**, Ea.
- According to the kinetic molecular theory, the average kinetic energy of the particles of a substance is directly proportional to the absolute temperature.
- As the temperature of the reacting species is raised, the average kinetic energy of the reacting particles increases considerably.
- This causes the particles of the reactants to collide more frequently and with greater energy. This results in increase in reaction rate.

4.3 Factors affecting the Rate of a Chemical Reaction

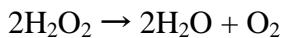
- The rates at which reactants are consumed and products are formed during chemical reactions vary greatly
- Even a chemical reaction involving the same reactants may have different rates under different conditions. Change in temperature, concentration, nature of reactant, surface area and presence of a catalyst, result in changes in rate of reaction.

i. Nature of the reactants

- The rate of a reaction depends on the chemical nature of the substances in the reaction.
- The combination of two oppositely charged ions usually occurs very rapidly. For example, the reaction of an acid with a base is:



- The acid-base reaction of HCl and NaOH is much faster than the decomposition of hydrogen peroxide, which involves the reorganization of molecules.



ii. Surface Area of Reactants

- Reactions can be classified as homogeneous (same phase) and heterogeneous (different phases).
- For example, the combustion of graphite is a heterogeneous reaction because it involves a solid with gas. In this case, the reaction occurs only at the interface (boundary) between two phases.
- A homogeneous reaction occurs only in one phase.
- For example: $\text{NO(g)} \rightarrow \frac{1}{2}\text{N}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)}$
- Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of reaction between two phases depends to a great extent on the surface area of contact between them.
- Finely divided solids, react more rapidly than the same amount of the substance in a large body because of the greater surface area available.

iii. Concentration of Reactants

- At a fixed temperature, the rate of a given reaction depends on the concentration of the reactants.
- Reaction rates often increases when the concentration of one or more of the reactants increases. This is because increasing the concentration produces more contacts between the reacting particles, which results in increasing the rate of reaction.
- In the case of reactions that involve gaseous reactants, an increase in pressure can increase the concentration of the gases which may lead to an increase in the rate of reaction. However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids

iv. Temperature of Reactants

- Temperature usually has a major effect on the rate of reaction. Molecules at higher temperatures have more thermal energy. Generally, an increase in the temperature of a reaction mixture increases the rate of chemical reactions. This is because, as the temperature of the reaction mixture rises, the average kinetic energy of the reacting particles increases. So, they collide more frequently and with greater energy.
- The effect of temperature on rate of reaction can be experienced in our daily life. For example, foods cook faster at higher temperature than at lower ones. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, the rate of a reaction in a homogeneous system is approximately doubled by an increase in temperature of only 10 °C.

v. Presence of a Catalyst

- A catalyst is a substance that changes reaction rate by providing a different reaction mechanism one with lower activation energy, E_a . Activation energy is the minimum energy required to start a chemical reaction. Catalysts are not used up by the reactions; rather they are recovered at the end of the reaction. Although a catalyst speeds up the reaction, it does not alter the position of equilibrium.

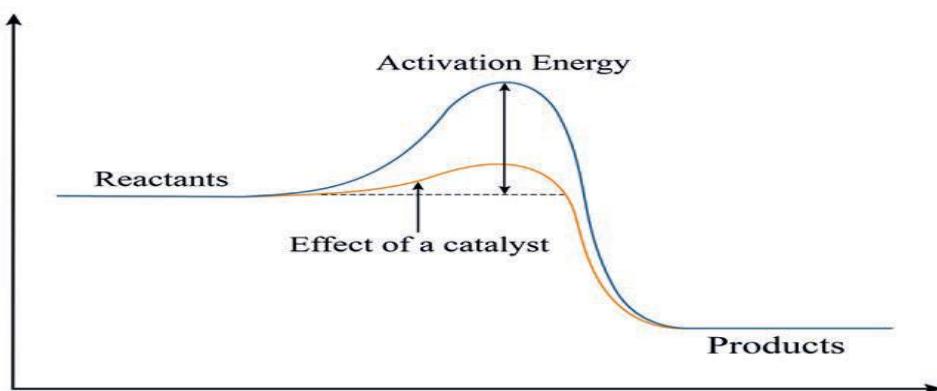


Figure 4.5 A catalyst provides an alternative pathway with a lower activation energy barrier for the reaction

- Chemical catalysts can be either positive or negative.
- Positive catalysts increase the rate of reaction by lowering the E_a
- Example 4.3** $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$; $\text{V}_2\text{O}_5(\text{s})$ as catalyst.
- Negative catalysts or inhibitors decrease the rate of reaction by increasing the value of E_a
- Example 4.4 $\text{OCl}^-(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{OI}^-(\text{aq}) + \text{Cl}^-(\text{aq})$; $\text{OH}^-(\text{aq})$ as inhibitor
- Example 4.3 represents heterogeneous catalysts as state of reactants and catalyst is different, while Example 4.4 represents homogeneous catalyst as both reactants and catalyst are in same state.
- A substance that catalyzes one reaction may have no effect on another reaction, even if that reaction is very similar. Many of the most highly specific catalysts are those designed by nature.
- The chemical reactions in living things are controlled by biochemical catalysts called enzymes.

UNIT SUMMARY

- Chemical kinetics is the study of the rates and mechanisms of chemical reactions.
- A chemical reaction occurs when atoms, molecules or ions undergo effective collisions.
- The higher the activation energy, the slower a chemical reaction and vice versa.

- In general, reaction rates increase with temperature, because higher temperature increases both the frequency of collisions and the number of molecules possessing enough energy to undergo effective collision.
- Reaction rate is expressed as the change in concentration of a reactant or product, per unit time.
- Reaction rates must be determined experimentally, often by gathering data on the variation of concentration over time.
- Reaction rates are influenced by the concentrations of reactants, temperature, catalysts and the degree of contact between reactants (surface area).

REVIEW EXERCISE

Part I: Choose the correct answer from the given alternatives

1. When the concentration of reactant molecules is increased, the rate of reaction increases. The best explanation is: As the reactant concentration increases,
 - a. the average kinetic energy of molecules increases.
 - b. the frequency of molecular collisions increases.
 - c. the rate constant increases.
 - d. the activation energy increases.

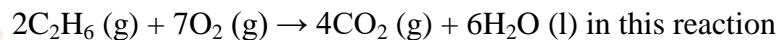
2. A catalyst:

- a. actually participates in the reaction.
- b. changes the equilibrium concentration of the products.
- c. does not affect a reaction energy path.
- d. always increases the activation energy for a reaction.

3. Which items correctly complete the following statement? A catalyst can act in a chemical reaction to:

- (I) increase the equilibrium constant.
- (II) Lower the activation energy.
- (III) Provide a new path for the reaction.
 - a. only I & II b. only II c. only II & III d. only I & III

4. The combustion of ethane (C_2H_6) is represented by the equation:



- a. the rate of consumption of ethane is seven times faster than the rate of consumption of oxygen.
- b. CO_2 is formed twice as fast as ethane is consumed.
- c. water is formed at a rate equal to two-thirds the rate of formation of CO_2 .
- d. the rate of consumption of oxygen equals the rate of consumption of water.

5. The speed of a chemical reaction

- a. is constant no matter what the temperature is.
- b. is independent of the amount of contact surface of a solid involved.
- c. between ions in aqueous solution is extremely rapid because there are no bonds that need to be broken.
- d. varies inversely with the absolute temperature

6. A graph of volume of hydrogen released vs time for a hypothetical reaction between zinc and dil. HCl is given in figure 4.6 On the basis of this mark the correct option.

a. Average rate up to 40 s is $\frac{V_3 - V_2}{40}$

b. Average rate up to 40 s is $\frac{V_3 - V_2}{40 + 30}$

c. Average rate up to 40 s is $\frac{V_3}{40}$

d. Average rate up to 40 s is $\frac{V_3 - V_1}{40 - 20}$

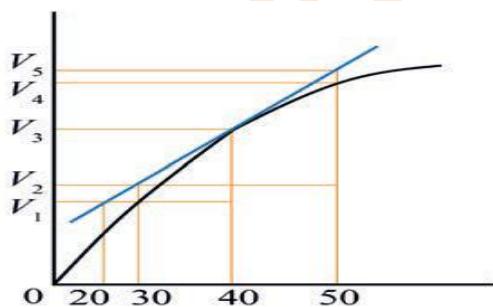


Figure 4.6 A reaction between Zinc and dilute hydrochloric acid

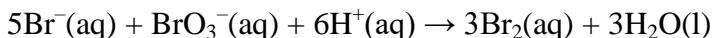
7. Consider the graph given in figure 4.6 , Which of the following options does not show instantaneous rate of reaction at 40th second?

a. $\frac{V_5 - V_2}{50 - 30}$ b. $\frac{V_4 - V_2}{50 - 30}$ c. $\frac{V_3 - V_2}{50 - 30}$ d. $\frac{V_3 - V_1}{40 - 20}$

8. Which of the following statements is correct?

- a. The rate of a reaction decreases with passage of time as the concentration of reactants decreases.

- b. The rate of a reaction is same at any time during the reaction.
 - c. The rate of a reaction is independent of temperature change.
 - d. The rate of a reaction decreases with increase in concentration of reactant(s).
9. Which of the following expressions is correct for the rate of reaction given below?



a. $\frac{\Delta[\text{Br}^-]}{\Delta t} = 5 \frac{\Delta[\text{H}^+]}{\Delta t}$ b. $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{6}{5} \frac{\Delta[\text{H}^+]}{\Delta t}$ c. $\frac{\Delta[\text{Br}^-]}{\Delta t} = \frac{5}{6} \frac{\Delta[\text{H}^+]}{\Delta t}$ d. $\frac{\Delta[\text{Br}^-]}{\Delta t} = 6 \frac{\Delta[\text{H}^+]}{\Delta t}$

10. During the decomposition of H_2O_2 to give di-oxygen, 48 g O_2 is formed per minute at certain point of time. The rate of formation of water at this point is
- a. $0.75 \text{ mol min}^{-1}$ b. 1.5 mol min^{-1} c. $2.25 \text{ mol min}^{-1}$ d. 3.0 mol min^{-1}

Part II: Give short answers to each of the following questions

11. What variable of a chemical reaction is measured over time to obtain the reaction rate?
12. How does an increase in pressure affect the rate of a gas phase reaction? Explain.
13. A reaction is carried out with water as the solvent. How does the addition of more water to the reaction vessel affects the rate of the reaction? Explain.
14. How does an increase in temperature affect the rate of a reaction? Explain the two factors involved.
15. What is the difference between an average rate and an instantaneous rate?
16. What is the difference between an initial rate and an instantaneous rate?
17. Give two reasons to measure initial rates in a kinetics study.
18. For the reaction $\text{A(g)} \rightarrow \text{B(g)}$, sketch two curves on the same set of axes that show
- a. The formation of product as a function of time
 - b. The consumption of reactant as a function of time
19. The compound AX_2 decomposes according to the equation
 $2\text{AX}_2(\text{g}) \rightarrow 2\text{AX}(\text{g}) + \text{X}_2(\text{g})$. In one experiment, $[\text{AX}_2]$ was measured at various times and these data were obtained:

Time (s)	0	1	2	6	10	20
$[\text{AX}_2] (\text{mol L}^{-1})$	0.05	0.0448	0.03	0.0249	0.0209	0.0088

- a. Find the average rate over the entire experiment.
- b. Is the initial rate higher or lower than the rate in part (a)? Use graphical methods to estimate the initial rate.

20. Express the rate of reaction in terms of the change in concentration of each of the reactants and products: $\text{A(g)} + 2\text{B(g)} \rightarrow \text{C(g)}$ When $[\text{B}]$ is decreasing at $0.5 \text{ mol L}^{-1} \text{ s}^{-1}$, how fast is $[\text{A}]$ decreasing?

21. Reaction rate is expressed in terms of changes in concentration of reactants and products.
Write a balanced equation for

$$\text{Rate} = -\frac{\frac{1}{2} \Delta [N_2O_5]}{\Delta t} = \frac{1}{4} \frac{\Delta [NO_2]}{\Delta t} = \frac{\Delta [O_2]}{\Delta t}$$

22. Although the depletion of stratospheric ozone threatens life on Earth today, its accumulation was one of the crucial processes that allowed life to develop in prehistoric times: $3O_2(g) \rightarrow 2O_3(g)$

- Express the reaction rate in terms of $[O_2]$ and $[O_3]$.
- At a given instant, the reaction rate in terms of $[O_2]$ is $2.17 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$. What is it in terms of $[O_3]$?

Answer to Review Questions

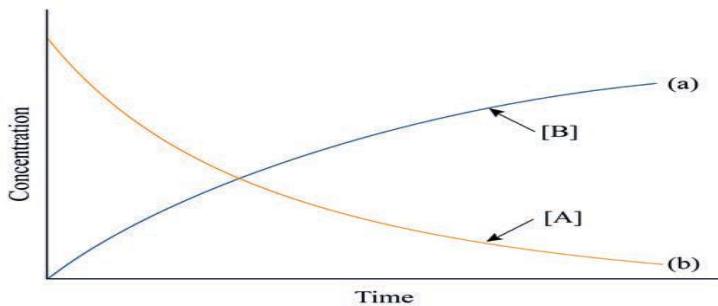
Part I: Choose the correct answer from the suggested options

1. B 2. A 3. D 4. B 5. C 6. C 7. B 8. A 9. C 10. D

Part II: Give short answers to each of the following questions

- This could be a color change, a temperature change, a pressure change, a mass change, or the appearance of a new substance (for example, amount of precipitate formed).
- Reaction rate is proportional to concentration. An increase in pressure will increase the concentration, resulting in an increased reaction rate.
- The addition of water will dilute the concentrations of all dissolved solutes, and the rate of the reaction will decrease.
- An increase in temperature affects the rate of a reaction by increasing the number of collisions between particles, but more importantly, the energy of collisions increases. Both these factors increase the rate of reaction.
- The slope of the line joining any two points on a graph of concentration versus time gives the average rate between the two points. The closer the points, the closer the average rate will be to the instantaneous rate.
- The initial rate is the instantaneous rate at the point on the graph where time = 0, that is, when reactants are mixed.
- Measuring initial rates is done for two practical reasons.

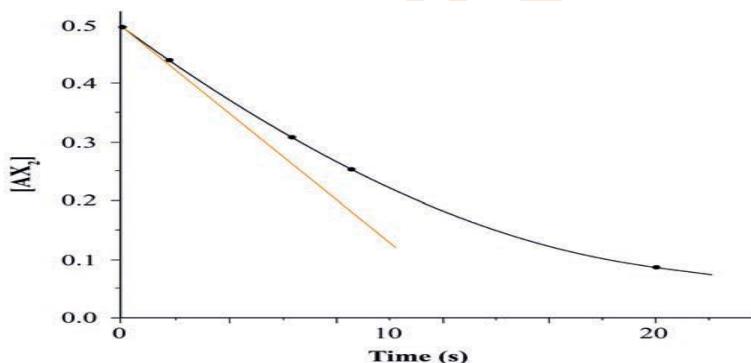
- we can approximate the product concentration as 0. For a reaction that is at all reversible or product-inhibited, the math is much easier if $[P] = 0$.
- we can often approximate the concentration of one (or more) of the reactants as fixed. For example, if you measure the rate only for an amount of time required for a few percent of the reactant to be consumed, you can get a pretty good fit to the data by assuming that reactant is fixed at its initial concentration. That makes it easy to produce plots of the initial rate vs the concentration of that reactant.



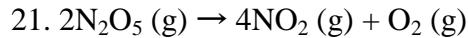
18.

19. a. $0.0010 \text{ mol L}^{-1}\text{s}^{-1}$

b. The initial rate is higher than the average rate because the rate will decrease as reactant concentration decreases.



20. Rate = $-\frac{\Delta[A]}{\Delta t} = \frac{1}{2} \frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t}$, $0.2 \text{ mol L}^{-1}\text{s}^{-1}$



22. a. Rate = $-\frac{1}{3} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{O}_3]}{\Delta t}$ b. $1.45 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$

UNIT 5

CHEMICAL EQUILIBRIUM

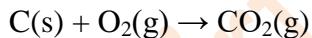
5.1 INTRODUCTION

- Do all reactions reach to completion? If not then how much of the reactants remain unreacted, that is, what is the extent of the reaction it took? Why does the reaction reach to completion? Why does it attain equilibrium? These questions can be answered after studying chemical equilibrium.
- In this unit, you will learn about chemical equilibrium, how it is attained, and factors that affect the position of chemical equilibrium.

5.2 Chemical Equilibrium

5.2.1 Reversible and Irreversible Reactions

- Many chemical reactions proceed to completion. In such types of reactions, the reactants are converted to the products and the amount of reactants left after the reaction is very small. Such reactions are called **irreversible reactions or one-way reactions**.
- When the equation for an irreversible reaction is written, a single arrow (\rightarrow) is used to indicate that the reaction proceeds in only one direction.
- For instance, the reaction between carbon and oxygen is an irreversible reaction:



- On the other hand, some reactions **do not go to completion**. Such reactions are called **reversible reactions or two-way reactions**. These reactions usually precede both in the forward and reverse reactions.
- The reaction in which the original reactants form products is the forward reaction and the reaction in which the products are converted to the original reactant is **the reverse (backward) reaction**.
- When the equation for a reversible reaction is written, a **double arrow (\rightleftharpoons)** indicates the reaction that goes from reactants to products to the right and from the products to the reactants to the left.

Reversible reactions have the following general form:

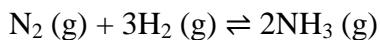


Where A and B are reactants, C and D are products and a, b, c, and d are balancing coefficients.

In this reaction:



For example, the formation of ammonia is a reversible reaction:



Exercise 5.1

Answer the following questions:

- How do you distinguish between reversible and irreversible reactions?
- Give examples of reversible and irreversible reactions.

Answer to Exercise 5.1.

Irreversible reaction

Products do not convert back
to reactants

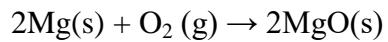
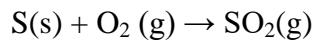
The reaction stops completely
and almost goes to completion

It can be carried out in an
open or closed vessel

It takes place in one direction.

It is represented by single
arrow “ \longrightarrow ”

2. i. Irreversible reactions



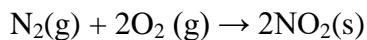
Reversible reaction

Products are convert back to
reactants

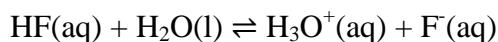
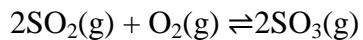
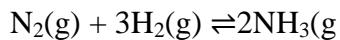
The reaction never goes to
completion all the time, some
reactants and products are present
in the resection mixture

It is generally carried out in a
closed vessel

It takes place in both directions. It
is represented by double arrow “
 \rightleftharpoons ”



ii. Reversible reaction



5.2.2 Attainment and Characteristics of Chemical Equilibrium

- For a reversible reaction, the rate with which the reactants form products is the forward reaction rate (r_f) and the rate with which the products combine to produce the original reactants is called the reverse reaction rate (r_r).
- At the beginning of the reaction, the forward reaction has a high rate, but gradually decreases with time.
- The reverse reaction has a very small rate at the beginning, but gradually an increase (as the products concentration increase) until equilibrium is established.
- The equilibrium is attained when the rate of the two opposing reactions become equal.
- That is at equilibrium:

$$\text{Rate of forward reaction } (r_f) = \text{Rate of reverse reaction } (r_r)$$

5.2.3 Conditions for attainment of Chemical Equilibrium

- Chemical equilibria are dynamic equilibria, i.e., reactants and products are interconverted continually, even though the overall composition of the reaction mixture does not change.
- Once the equilibrium is established, a change in one direction is balanced by changes in the other direction.
- To understand the concept, consider Figure 5.1, which shows the change in the reaction rate with time for the forward and reverse reactions.
- The rate of the forward reaction depends upon the concentration of reactants, whereas the rate of the reverse reaction depends upon the concentration of the products.
- Initially, only the reactants are present, therefore, the rate of the forward reaction is fast. The reaction in the reverse direction does not take place as no product is present yet.
- As the reaction progresses, the concentration of the reactants decreases and hence, the rate of forward reaction also decreases.
- However, due to the increase in the concentration of products, the rate of the reverse reaction increases.
- As the reaction further progresses a point will be reached when the rate of forward reaction becomes equal to the rate of reverse reaction.

- When this stage is attained, the concentrations of reactants and products do not change. The reaction has reached **chemical equilibrium**.

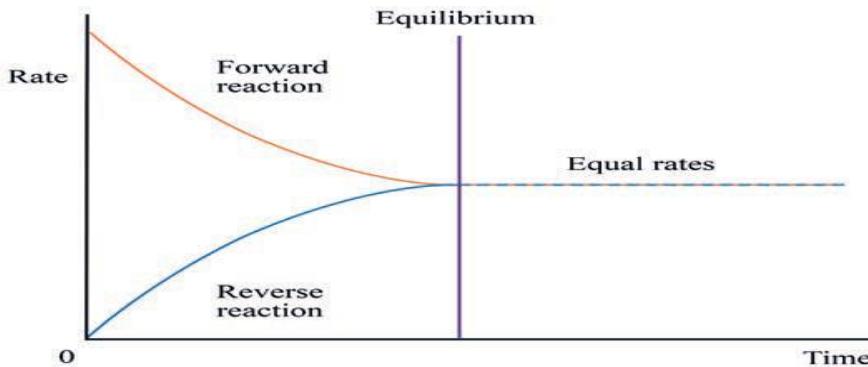


Figure 5.1 Change in the rate of reaction with time for forward and reverse reactions

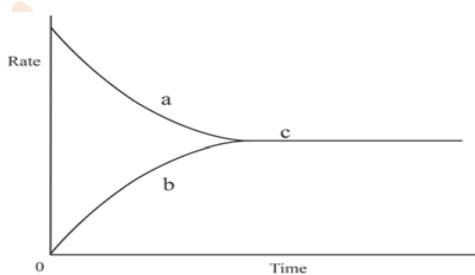
- Note that the concentrations of products and reactants are not necessarily equal at equilibrium, only the rate of forward and reverse reactions are equal. Generally, a reaction at equilibrium has the following characteristics:

- The reaction is reversible in nature.
- There is no net change in the concentrations of the reactants and products of the reaction.
- The rates of the forward and reverse reactions are equal.
- The reaction should take place in a closed vessel to react at equilibrium.
- The equilibrium is dynamic in nature.
- The concentrations of reactants and products are generally not equal.

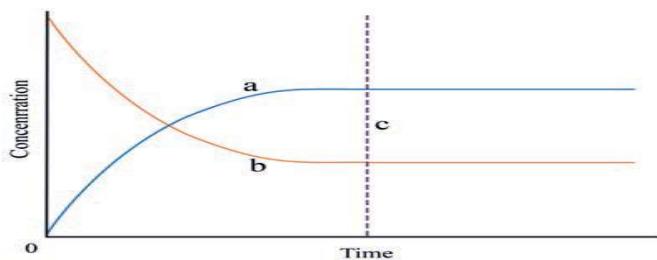
Exercise 5.2

Answer the following questions

1. Explain trends of the rates of the forward and reverse reactions for the following graph, using the labels a, b and c.



2. Explain what happens to the Concentration of the reactants and the concentration of the products in the graph using the labels a, b and c.



3. What are the conditions that remain constant at equilibrium?

Answer to Exercise 5.2

1. In the given **Figure (a)** rate of forward reaction (b) rate of reverse reaction, and (c) Equilibrium point. The rate of the forward reaction decreases and the rate of the reverse reaction increases.
2. In the given **Figure (a)** Concentration of product (b) concentration of reactants, and(c) equilibrium point. Concentration of reactants decreases, and concentration of product increases.
3. The conditions that remain constant at equilibrium include:
 - a. concentration of the reactants and the products.
 - b. the rate of forward and reverse reaction.

5.2.4 Equilibrium Expression and Equilibrium Constant

A. Law of Mass Action

- Mathematically the equilibrium constant is written based on the law of mass action or law of concentration action proposed by Cato Maximilian Guldberg and Peter Waage, in 1864.
 - **The law of mass action states** that “the rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respective coefficient in the balanced chemical reaction.”
 - The general equation that represents a reversible reaction is:
- $$aA + bB \rightleftharpoons cC + dD$$
- For the forward reaction A and B are reactants, and C and D are products. Assume that the reaction is homogeneous, in which all the reactants and the products are in the same state.
 - The rate of forward reaction (r_f) depends upon the concentrations of A and B as well as the rate of reverse reaction (r_r) depends upon the concentrations of C and D. These relations are expressed as follows:
 - $r_f \propto [A]^a[B]^b$ or $r_f = k_f[A]^a[B]^b$

- $r_r \propto [C]^c[D]^d$ or $r_r = k_f[C]^c[D]^d$
- Where $[A]$, $[B]$, $[C]$ and $[D]$ are the concentrations of A, B, C and D, and k_f and k_r are rate constants for the forward and reverse reactions, respectively.
- At equilibrium, the rate of forward reaction is equal to the rate of reverse reaction.
- Therefore, $r_f = r_r$ or $k_f[A]^a[B]^b = k_r[C]^c[D]^d$
- k_f and k_r are constant. Therefore, the ratio of k_f to k_r is also constant.
- $\frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_{eq}$
- The ratio of k_f and k_r is represented by K_{eq} , which is called **equilibrium constant**. $[A], [B], [C]$ and $[D]$ are concentrations of A, B, C, D, and A at equilibrium, respectively.
- When their concentrations are expressed in molarities, the K_{eq} is shown by K_c .
- When the reaction reactants and the products are gaseous, their concentrations can be expressed in terms of partial pressures.
- In such cases, the K_{eq} is denoted by K_p .

B. Equilibrium Constant Expression involving Concentration, K_c

- In homogeneous reactions, all reactants and products are present in the same physical state. While writing equilibrium constant expressions for such reactions, the following rules are followed.

- The concentrations of all the substances formed as products are written in the numerator (the top of the fraction).
 - The concentrations of all the reactants are written in the denominator (the bottom of the fraction).
 - The equilibrium concentrations of each species are raised to a power equal to the coefficient of that species written in the balanced chemical equation.
- For a general reaction at equilibrium:

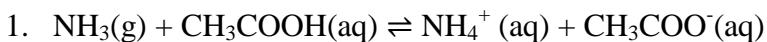


The expression for K_c is: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

- The unit of K_c depends upon the number of moles of the reactants and products involved in the reaction. Therefore, for the above general reaction, the K_c unit will be:

$$\begin{aligned} K_c &= \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{[\text{mol L}^{-1}]^c [\text{mol L}^{-1}]^d}{[\text{mol L}^{-1}]^a [\text{mol L}^{-1}]^b} \\ &= (\text{mol L}^{-1})^{(c+d)-(a+b)} \end{aligned}$$

Example 5.1, K_c expressions and units as well as K_c value determinations:



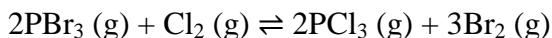
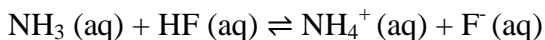
$$K_c = \frac{[NH_4^+][CH_3COO^-]}{[NH_3][CH_3COOH]} = \frac{[\text{mol}\cdot L^{-1}][\text{mol}\cdot L^{-1}]}{[\text{mol}\cdot L^{-1}][\text{mol}\cdot L^{-1}]} = 1$$



$$K_c = \frac{[H^+][F^-]}{[HF]} = \frac{[\text{mol}\cdot L^{-1}][\text{mol}\cdot L^{-1}]}{[\text{mol}\cdot L^{-1}]} = \text{mol}\cdot L^{-1}$$

Exercise 5.3

1. Write the equilibrium constant expressions (KC) for the following reactions:



3. For the reaction N₂ (g) + 3Cl₂ (g) \rightleftharpoons 2NCl₃ (g) an analysis of an equilibrium mixture is performed at a certain temperature. It is found that [NCl₃] = 1.9 × 10⁻¹ M, [N₂] = 1.4 × 10⁻³ M, and [Cl₂] = 4.3 × 10⁻⁴ M. Calculate KC for the reaction at this temperature.

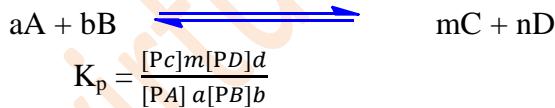
Answer to Exercise 5.3

1. a. $K_c = \frac{[NH_4^+][F^-]}{[NH_3][HF]}$ b. $K_c = \frac{[PCl_3]^2[Br_2]^3}{[PBr_3]^2[Cl_2]^3}$

2. $K_c = \frac{[NCl_3]^2}{[N_2][Cl_2]^3} = \frac{(1.9 \times 10^{-1})^2}{[1.4 \times 10^{-3}] \times (4.3 \times 10^{-4})^3} = 3.2 \times 10^{11} \text{ M}^{-2}$

C. Equilibrium Constant Expression involving Partial Pressure, K_p

- When all the reactants and the products are gases, their concentrations can be written in terms of partial pressures.
- In such cases the equilibrium constant is denoted by K_p, which is expressed as:
For a general reaction at equilibrium:



For the formation of ammonia: N₂ (g) + 3H₂ (g) \rightleftharpoons 2NH₃ (g)

- The expression of equilibrium constant in terms of molarities is:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

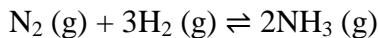
The expression of K_p is: $K_p = \frac{[PNH_3]^2}{[PN_2][PH_2]^3}$

- The unit of K_p is decided by the unit of pressure. If the partial pressure is expressed in atm, then the unit of K_p, will be:

$$K_p = \frac{[P_C]^m[P_D]^n}{[P_A]^a[P_B]^b} = \frac{[\text{atm}]^m[\text{atm}]^n}{[\text{atm}]^a[\text{atm}]^b} = (\text{atm})^{(m+n)-(a+b)}$$

If the partial pressure is measured in kPa, then the unit of K_p will be (kPa)^{(m+n)-(a+b)}

Example 5.2. 1. KP expressions and units as well as K P value determinations:



$$K_p = \frac{[PNH_3]^2}{[PN_2][PH_2]^3} = \frac{(atm)^2}{(atm)(atm)^3} = \frac{1}{(atm)^2}$$

2. The reaction for the formation of nitrosyl chloride was studied at 25 °C 2NO (g) + Cl₂ (g) ⇌ 2NOCl (g)

At equilibrium, the partial pressures were found to be 1.2, 5.0 × 10⁻² and 3.0 × 10⁻¹ atm for NOCl, NO and Cl₂, respectively. Calculate the value of KP for this reaction at 25 °C.

Solution:

Given: P_{NOCl} = 1.2 atm, P_{NO} = 5.0 × 10⁻² atm and P_{Cl₂} = 3.0 × 10⁻¹ atm

K_P expression for the reaction is

$$K_p = \frac{[PNOCl]^2}{[PNO]^2[PCL_2]}$$

Substitution of the give values in the expression gives

$$K_p = \frac{[1.2\text{atm}]^2}{[5.0 \times 10^{-2}\text{ atm}]^2[3.0 \times 10^{-1}\text{ atm}]} = 1.920 \text{ atm}^{-1}$$

Exercise 5.4

1. Write the equilibrium constant expressions (KP) for the following reactions:

- a. 2SO₂ (g) + O₂ (g) ⇌ 2SO₃ (g)
- b. N₂ (g) + O₂ (g) + Br₂ (g) ⇌ 2NOBr (g)

2. The following equilibrium pressures were observed at a certain temperature for the reaction 2NO₂(g) ⇌ 2NO (g) + O₂ (g)

$$P_{NO_2} = 0.55 \text{ atm}$$

$$P_{NO} = 6.5 \times 10^{-5} \text{ atm},$$

$$P_{O_2} = 4.5 \times 10^{-5} \text{ atm}$$

Calculate the value for the equilibrium constant at this temperature

Answer to Exercise 5.4

1. a. $K_p = \frac{[PSO_3]^2}{[PSO_2]^2[P O_2]}$ b. $K_p = \frac{[PNOBr]^2}{[PN_2][P O_2][PBr_2]}$

$$2. \frac{(NO_2)^2 \times P O_2}{[PNO_2]} = \frac{(6.5 \times 10^{-5})^2 \times 4.5 \times 10^{-5}}{(0.55)^2} = 6.28 \times 10^{-13} \text{ atm}$$

D. Equilibrium Constant for Heterogeneous Reactions

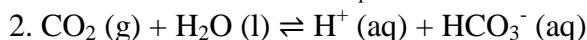
- In heterogeneous reactions, the reactants and products are present in more than one physical state.

- For example, thermal decomposition of calcium carbonate is an example of heterogeneous reaction.
- $$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$
- $$\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$$
- $$\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$$
- When we write the equilibrium constant expression for heterogeneous reactions, we do not include the concentration of pure solids or pure liquids in the expression.
 - This is because; the position of equilibrium does not depend on the amounts of pure solids or pure liquids present.
 - The molar concentrations of pure solids liquids are constant at a given temperature.

Example 5.3, The equilibrium constant expressions for some heterogeneous reactions are shown below:



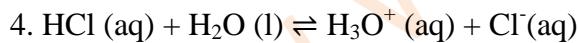
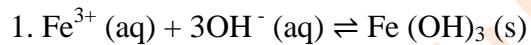
$$K_c = [\text{CO}_2] \quad \text{or} \quad K_p = P_{\text{CO}_2}$$



$$K_c = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]}$$

Exercise 5.5

Write the equilibrium constant expression for the following reactions:



Answer to Exercise 5.5

1. $K_c = \frac{1}{\text{Fe}^{3+}[\text{OH}^-]^3}$

2. $K_c = [\text{Cl}_2] \quad \text{or} \quad K_p = \text{PCl}_2$

3. $K_c = [\text{N}_2][\text{Br}_2]^3 \quad \text{or} \quad K_p = [\text{P}_N][\text{P}_{\text{Br}}]^3$

4. $K_c = [\text{H}_3\text{O}^+][\text{OH}^-]$

E. Relation between K_c and K_p

For the general reaction



K_C and K_P expressions are:

$$K_C = \frac{[C]^c [D]^d}{[A]^a [B]^b} = \frac{C_C^c C_D^d}{C_A^a C_B^b}$$

$$K_P = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

- Assume that all gaseous species behave like an ideal gas. Thus, according to the ideal gas equation, the partial pressure (P) of a gas is given by: $P = nRT/V$ and $n/V = C$
- Where n is amount of the gaseous species in moles, R is gas constant, T is temperature, in kelvin, V is volume of the reaction mixture and C is concentration in molarity.
- Thus, partial pressure of each species for the above general reaction is:

$$P_A = nART/V = C_A RT$$

$$P_B = nBRT/V = C_B RT$$

$$P_C = nCRT/V = C_C RT$$

$$P_D = nDRT/V = C_D RT$$

$$K_P = \frac{[n.C.RT/V]^c [n.D.RT/V]^d}{[n.A.RT/V]^a [n.B.RT/V]^b} = \frac{C_C^c C_D^d}{C_A^a C_B^b} (RT)^{\Delta n}$$

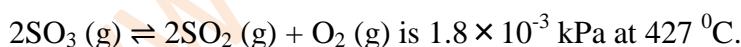
Where $\Delta n = (c + d) - (a + b)$ for gaseous species.

$$K_P = K_C (RT)^{\Delta n}$$

When the number of gaseous reactants and products are equal then, $a + b = c + d$

Therefore, $\Delta n = 0$ and, hence $K_P = K_C$

Example 5.4, The equilibrium constant (K_P) for the reaction.



Calculate K_C for the reaction at the same temperature

Solution:

Given: $K_P = 1.8 \times 10^{-3}$ kPa = 1.8 Nm^{-2} , $T = 427^\circ\text{C} = 700 \text{ K}$ and $R = 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1}$

We know that $K_P = K_C (RT)^{\Delta n}$

For the given reaction, $\Delta n = (2 + 1) - 2 = 1$

Therefore, $K_c = K_p/(RT)$

$$K_c = \frac{K_p}{RT} = \frac{1.8 \text{ atm}^{-2}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 1.700 \text{ K}} = 3.14 \times 10^{-4} \text{ mol m}^{-3}$$

Exercise 5.6

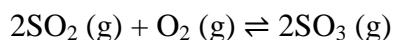
1. At 327°C , the equilibrium concentrations are

$[\text{CH}_3\text{OH}] = 0.15 \text{ M}$, $[\text{CO}] = 0.24 \text{ M}$ and $[\text{H}_2] = 1.1 \text{ M}$ for the reaction:



Calculate K_p at this temperature.

2. At 1100 K , $K_p = 0.25$ for the reaction:



What is the value of K_c at this temperature?

3. When 0.500 mol of N_2O_4 is placed in a 4.00 L reaction vessel and heated

at 400 K , 79.3% of the N_2O_4 decomposes to NO_2 . The decomposition reaction is: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, Calculate K_c and K_p of the reaction at 400 K .

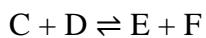
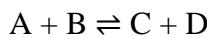
Answer to Exercise 5.6

1. $K_p = 4,686.34 \text{ atm}$

2. $K_c = 22.55$

3. $K_c = 1.51$, $K_p = 49.6$

- Consider the reactions in which the product species in one equilibrium system are involved in the second equilibrium process.
- $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ (i)
- $\text{C} + \text{D} \rightleftharpoons \text{E} + \text{F}$ (ii)
- The equilibrium constant expressions for reaction (i) and (ii), respectively, are
- $K_1 = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$ and $K_2 = \frac{[\text{F}][\text{E}]}{[\text{C}][\text{D}]}$
- The overall reaction is given by the sum of the two reactions:

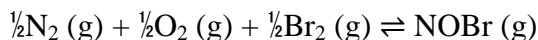


- The equilibrium constant expression for the overall reaction is:

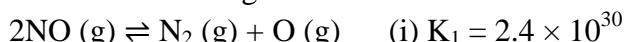
$$K_{\text{overall}} = \frac{[F][E]}{[A][B]} = K_1 \times K_2 = \frac{[C][D]}{[A][B]} \times \frac{[F][E]}{[C][D]}$$

- Note that if a reaction is the sum of two or more reactions, the equilibrium constant of the overall reaction is equal to the product of the equilibrium constants of the individual reaction.
- That is: $K_{\text{overall}} = K_1 \times K_2 \times K_3 \dots \dots$

Example 5.5, Determine K_C for this reaction

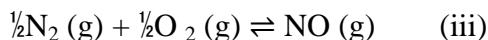


From the following information at 298 K.



Solution:

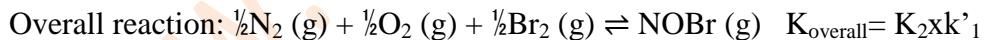
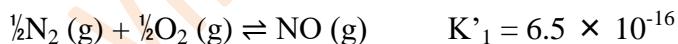
To calculate K_C of the overall reaction, reactions (i) and (ii) must add up to give the overall reaction. To do this, first reverse reaction (i) and multiply $\frac{1}{2}$, so that it will have the form:



Since the reaction equation is reversed and multiplied by $\frac{1}{2}$, the equilibrium constant for reaction (iii), K'_1 is calculated as:

$$K'_1 = (1/K_1)^{1/2} = (1/2.4 \times 10^{30})^{1/2} = 6.5 \times 10^{-16}$$

Now, add reactions (ii) and (iii):



Thus, the equilibrium constant for the overall reaction is:

$$K_{\text{overall}} = K_2 \times K'_1 = 1.4 \times 6.5 \times 10^{-16} = 9.1 \times 10^{-16}$$

Exercise 5.7

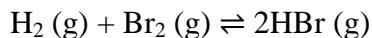
1. The following equilibrium constants were determined at 1123 K:



Write the equilibrium constant expression K_c and calculate the equilibrium constant at 1123 K for the following reaction.

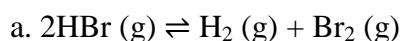


2. For the reaction:

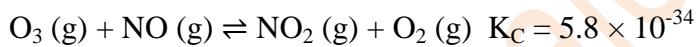


$$K_p = 7.1 \times 10^4 \text{ at } 700 \text{ K.}$$

What is the value of K_p for the following reactions at the same temperature?



3. Calculate a value for the equilibrium constant for the reaction:



Answer to Exercise 5.7

1. $K_C = \frac{[COCl_2]^2}{[CO_2]^2[Cl_2]^2} = K_{C1} \times (K_{C2})^2 = 4.24 \times 10^{15}$

2. a. 1.41×10^{-5}

b. 2.66×10^2

3. 2.53×10^{81}

5.2.5 Application of Equilibrium Constant

- Useful information can be obtained from the value of equilibrium constant of a given reaction at a particular temperature.
- The equilibrium constant of a reaction enables us to:
 - predict the composition of an equilibrium mixture (or predict extent of reaction);
 - predict the direction of the reaction

- Calculate the equilibrium concentrations of reactants and products from initial concentrations.

A. predict the composition of an equilibrium mixture

- K_C or K_P value is used predict the extent of the reactions at equilibrium.
- Very large values of K_C or K_P indicate that at equilibrium the reaction system consists of mainly products and the equilibrium lies to the right, i.e., the reaction goes near to completion.
- An equilibrium mixture contains about as much product as can be formed from the given initial amounts of reactants.
- However, if K_C or K_P values are very small, the equilibrium mixture consists of mainly reactants and the reaction lies far to the left.
- Note that a reaction goes essentially to completion if K_C or $K_P > 10^{10}$ and not at all if K_C or $K_P < 10^{-10}$.

Exercise 5.8

1. Predict whether the formation of product is favored for the following reactions:
 - a. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_C = 3.6 \times 10^8$
 - b. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_C = 5.0 \times 10^{-3}$
 - c. $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ $K_C = 4.45 \times 10^{-2}$
2. Arrange the following reactions in order of their increasing tendency to proceed towards completion (least extent to greatest extent):
 - a. $CO + Cl_2 \rightleftharpoons COCl_2$ $K_C = 13.8$
 - b. $2CO_2 \rightleftharpoons 2CO + O_2$ $K_C = 2.0 \times 10^{-6}$
 - c. $2NOCl \rightleftharpoons 2NO + Cl_2$ $K_C = 4.7 \times 10^{-4}$

Answer to Exercise 5.8

1. Given the equations
 - a. Formation of the product is favored, since K_C is extremely large.
 - b. Formation of the product is not favored, since K_C is small.
 - c. Formation of the product is favored, since K_C is extremely small
2. Increasing tendency to proceed towards completion (least extent to greatest extent). $K_c = 2.1 \times 10^{-4} < (c) K_c = 4.7 \times 10^{-4} < (a) K_c = 13.8$

B. predict the direction of the reaction

- To predict the direction of a reaction of a reaction, we first calculate the reaction quotient (Q_C) and compare it with the value of the equilibrium constant.
- The reaction quotient is the ratio of concentrations of products to the concentrations of reactants each raised to the power equal to its stoichiometric coefficient.
- Q_C has the same form as K_C , but involves concentrations that are not necessarily equilibrium concentrations.
- For the general reaction:



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- Where $[A]$, $[B]$, $[C]$ and $[D]$ are concentrations at any stage during the reaction.
- At the initial stages of the reaction, the amount of product formed is low, therefore, the value of Q is small.
- As the reaction progresses, the value of Q also increases due to the increase in concentration of the products.
- When the reaction attains equilibrium, Q becomes equal to the equilibrium constant.
- To predict the direction of the reaction, Q is compared with K_{eq} :
 1. $Q = K_{eq}$, the reaction is at equilibrium.
 2. $Q < K_{eq}$, then the reaction will proceed to the right (the forward direction) to consume the reactants and to form more products until the equilibrium is reached.
 3. $Q > K_{eq}$, the reaction will proceed to the left (the reverse direction) to reduce the products until the equilibrium is reached.

Example 5.6 At a certain temperature, the reaction:

$\text{CO (g)} + \text{Cl}_2 (\text{g}) \rightleftharpoons \text{COCl}_2 (\text{g})$ has an equilibrium constant $K_c = 13.8$. Is the following mixture an equilibrium mixture? If not, to which direction (forward or backward) will the reaction proceed to reach equilibrium?

$[\text{CO}]_0 = 2.5 \text{ mol L}^{-1}$; $[\text{Cl}_2]_0 = 1.2 \text{ mol L}^{-1}$, and $[\text{COCl}_2]_0 = 5.0 \text{ mol L}^{-1}$.

Solution:

Given: $[\text{CO}]_0 = 2.5 \text{ mol L}^{-1}$ $[\text{COCl}_2]_0 = 5.0 \text{ mol L}^{-1}$

$[\text{Cl}_2]_0 = 1.2 \text{ mol L}^{-1}$ $K_C = 13.8$

The expression for Q_C is:

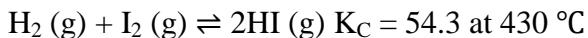
$$Q_C = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{5.0 \text{ mol L}^{-1}}{2.5 \text{ mol L}^{-1} \times 1.2 \text{ mol L}^{-1}} = 1.67$$

$Q_C < K_C$ thus the reaction mixture is not an equilibrium mixture. So, the reactants should combine to form more products to reach equilibrium, i.e., the reaction should proceed further to the right (the forward direction).

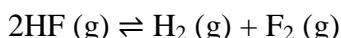
Exercise 5.9

1. At a start of a reaction, there are 0.0218, 0.0145, ad 0.0783 moles of H₂, I₂ and HI, respectively, in a 3.5 liter reaction vessel at 430 °C.

Decide whether or not the reaction is at equilibrium. If not, predict in which direction the reaction will proceed. The equilibrium reaction is:



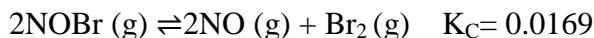
2. At a very high temperature, the following reaction has $K_C = 1.0 \times 10^{-13}$



At a certain time, the concentrations of HF, F₂ and H₂ were 0.4 M,

0.004 M and 0.001 M, respectively. Is the system at equilibrium? If not, what must happen for the equilibrium to be reached?

3. The decomposition of NOBr is represented by the equation:



At equilibrium the concentrations of NO and Br₂ are 1.05×10^{-2} M and 5.24×10^{-3} M, respectively. What is the concentration of NOBr?

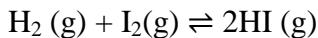
Answer to Exercise 5.9

1. $Q_C = 19.4$ which is less than K_C . Thus, the reaction mixture is not an equilibrium mixture. The reactants should combine to form more products to reach equilibrium, i.e., the reaction should proceed further to the right (the forward direction).
2. $Q_C = 2.5 \times 10^{-5}$ which is greater than K_C . Implies that the reaction mixture is not an equilibrium mixture. The reaction should proceed to the left (the reverse direction) to reduce the products until the equilibrium is reached.
3. 5.7×10^{-2} M

C. Calculate the equilibrium concentrations

- Once equilibrium constant is determined for a reaction, it can be used to calculate the concentrations or partial pressures in an equilibrium mixture. To calculate equilibrium concentrations, follow the following steps:
- Write the balanced equation for the reaction and then the K_C or K_P expressions.
 - List the initial concentrations.
 - Calculate Q_C or Q_P to determine the direction of the reaction, if initial concentrations of the reactants and products are given.
 - Define the change in concentration needed to reach equilibrium and find the equilibrium concentrations by using the change of the initial concentrations.
 - Substitute the equilibrium concentrations into the K_C or K_P expression, solve for the unknown.
 - Check whether the calculated equilibrium concentrations give the correct value of K_C or K_P .

Example 5.7 The equilibrium constant, K_C is 69 for the following reaction.



Given that 1 mole of H_2 and 2 moles of I_2 were added to a 500 mL reaction vessel.

Determine the molar concentrations in the mixture at equilibrium.

Solution:

1. The equation for the reaction is

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_C = \frac{[HI]^2}{[H_2][I_2]} = 69$$

$$[HI]_{\text{initial}} = [HI]_0 = 0$$

$$[H_2]_0 = \frac{1\text{ mol}}{0.5\text{ mL}} = 2 \text{ mol L}^{-1} = 2\text{ M}$$

$$[I_2]_0 = \frac{2\text{ mol}}{0.5\text{ mL}} = 4 \text{ mol L}^{-1} = 4\text{ M}$$

2. No need to calculate QC since $[HI]_0 = 0$

3. Let the number of moles of H_2 (or I_2) consumed per liter to reach an equilibrium is x .

Since the stoichiometric proportion of each reactant (H_2 and I_2) and the product HI is 1:2, for every x of both reactants consumed the concentration of HI formed is $2x$. These changes are shown here:

Concentration	H_2	I_2	\rightleftharpoons	$2HI$
Initial	2.0 M	4.0 M		0
Change	-x	-x		+2x
Equilibrium	2.0 M-x	2.0 M-x		2x

4. Substituting the equilibrium concentrations:

$$K_C = \frac{[HI]^2}{[H_2][I_2]} \quad 64 = \frac{(2x)^2}{(2.0 M-x)(2.0 M-x)} = \frac{(2x)^2}{x^2 - 6x + 8} = \frac{4x^2}{x^2 - 6x + 8}$$

By rearranging, we get:

$$4x^2 = 64x^2 - 384x + 512$$

By rearranging again, we get:

$$60x^2 - 384x + 512 = 0$$

This is a quadratic equation of the general formula $ax^2 + bx + c = 0$

The values of x can be obtained from the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this example $a = 60$, $b = -384$ and $c = 512$. Therefore:

$$x = \frac{-(-384) \pm \sqrt{(-384)^2 - 4 \times 60 \times 512}}{2 \times 60}$$

$$x = \frac{384 \pm \sqrt{2.5 \times 10^4}}{120}$$

$$x = \frac{384 \pm 158}{120}$$

$$x = 1.9 \text{ M or } 4.5 \text{ M}$$

But the change in concentration cannot be greater than the initial concentrations of the H₂, i.e., 2 M. Thus, only 1.9 is a reasonable value. Therefore, the equilibrium concentration of each species is:

$$[\text{H}_2] = 2.0 - x = 2.0 \text{ M} - 1.9 \text{ M} = 0.1 \text{ M}$$

$$[\text{I}_2] = 4.0 - x = 4.0 \text{ M} - 1.9 \text{ M} = 2.1 \text{ M}$$

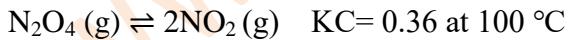
$$[\text{HI}] = 2x = 2(1.9 \text{ M}) = 3.8 \text{ M.}$$

$$\text{Check , Kc} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(3.8 \text{ M})^2}{(0.1 \text{ M})(2.1 \text{ M})} = 68.76 \approx 69$$

Therefore, the calculated equilibrium concentrations are correct.

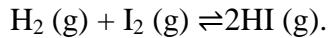
Exercise 5.10

1. for the equilibrium:



A sample of 0.25 mol N₂O₄ is allowed to dissociate and come to equilibrium in a 1.5 L flask at 100°C. What are the equilibrium concentrations of NO₂ and N₂O₄?

2. At 400°C , the equilibrium constant for the reaction is 64:



A mixture of 0.250 mol H₂ and 0.250 mol I₂ was introduced into an empty 0.75 L reaction vessel at 400°C , find the equilibrium concentrations of all components.

Answer to Exercise 5.10

- For the equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

The equilibrium constant expression is written as

$$= \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.36$$

Initial concentration of N_2O_4 is 0.25 mol/1.5 L, which is 0.167 M.

$$\text{Therefore, } \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{(0.167-x)} = 0.36$$

By solving the equation, be sure you get $[\text{NO}_2] = 0.17 \text{ M}$, $[\text{N}_2\text{O}_4] = 0.085 \text{ M}$

- The concentration table may be constructed as follows:

Concentration	H_2	+	I_2	\rightleftharpoons	2HI
Initial (M)	0.33		0.33		0
Change (M)	-x		-x		+2x
Equilibrium (M)	0.33 - x		0.33 - x		2x

The equilibrium constant expression becomes:

$$\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(0.33-x)(0.33-x)} = 64$$

After solving for x, we get:

$$[\text{HI}] = 0.532 \text{ M} \text{ and } [\text{H}_2] = [\text{I}_2] = 6.7 \times 10^{-2} \text{ M}$$

5.2.6 Changing Equilibrium Conditions; Le Chatelier's Principle

- Consider a chemical reaction that is initially at equilibrium.
- Often a change in conditions will displace the reaction from equilibrium.
- The reaction then shifts toward one direction or the other (left to right or right to left as the equation is written) as it changes to a new equilibrium state.
- The direction of an equilibrium reaction will shift when a change in conditions occurs as predicted by Le Chatelier's principle.
- Le Châtelier's principle states that if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.
- The factors whose change may affect reaction equilibrium include **concentration of a reactant or product, reaction volume or applied pressure, and temperature**.

A. Effect of Change in The Concentration

- When a system at equilibrium is disturbed by a change of concentration of one of the components, the system reacts in the direction that reduces the change.
- That is:
 - If the concentration increases, the system reacts to reduce some of it.
 - If the concentration decreases, the system reacts to produce some of it.
- Consider the general reaction:

- $A + B \rightleftharpoons C + D$
- An increase in the concentration of A or B, or both, shifts the equilibrium position to the right, that is, toward the formation of more products.
- Similarly, a decrease in the concentration of C or D, or both, shifts the equilibrium position to the right.
- However, an increase in the concentration of C or D, or both (or a decrease in A or B, or both) shifts the equilibrium position to the left.
- Note that adding or removing reactants or products changes the value of Q_C . It does not change the value of K_C .

Exercise 5.11

A and B react to produce C according to the following chemical equation:



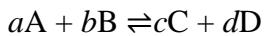
Amounts of A and B are added to an equilibrium reaction mixture of A, B, and C such that when equilibrium is again reached, the amounts of A and B are doubled in the same volume. How is the amount of C changed?

Answer to Exercise 5.11

- The amount of C is also doubled when the equilibrium is re-established.

B. Effect of Change in Pressure

- A change in pressure affects only equilibrium systems that involve gases.
- Pressure changes can occur in three ways:
 - changing the concentration of a gaseous component
 - adding an inert gas
 - changing the volume of the reaction vessel.
- Adding an inert gas has no effect on the equilibrium position. The reason is that inert gas molecules do not take part in the reaction and therefore cannot affect the equilibrium in any way.
- However, the addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.
- A pressure change obtained by changing the volume can affect the yield of product in a gaseous reaction if the reaction involves a change in total moles of gas.
- According to Le Châtelier's principle, if a pressure at equilibrium is increased (volume decreased) then the reaction will proceed in the direction that relieves the pressure.
- Thus, an increase in pressure of the system at a constant temperature shifts the equilibrium in the direction that produces a smaller number of gaseous molecules,
- Whereas a decrease in pressure shifts in the direction of greater number (moles) of gaseous molecules.
- For a general reaction:

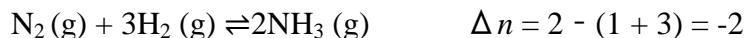


- The effect of pressure is decided by:

$$\Delta n, \Delta n = (c + d) - (a + b)$$

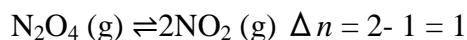
- If $\Delta n > 0$, the total moles of products is greater than the total moles of reactants.
Lowering of pressure will favor the reaction in the forward direction.
- If $\Delta n < 0$, the total moles of products is less than the total moles of reactants.
Increasing the pressure will favor the reaction in the forward direction.
- If $\Delta n = 0$, the change in pressure has no effect on the position of equilibrium.

For example, in the formation of ammonia:



Therefore, an increase in pressure at equilibrium will favor the forward reaction.

For the dissociation of di-nitrogen tetroxide:



The decrease in pressure at equilibrium, favors the forward reaction.

Exercise 5.12

1. Look at each of the following equations and decide whether an increase of pressure obtained by decreasing the volume will increase, decrease, or have no effect on the amounts of products.

- $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
- $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$
- $C(s) + S_2(g) \rightleftharpoons CS_2(g)$

Answer to Exercise 5.12

- The increase in pressure at equilibrium, favors the forward reaction.
- The increase in pressure at equilibrium, favors the reverse reaction.
- The change in pressure has no effect on the position of equilibrium

C. The Effect of Change in Temperature

- Temperature has a profound effect on most reactions. Reaction rates usually increase with an increase in temperature, meaning that equilibrium is reached sooner.
- Many reactions have very low rates at room temperature, but speed up at higher temperatures.
- Change of temperatures also changes the equilibrium constant values of a reaction.
- Consider the KC values of the methanation reaction at different temperatures:
 $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \quad \Delta H^\circ = -206.2 \text{ kJ}$

K_C for methanation at different temperatures

298	4.7×10^{27}
800	1.38×10^5
1000	2.54×10^2
1200	3.92

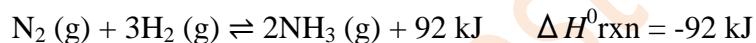
- Reversible reactions are endothermic in one direction and exothermic in the other.

Consider a general reaction:



- If we consider heat as a reaction component of the aquarium system, a rise in temperature “adds” heat to the system and a drop in temperature “removes” heat from the system.
- As with a change in any other component, the system shifts to reduce the effect of the change. Therefore, an increase in temperature at a constant pressure and concentration favors the endothermic reaction.
- Whereas, a decrease in temperature favors the exothermic reaction.

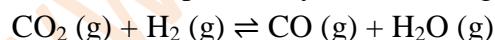
For example, formation of ammonia is an exothermic process:



- From the equation we can see that 92 kJ of heat is released when NH₃ is produced from N₂ and H₂.
- Therefore, the forward reaction is exothermic, while the reverse reaction is endothermic.
- Thus, an increase in temperature favors the decomposition of ammonia to N₂ and H₂, i.e., shifts the equilibrium to the left or reactant side.
- Whereas, a decrease in temperature favors the formation of ammonia (shifts the equilibrium to the right or product side).

Exercise 5.13

Consider the possibility of converting CO₂ to CO by the endothermic reaction:



Is a high or a low temperature more favorable for the production of carbon monoxide? Explain.

Answer to Exercise 5.13

- Higher temperature favours converting of CO₂ to CO. i.e., higher temperature shifts the equilibrium to the right. Whereas, low temperature favours the reverse reaction or shifts the equilibrium to the left.

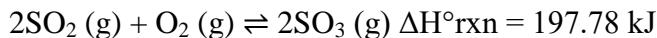
D. Effect of Catalyst

- A catalyst is a substance that increases the rate of a reaction but is not used up in the reaction.

- A catalyst is shown over the arrow in an equation for a chemical reaction and does not appear in equilibrium constant or in the reaction quotients.
- Addition of a catalyst **does not shift the equilibrium position**. Because a catalyst increases the rates of both forward and reverse reactions by the same factor, it has no effect on the equilibrium composition of a reaction mixture. It speeds up reaching equilibrium but does not change either the value of the equilibrium constant or the equilibrium concentrations.

Exercise 5.14

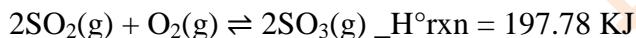
Predict the effect of the following changes on equilibrium;



- increasing pressure at constant temperature
- increasing temperature at constant pressure
- adding a catalyst.

Answer to Exercise 5.14

Predict the effect of the following changes on equilibrium



- Favors forward reaction
- Favor forward reaction
- Equally affect both forward and reverse reaction or it cannot shift the equilibrium position.

5.7.2 Equilibrium and Industry

- Industrial processes are designed to give maximum possible yield of the products.
- The conditions for carrying out the reactions are varied based on Le Chatelier's principle.
- The following processes demonstrate application of Le Chatelier's principle in the industry.

A. Haber Process for the Manufacture of Ammonia

- In 1909, Fritz Haber established the conditions under which atmospheric nitrogen, N_2 , would be converted to ammonia, NH_3 , by reacting it with hydrogen, H_2 .
- The Haber synthesis was developed into an industrial process by Carl Bosch.
- The reaction between N_2 and H_2 to produce NH_3 is an exothermic equilibrium reaction.
- It releases 92.4 kJ/mol of energy at 298 K.

Hear, Pressure
Catalyst



- According to Le Chatelier's principle, the production of ammonia is favored by high pressure and low temperature. However, the rate of the reaction at

lower temperature is extremely slow, so a higher temperature must be used to speed up the reaction which results in a lower yield of ammonia. The equilibrium expression for the reaction is:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

- As the temperature increases, the equilibrium constant decreases and the yield of ammonia decreases.

Temperature (°C)	K _{eq}
25	6.4×10^2
200	4.4×10^{-1}
300	4.3×10^{-3}
400	1.6×10^{-4}
500	1.5×10^{-5}

- In the industrial production of NH₃ by Haber process, the reaction rate is increased by:
 - Adding a catalyst such as iron. It speeds up the reaction by lowering the activation energy so that the N₂ bonds and H₂ bond can be more readily broken.
 - Increasing reaction temperature. When temperature is increased, reactant molecules will get sufficient energy to overcome the energy barrier (activation energy) so that the reaction is faster at higher temperatures, but the yield of ammonia is lower at higher temperature.
- At 200 °C and pressure above 750 atm, the yield of ammonia is almost 100 %, i.e., the reactants are completely converted to ammonia. Increasing the pressure increases the final yield of ammonia, however high pressures are expensive to produce and difficult to manage. So, the Haber process is carried out at pressures between 200 and 400 atm and a temperature of 500 °C.
- The effect of temperature and pressure on the percentage yields of ammonia for the Haber process is shown in figure 5.2

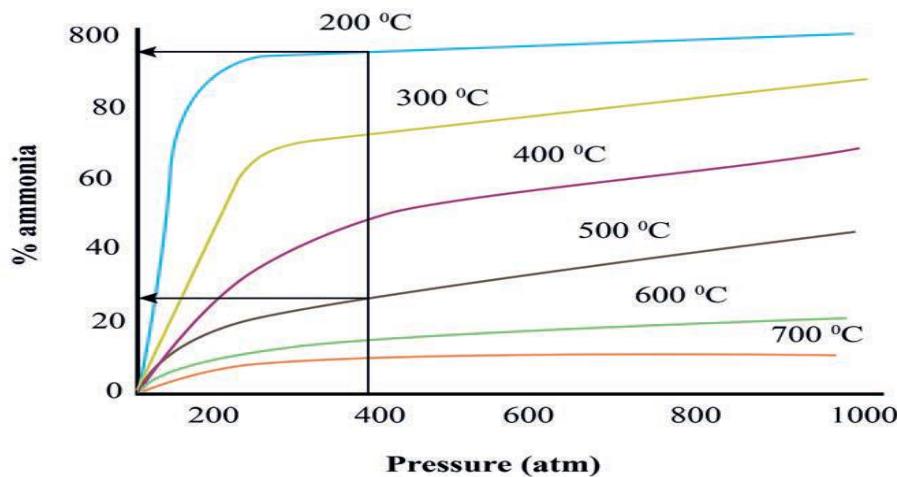


Figure 5.2 The effect of temperature and pressure on the percentage yields of ammonia for Haber process

- In the commercial production of ammonia, NH₃ is continuously removed as it is produced. Removing the products causes more N₂ and H₂ to combine according to Le Chatelier's principle. The reaction never reaches equilibrium as the gas mixture leaving the reactor is cooled to liquefy and remove the ammonia. The remaining mixture of reactant gases is recycled through the reactor. The heat released by the reaction is removed and used to heat the incoming gas mixture.
- Figure 5.3 shows a simplified flow diagram for the Haber process:

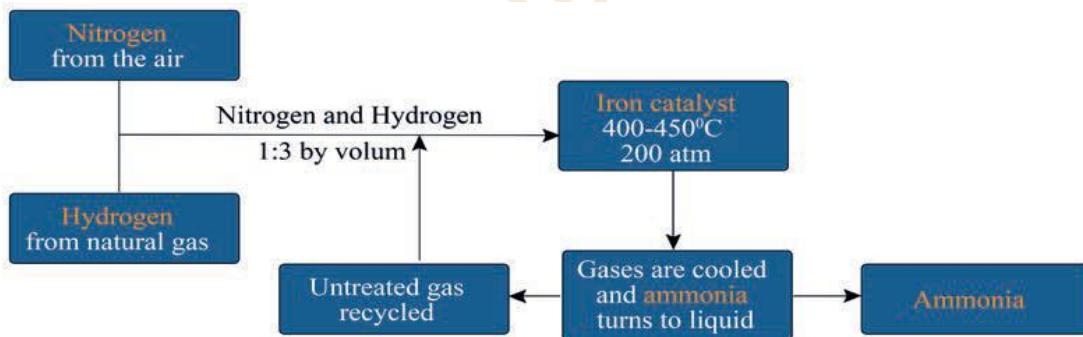


Figure 5.3 A flow Diagram of the Haber Process

Exercise 5.15

Answers the following questions:

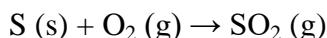
1. Which compound is manufactured by the Haber process?
2. What are the raw materials used in the Haber process?
3. What is the role of iron in the Haber process?

Answer to Exercise 5.15

1. Ammonia
2. Nitrogen and hydrogen
3. Catalyst, to speed up the ammonia production process.

B. Contact Process for the Manufacture of Sulfuric Acid

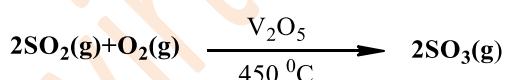
- The Contact process is the production of sulphuric acid, H₂SO₄, by the catalytic oxidation of sulphur dioxide, SO₂, to sulphur trioxide, SO₃. It is a reversible reaction:
- 2SO₂(g) + O₂(g) ⇌ 2SO₃(g) ΔH = -196 kJ
- The Contact process involves the following steps:
 - i. Preparation of sulphur dioxide gas, SO₂, by burning pure sulphur in the presence of excess air:



To improve the efficiency of a catalyst (in the next step), various impurities present in the mixture of SO₂ and air are first removed.

- ii. Conversion of SO₂ to sulphur trioxide, SO₃

Oxidation of SO₂ to SO₃ takes place at 450 °C in the presence of a catalyst, a vanadium (V) oxide (V₂O₅):



- iii. Converting sulfur trioxide into sulfuric acid, H₂SO₄

- SO₃(g) is dissolved in concentrated H₂SO₄ (98 %) to produce disulphuric acid or pyrosulphuric acid, also known as fuming sulphuric acid or oleum, H₂S₂O₇:

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$
- Converting sulfur trioxide to sulfuric acid cannot be done just by adding water, as the reaction is so uncontrollable that it creates a fog of sulfuric acid:

- iv. Dilution of H₂S₂O₇ to obtain H₂SO₄

- A calculated amount of water is added to obtain sulphuric acid of desired strength:



- The oxidation of SO_2 to SO_3 (step ii) is an exothermic reaction. So, according to Le Chatelier's principle, higher temperatures will force the equilibrium position to shift to the left, favoring the production of SO_2 , whereas lower temperatures would favor the production of SO_3 . However, the rate of reaching equilibrium at the lower temperatures is extremely low. At higher temperature, equilibrium is reached rapidly but the yield of SO_3 is lower. The temperature about 450°C is a compromising situation whereby a faster reaction rate results in a slightly lower yield.
- Similarly, at higher pressures, the equilibrium position shifts to the least numbers of gaseous molecules, i.e., SO_3 . In the Contact process, V_2O_5 is also used to speed up the rate of the reaction. Figure 5.4 shows the Contact process for the manufacture of H_2SO_4 .

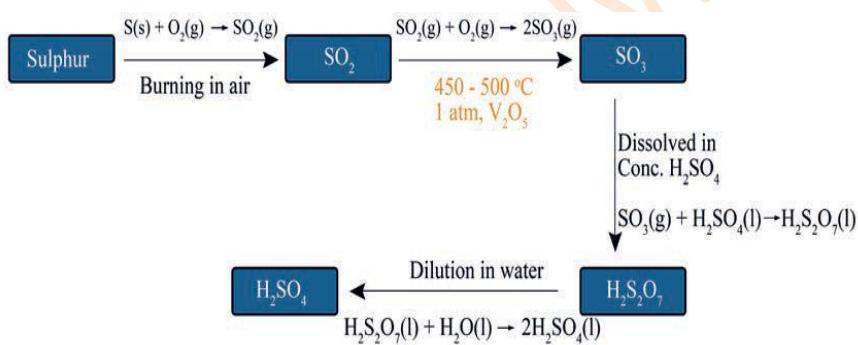


Figure 5.4 A flow Diagram of the Contact Process

Exercise 5.16

Answer the following questions:

1. What is a mixture of H_2SO_4 and free SO_3 ?
2. What are the raw materials for making SO_2 in the Contact process?
3. Why is SO_3 not directly added to make H_2SO_4 ?

Answer to Exercise 5.16

1. It is disulphuric acid or pyrosulphuric acid, also known as fuming sulphuric acid or oleum, $\text{H}_2\text{S}_2\text{O}_7$
2. Elemental sulphur
3. Because the reaction is explosive or uncontrollable.

UNIT SUMMARY

- A system is said to be at equilibrium when its macroscopic properties like temperature, pressure, concentration and energy do not change with time without any outside help.
- The equilibrium is dynamic in nature which means that although the macroscopic properties do not change, the processes do not stop at molecular level.
- Chemical equilibrium is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.
- According to the law of mass action the rate at which A and B combine is directly proportional to the product of their concentration terms each raised to the power of its respected coefficient in the balanced chemical reaction.
- For a general reaction at equilibrium $aA + bB \rightleftharpoons mM + nN$ the expression for K_C is:

$$K_C = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

- The expression for K_P is $K_P = \frac{[P_M]^m [P_N]^n}{[P_A]^a [P_B]^b}$ provided that all A, B, M and N are in gaseous state
 - The unit of K_C is $(\text{mol L}^{-1})^{(m+n)-(a+b)}$ and the unit of K_P is $(\text{atm})^{(m+n)-(a+b)}$
 - $K_P = K_C (RT)^{\Delta n}$
 - When $K_C > 1$ the formation of products is favored at equilibrium.
 - When $K_C < 1$, So the formation of products is not favored at equilibrium.
 - When $K_C = 1$, it indicates that the reactants and the products are present in equal amounts.
 - The reaction quotient is the ratio of concentrations of products to the concentrations of reactants raised to the power of their respective coefficients at any stage after the start of the reaction.
 - For the reaction, $aA + bB \rightleftharpoons mM + nN$ the expression for the reaction quotient is:
- $$Q = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$
- When $Q < K$, then the reaction will proceed in the forward direction and more products will be formed till the equilibrium is reached.
 - When $Q > K$, then the reaction will proceed in the reverse direction and more reactants will be formed till the equilibrium is reached.
 - When $Q = K$, then the reaction has reached equilibrium.
 - Le Chatelier's principle gives the effect of any one or more of temperature, pressure or concentration on equilibrium.
 - For exothermic reactions the yield of products is increased by performing the reaction at lower temperatures.

- For endothermic reactions the yield of products is increased by performing the reaction at higher temperatures.
- When $\Delta n > 0$ the decrease in pressure favors the formation of products.
- When $\Delta n < 0$ the increase in pressure favors the formation of product
- Removing the products from the reaction vessel shifts the reaction in the forward direction.

REVIEW EXERCISE

Part I: Multiple Choice Type Questions

Choose the correct answer from the given alternatives

1. Which of the following is correct about a reaction at equilibrium?
 - a. The concentrations of reactants and products are equal.
 - b. The system is static in nature.
 - c. The forward and backward rates are equal.
 - d. None.
2. For a reaction to shift towards the product direction, which of the following conditions holds true?
 - a. $Q_c = K_c = 0$
 - b. $Q_c < K_c$
 - c. $Q_c > K_c$
 - d. $Q_c = K_c$
3. Given the equation $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$, the expression for K_c is:
 - a. $\frac{2[CO]}{[2[C][O]]}$
 - b. $\frac{[CO]^2}{[C]^2 [O]}$
 - c. $\frac{[CO]^2}{[O^2]}$
 - d. $\frac{2[CO]}{[O^2]}$
4. In which of the following cases does the reaction go fastest towards completion:
 - a. $K = 10^3$
 - b. $K = 10^{-2}$
 - c. $K = 10$
 - d. $K = 1$
5. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 atm and 4.0 atm, respectively, at equilibrium. What is the value of K_p for this reaction?
 - a. 0.5 atm
 - b. 4.0 atm
 - c. 8.0 atm
 - d. 32.0 atm
6. The equilibrium partial pressures of SO_2 , O_2 and SO_3 are 0.1 atm, 0.25 atm and 0.5 atm respectively. The equilibrium constant for the reaction
$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$$
is:
 - a. 0.1
 - b. 10
 - c. 0.05
 - d. 20
7. Which of the following is likely to happen when pressure is applied to the following system at equilibrium: $H_2O(s) \rightleftharpoons H_2O(l)$
 - a. More water will be formed
 - b. More ice will be formed
 - c. Water will evaporate
 - d. No change occur
8. The equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is

K_1 and for the reaction $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ is K_2 . The relation between K_1 and K_2 is:

- a. $K_1 = K_2$
- b. $K_1 = 1/K_2$
- c. $K_1 = -K_2$
- d. $K_1 = (K_2)^{0.5}$

9. What will happen when CaO is added to the following reaction at equilibrium?



- a. No change occurs.
- b. Reaction shifts in the forward direction
- c. More CaCO_3 is formed
- d. Total pressure increases

10. Under what conditions are K_p and K_c equal?

- a. $\Delta n = 1$
- b. $\Delta n = 0$
- c. $\Delta n = -1$
- d. They can never be equal

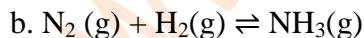
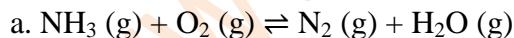
Part II . Answer the following Question

11. For the reaction at equilibrium: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

$\Delta H = -196 \text{ kJ/mol}$. Predict the direction of the change on:

- a. Removal of SO_2
- b. Addition of noble gas (argon) at constant pressure
- c. Decreasing volume of the system
- d. Increasing temperature of the system
- e. Addition of a catalyst

12. Balance the following equations and write the equilibrium constant expressions, in terms of K_C and K_P .



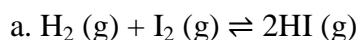
13. For the reaction at 200°C : $2\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons 3\text{C}(\text{g})$ the equilibrium constant is 3.0. Given the following information,

Species	Concentration
[A]	2.0M
[B]	3.0M
[C]	2.0M

predict the direction in which the reaction should proceed to reach equilibrium.

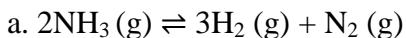
14. Given the reaction: $2\text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g}) + \text{O}_2(\text{g})$ what is the concentration of CO in equilibrium at 25 °C in a sample of gas originally containing 1.00 mol L⁻¹ of CO₂? For the dissociation of CO₂ at 25 °C, K_C = 2.96×10^{-92} .

15. Hydrogen and iodine react according to the equation:



Suppose 1.00 mol H₂ and 2.00 mol I₂ are placed in a 1.00 L vessel. How many moles of substances are in the gaseous mixture when it comes to equilibrium at 458 °C? The equilibrium constant K_c at this temperature is 49.

16. 5.0 moles of ammonia were introduced into a 5.0 L reaction chamber in which it partially decomposed at high temperatures;



b. At equilibrium at a particular temperature, 80.0% of the ammonia had reacted. Calculate K_c for the reaction.

17. 1.25 mol NOCl was placed in a 2.50 L reaction chamber at 427 °C. After equilibrium was reached, 1.10 moles of NOCl remained. Calculate the equilibrium constant K_c for the reaction.

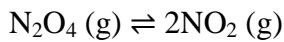


18. A sample of nitrosyl bromide was heated to 100°C in a 10.0 L container in order to partially decompose it.



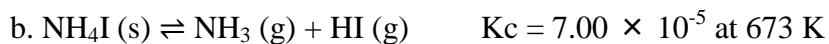
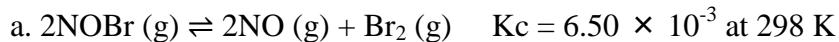
At equilibrium the container was found to contain 0.0585 mole of NOBr, 0.105 mole of NO, and 0.0524 mole of Br₂. Calculate the value of K_c.

19. The brown gas NO₂ and the colorless gas N₂O₄ exist in equilibrium.



0.625 mole N₂O₄ was introduced into a 5.00 L vessel and was allowed to decompose until it reached equilibrium with NO₂. The concentration of N₂O₄ at equilibrium was 0.0750 M. Calculate K_C for the reaction.

20. Calculate K_P for the following reactions at the indicated temperature.



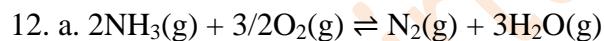
Answer to Review Questions and Problems

Part I: Multiple Choice Type Questions

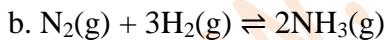
1. C 2. B 3. C 4. A 5. C 6. A 7. D 8. B 9. C 10. B

Part II: Answer the following Questions

11. a. removal of SO₂ shifts the equilibrium to the left direction
 b. addition of noble gas (argon) at constant pressure does not affect the equilibrium.
 c. decreasing the volume of the system shifts the equilibrium to the right direction.
 d. increasing the temperature of the system shifts the equilibrium to the left direction. addition of a catalyst has no effect on the equilibrium.



$$K_C = \frac{[N_2][H_2O]^3}{[NH_3]^2[O_2]^{3/2}} \quad \text{or} \quad K_P = \frac{(PN_2)(PH_2O)^3}{[PNH_3]^2[PO_2]^{3/2}}$$



$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \text{or} \quad K_P = \frac{(PNH_3)^2}{[PN_2][PH_2]^3}$$



$$K_C = (P_{CO_2}) \quad \text{or} \quad K_P = (P_{CO_2})$$

13. QC = 0.67; QC (0.67) < KC (3.0), hence, the reaction should proceed to the right to reach equilibrium.



15. The equilibrium composition is 0.07 mol H₂, 1.07 mol I₂, and 1.86 mol HI.

16. KC = 0.58

17. KC = 1.96×10^{-3}

18. KC = 0.90

19. KC = 0.13

20. a. KP = 0.159 b. KP = 0.213

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UNIT 6

SOME IMPORTANT OXYGEN CONTAINING ORGANIC COMPOUNDS

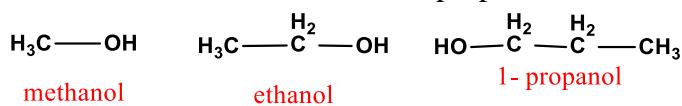
6.1 INTRODUCTION

Classification of organic compounds

- The oxygenated hydrocarbons include alcohols, ethers, aldehydes, ketones, carboxylic acids and esters.
- Alcohols occur widely in nature and have many industrial and pharmaceutical applications. Methanol, for example, is one of the most important of all industrial chemicals.
- Ethers are relatively resistant to chemical transformation and are often used as solvents in chemical reactions.
- Aldehydes and ketones contain a carbonyl group that consists of a carbon–oxygen double bond ($\text{C}=\text{O}$).
- Many compounds found in nature have aldehyde or ketone functional groups. Aldehydes have pungent odors, whereas ketones tend to smell sweet.
- Carboxylic acids and esters are present in many fruits and flowers.
- Many carboxylic acids are used as food additives in jams, jellies, candies and pickles, etc.

6.2 Alcohols and Ethers

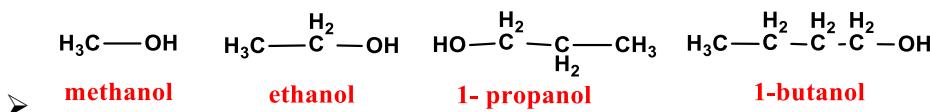
- Alcohols are derivatives of hydrocarbons in which one or more of the hydrogen atoms in the hydrocarbon have been replaced by a **hydroxyl group** ($-\text{OH}$).
- The functional group in an alcohol is an **$-\text{OH}$ (hydroxyl) group**, which is responsible for imparting certain chemical and/or physical properties to the compound.
- In alcohols, the hydroxyl group is directly attached to carbon atom(s) of an aliphatic system.
- Most people think of two common alcohols: the substance that intoxicates people, and the one used in clinics and hospitals. However, there are many types of alcohol.
- The only alcohol present in all alcoholic beverages is called **ethanol**.
- Other alcohols are used for different purposes.



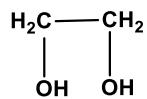
6.2.1 Classification of Alcohols

- Alcohols may be classified as mono-, di-, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl ($-OH$) groups respectively in their structures.

i. **Monohydric alcohols** are alcohols containing only one hydroxyl group.

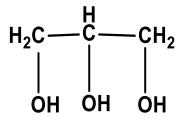


ii. **Dihydric alcohols** are those containing two hydroxyl groups per molecule. They are also named glycols or diols.



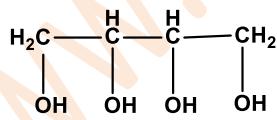
ethane-1,2-diol (Ethylene glycol)

iii. **Tri-hydric alcohols** are those containing three hydroxyl groups in their molecular structure



propane-1,2,3-triol (Glycerine or glycerol)

iv. **Polyhydric alcohols** are those alcohols containing three or more hydroxyl groups in their molecular structure.



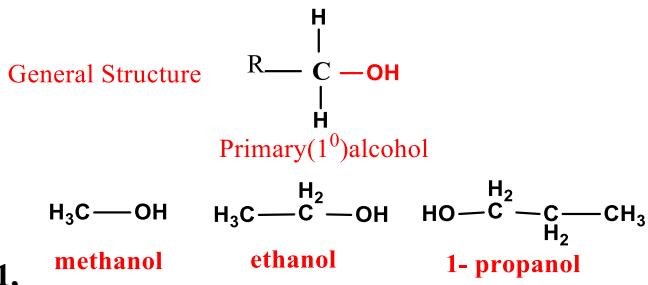
butane-1,2,3,4-tetraol

Classification of Monohydric Alcohols

- Monohydric alcohols may be further classified according to the carbon atom to which the hydroxyl group is attached.

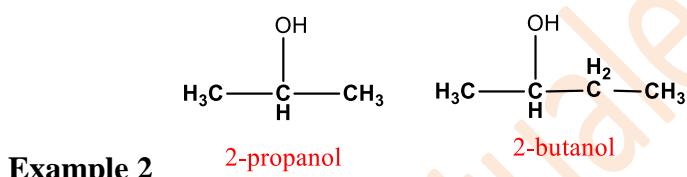
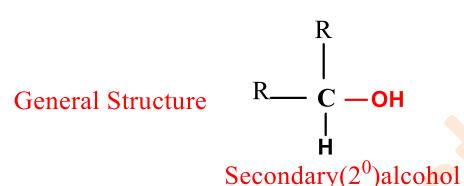
Primary alcohols

- In a primary alcohol, the carbon with the hydroxyl group is only attached to one alkyl group.



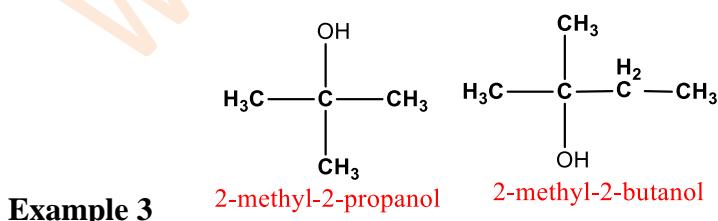
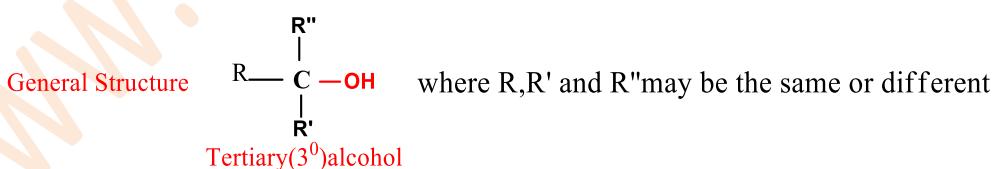
Example 1, Secondary alcohols

- In a secondary alcohol, the carbon with the hydroxyl group is attached to two alkyl groups.



Example 2 Tertiary alcohols

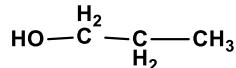
- In a tertiary alcohol, the carbon with the hydroxyl group is attached to three other alkyl groups.



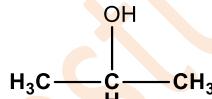
Example 3

6.2.2 Nomenclature of Alcohols

- The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it.
- In the IUPAC system, an alcohol is named by replacing the e of the corresponding alkane name with **ol**.
- $\text{CH}_3\text{-H}$ $\text{CH}_3\text{-OH}$ $\text{CH}_3\text{CH}_2\text{-H}$ $\text{CH}_3\text{CH}_2\text{-OH}$
Methane **Methanol (methyl alcohol)** **Ethane** **Ethanol (ethyl alcohol)**
- When an alcohol consists of a chain with three or more carbon atoms, the chain is numbered to give the position for the –OH group and any substituents on the chain.
- For this, the longest carbon chain (parent chain) is numbered starting at the end nearest to the hydroxyl group.
- The positions of the –OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached.

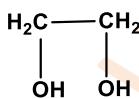


1-propanol (propyl alcohol)

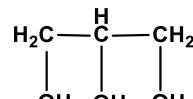


2-propanol(Isopropyl alcohol)

- For naming polyhydric alcohols, the '**e**' of alkane is retained and the ending '**ol**' is added.
- The number of –OH groups is indicated by adding the multiplicative prefix, *di*, *tri*, etc., before '**ol**'.



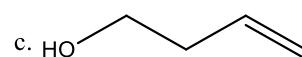
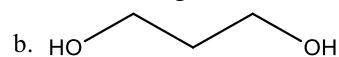
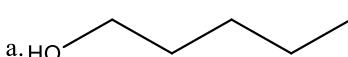
ethane-1,2-diol (Ethylene glycol)



propane-1,2,3-triol (Glycerine or glycerol)

Exercise 6.1

1. Give the general formula for the homologous series of monohydric alcohols.
2. Classify the following alcohols as monohydric, dihydric and trihydric alcohols.
 - a. 2-propanol
 - b. 1,3-propanediol
 - c. 1,2, 3-butanetriol
3. Classify the following monohydric alcohols as primary, secondary or tertiary alcohols.
 - a. 1-pentanol
 - b. 2-pentanol
 - c. 2-methyl-2-butanol
4. Give the IUPAC name for the following alcohols:



Answer to Exercise 6.1

1. $C_nH_{2n+1}OH$, where $n \geq 1$.
2. a. monohydric b. dihydric c. trihydric
3. a. primary b. secondary c. tertiary
4. 1-pentanol b. 1, 3-propanediol c. 3-buten-1-ol

6.2.3 Physical Properties of Alcohols

- The hydroxyl group in an alcohol is polar due to the high electronegativity of oxygen. As a result, there is significant hydrogen bonding in alcohols.

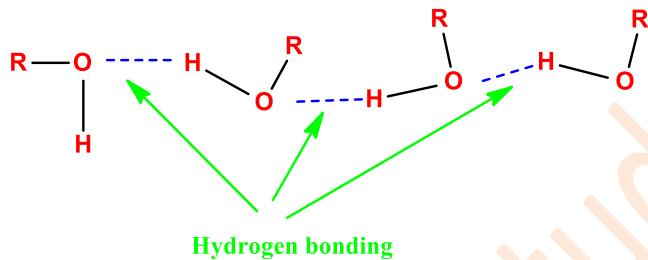


Figure 6.1 Hydrogen bonding between molecules of alcohols

- Due to the hydrogen bonding in alcohols, they have higher melting and boiling points than hydrocarbons of comparable molecular size (mass).
- Table 6.1 gives some physical constants of the first six monohydric alcohols. Hydrogen bonding is also the cause for even lower members to be liquids at room temperature.
- **Table 6.1:** IUPAC Names, Condensed Structure and Physical Constants of the First Six Monohydric Alcohol

Structure of monohydric alcohol	IUPAC name	Melting point (°C)	Boiling point (°C)	Density (g/mL)
CH_3OH	Methanol	-97	64.7	0.792
CH_3CH_2OH	Ethanol	-117	78.3	0.789
$CH_3CH_2CH_2OH$	1-Propanol	-126	97.2	0.804
$CH_3(CH_2)_2CH_2OH$	1-Butanol	-90	117.7	0.810
$CH_3(CH_2)_3CH_2OH$	1-Pentanol	-78.5	138	0.817
$CH_3(CH_2)_4CH_2OH$	1-Hexanol	-52	156.5	0.819

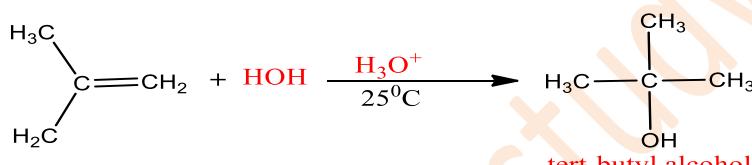
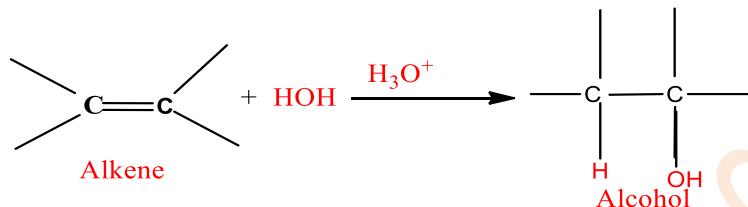
6.2.4 Preparation of Alcohols

The general laboratory methods of preparation of alcohols are:

A. Acid-catalyzed hydration of alkenes:

- Water is added to the double bond of an alkene in the presence of dilute acid such as H_2SO_4 or H_3PO_4 .

General Reaction:



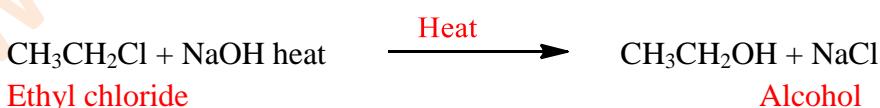
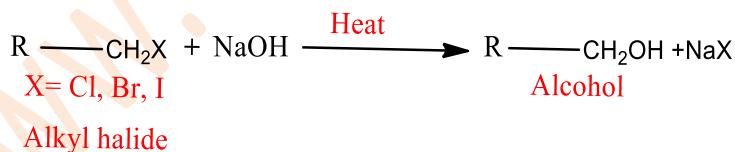
Example 4,

- Note that hydrogen of the water goes to the carbon of the alkene **that contains more hydrogen's.**

B. Hydrolysis of alkyl halides:

- Warming alkyl halides with sodium hydroxide forms alcohols.

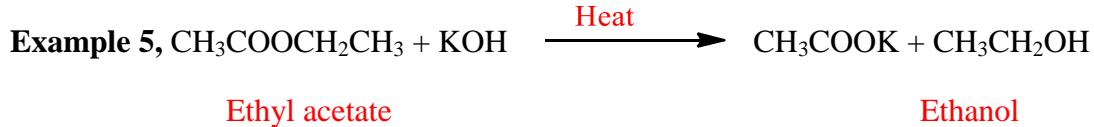
General Reaction:



C. Hydrolysis of Esters:

- Heating esters with potassium hydroxide produces alcohols.

General reaction:



- Methods **B** and **C** involve the replacement of other groups by the –OH group. Hence, they are examples of substitution reactions.

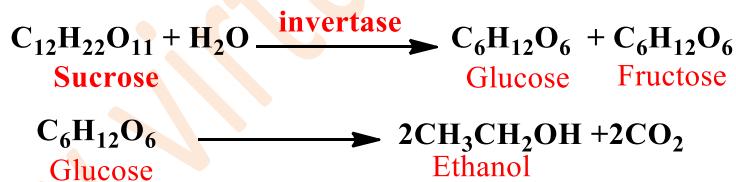
Ethanol (Ethyl Alcohol), $\text{CH}_3\text{CH}_2\text{OH}$

- Ethanol is the second member of the homologous series of monohydric alcohols.
- It is one of the constituents of all alcoholic beverages. ‘Tella’, ‘Tej’, Beer, Wine, ‘Katikalla’, Ouzo, Gin and Whisky contain ethanol.
- There are a number of methods for preparing ethanol using different materials.

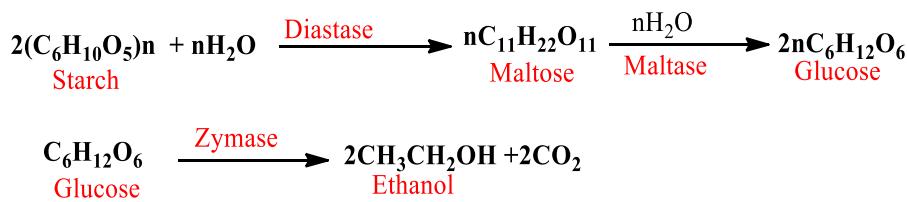
Industrial preparation of ethanol

Ethanol is manufactured industrially by:

1. Fermentation of carbohydrates such as sugar. Fermentation is the slow decomposition of carbohydrates such as sucrose, starch and cellulose in the presence of a suitable enzyme. It results in the formation of ethanol and carbon dioxide:

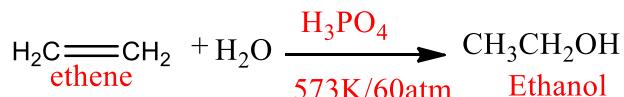


Fermentation can produce an alcoholic beverage whose ethanol content is 12- 15% only. Most liquor factories in Ethiopia use molasses, a by-product of sugar industries, as a raw material to produce ethanol. In the brewing industry, germinated barley called malt is used as the starting material. The whole process taking place in breweries is summarized as follows:



2. Catalytic Hydration of Ethene: Most ethanol is manufactured at present by this method.

In this process, ethene is treated with steam at 573 ° K and 60 atm pressures in the presence of phosphoric acid, H₃PO₄, catalyst.



6.2.5 Chemical Properties of Alcohols

- Reactions of alcohols may involve the cleavage of the oxygen–hydrogen bond (–O–H) or the carbon–oxygen bond (–C–O).

1. Reactions of alcohols involving cleavage of –O–H bond

a. Reaction with Active Metals

- Alcohols react with Li, Na, K, Mg, and other active metals to liberate hydrogen and to form metal alkoxides.
- General reaction:



Example 6



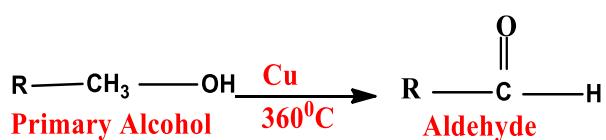
b. Oxidation of alcohols

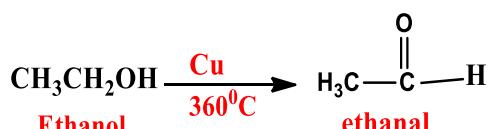
- The oxidation products of alcohols depend on the type of alcohol and the nature of oxidizing agents. Oxidation of alcohols is a very important method for the production of other oxygen-containing organic compounds, such as aldehydes, ketones and carboxylic acids.

i. Oxidation of primary alcohols

- Depending on the oxidizing agent used, a primary alcohol is oxidized to an aldehyde which in turn is oxidized to a carboxylic acid in the presence of mild oxidizing agents such as copper metal, primary alcohols yield aldehydes.

General reaction:

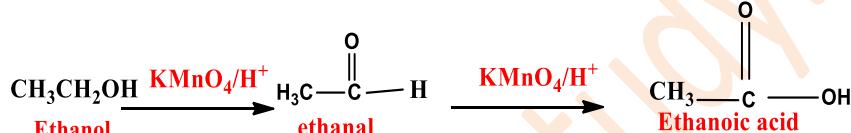
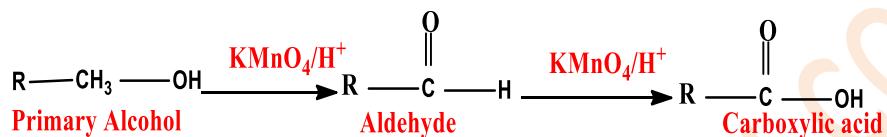




Example 7,

- Strong oxidizing agents, such as acidified KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ or CrO_3 in H_2SO_4 , oxidize primary alcohol first to aldehydes and then to carboxylic acids. It is difficult to stop the reaction at the aldehyde stage.

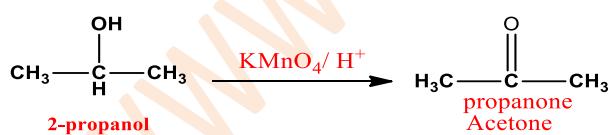
General reaction:



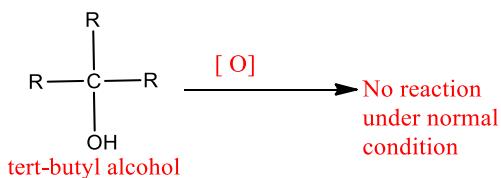
Example 8,

ii. Oxidation of secondary alcohols yields ketones

General reaction:



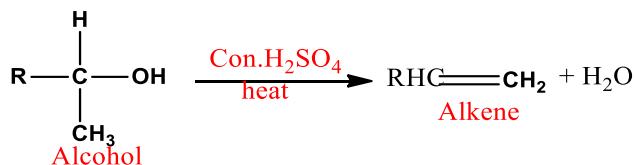
iii. Tertiary alcohols and ketones are generally resistant to oxidation



2. Reactions involving cleavage of carbon–oxygen (C – O) bond in alcohols

a. Dehydration of alcohols: Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with an acid such as concentrated H₂SO₄ or H₃PO₄ and heating.

General reaction:



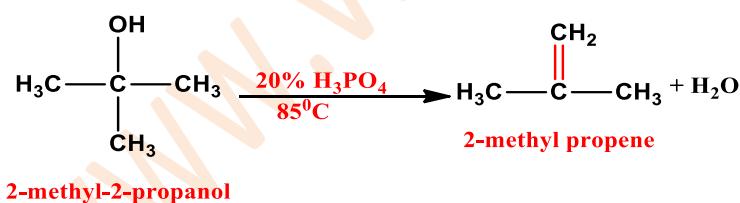
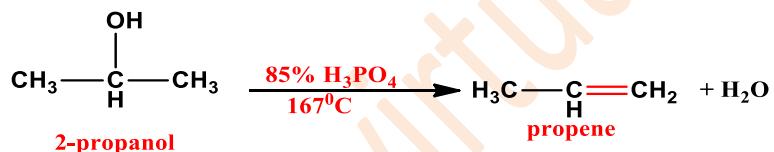
- In general, dehydration of primary alcohols is difficult and requires concentrated acid and high temperature.

Example 9



Secondary and tertiary alcohols dehydrate under milder conditions.

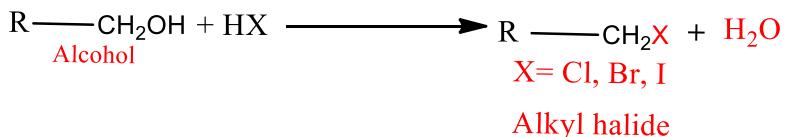
Example 10



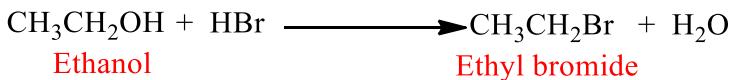
- Arrange primary, secondary, and tertiary alcohols in the degree of dehydration order.

b. Reactions of alcohols with hydrogen halides: Alcohols react with hydrogen halides to form alkyl halides.

General reaction:

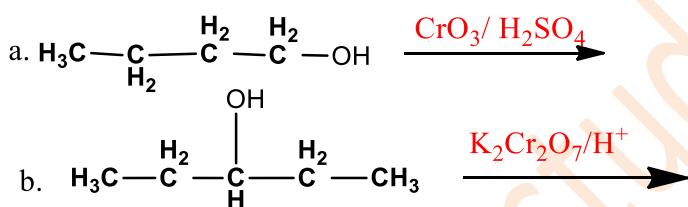


Example 11



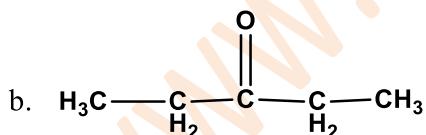
Exercise 6.2

- What is the functional group in alcohols?
- Classify the following alcohols as primary, secondary and tertiary alcohols:
 - 3-hexanol
 - 2-methyl-2-pentanol
 - 3-methyl-2-butanol
 - 1-heptanol
 - 2-methyl-1-propanol
 - 2,3-dimethyl-2-butanol
- Compare boiling points of alcohols and hydrocarbons of similar molecular mass. Explain if there is any difference.
- Complete the following chemical reactions in your exercise book:



Answers to Exercise 6.2

- The hydroxyl ($-\text{OH}$) group
- a. secondary b. tertiary c. secondary d. primary e. primary f. tertiary
- The boiling points of alcohols are higher than hydrocarbons of similar molecular weight because of the presence of strong intermolecular force, H-bonding in alcohols.
- a. $\text{CH}_3\text{CH}_2\text{COOH}$

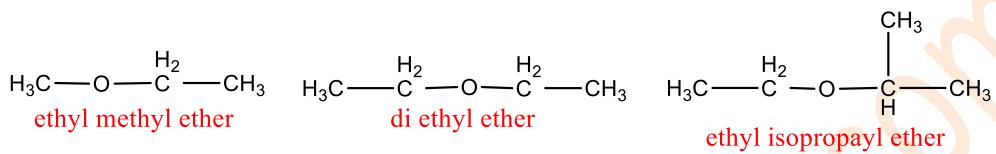


6.2.6 Structure and Nomenclature of Ethers

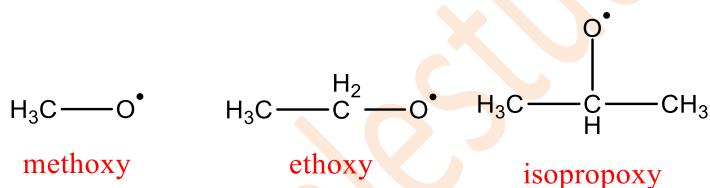
- Ethers are compounds in which an oxygen is bonded to two alkyl substituents ($\text{R}-\text{O}-\text{R}'$), where R and R' may be the same or different. If the alkyl substituents are identical, the ether is symmetrical ether. If the substituents are different, the ether is an unsymmetrical ether.



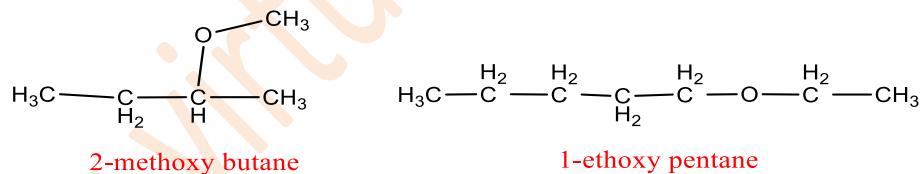
- The common name of an ether consists of the names of the two alkyl substituents (in alphabetical order), followed by the word “ether”.
- The smallest ethers are almost always named by their common names.
- **Example 12**



- The IUPAC system names ether as an alkane with an RO– substituent. The substituents are named by replacing the “yl” ending in the name of the alkyl substituent with “oxy”.

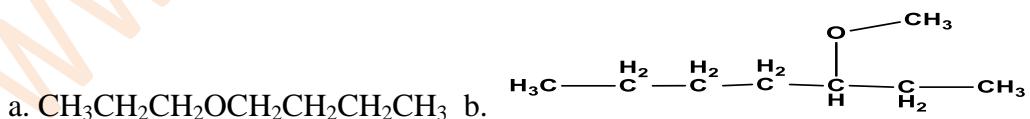


Example 13.



Exercise 6.3

1. Give the systematic (IUPAC) name for each of the following ethers:



Answers to Exercise 6.3

1. a. 1-propoxybutane b. 3-methoxyheptane
2. a. butylpropyl ether b. methyl (1-ethylpentyl) ether

6.2.7 Physical Properties of Ethers

- Ethers are polar compounds in which oxygen bears a partial negative charge and each carbon bonded to it bears a partial positive charge.
- The boiling points of ethers are much lower than those of alcohols of comparable molecular weight. For example, the boiling points of ethanol (78°C) is much higher than its constitutional isomer dimethyl ether (-24°C). The difference in boiling points between these two compounds is due to the polar O–H group in the alcohol, which is capable of forming intermolecular hydrogen bonds with water (figure 6.2) and are more soluble in water than are hydrocarbons of comparable molecular weight and shape.

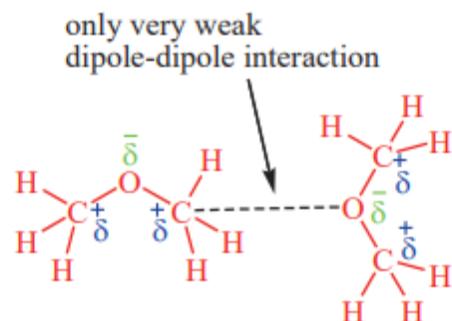
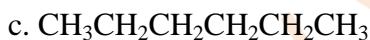
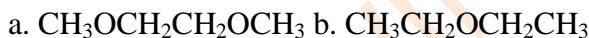


Figure 6.2, hydrogen bond between water and ethers

Exercise 6.4

1. Arrange these compounds in order of increasing solubility in water:



2. Arrange these compounds in order of increasing boiling point:



3. Write the condensed structures of both isomers with the formula $\text{C}_2\text{H}_6\text{O}$. Label the functional group of each isomer.

Answers to Exercise 6.4

1. a > b > c

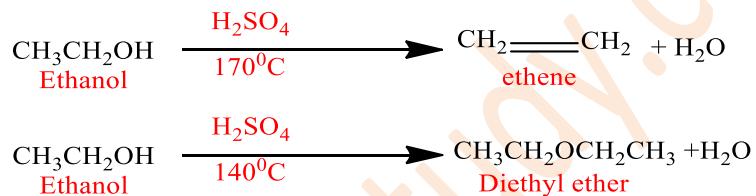
2. b > c > a

3. $\text{CH}_3\text{-O-CH}_3$ (Ether) and $\text{CH}_3\text{CH}_2\text{OH}$ (Alcohol)

6.2.8 Preparation of Ethers

1. Dehydration of alcohols

- Alcohol undergoes dehydration in the presence of protic acids (sulphuric acid, phosphoric acid) to produce alkenes and ethers under different conditions. For example, ethanol is dehydrated to ethene at 170°C in the presence of sulphuric acid.
- On the other hand, ethanol yields ethoxy-ethane in the presence of sulphuric acid at 140°C . The method is limited to use with primary alcohols.

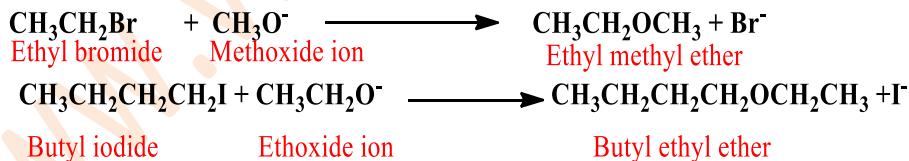


2. Williamson ether synthesis

In this method, an alkyl halide is made to react with an alkoxide which leads to the formation of ether.



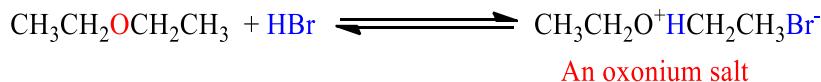
Example 14



6.2.9 Reactions of Ethers

- Ethers, $\text{R}-\text{O}-\text{R}$, resemble hydrocarbons in their resistance to chemical reaction.
- They do not react with oxidizing agents, such as $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 .
- Ethers are not affected by bases, however, they can react with proton donors to form oxonium salts.

Example 15



Heating dialkyl ethers with very strong acids (HI, HBr, and H₂SO₄) cleaves the ether linkage:



Ethers are not affected by most reagents at moderate temperatures. Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out many organic reactions.

Exercise 6.5

1. What are the common uses of ethers in medicine and industry?
2. Outline how the alkoxide ion is prepared for the Williamson ether synthesis using a chemical equation.

Answer to Exercise 6.5

1. Ethers are not affected by most reagents at moderate temperatures. Because of their good solvent properties and general inertness to chemical reaction, ethers are excellent solvents in which to carry out many organic reactions. Diethyl ether is used as an aesthetic in hospitals. Anesthetics help in making people go to sleep or become unconscious during surgery. The discovery of ether allowed physicians to use more refined techniques of surgery and medications.
2. The alkoxide ion for the Williamson ether synthesis is prepared by using sodium metal or sodium hydride (NaH) to remove a proton from an alcohol.

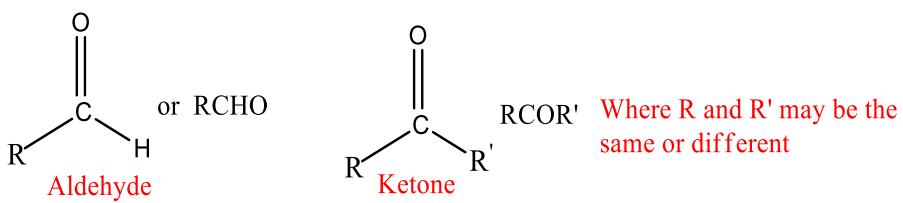


Example:



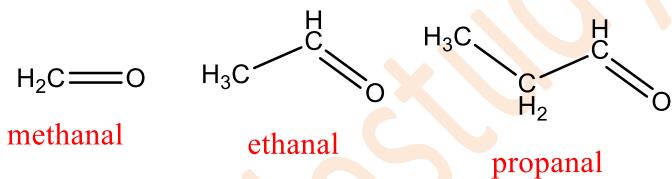
6.3 Aldehydes and Ketones

- The functional group of an aldehyde is a carbonyl group (C=O) bonded to a hydrogen atom.
 - In methanal (formaldehyde), the carbonyl group is bonded to two hydrogen atoms.
 - In other aldehydes, it is bonded to one hydrogen atom and one carbon atom.
- The functional group of a ketone is a carbonyl group bonded to two carbon atoms.

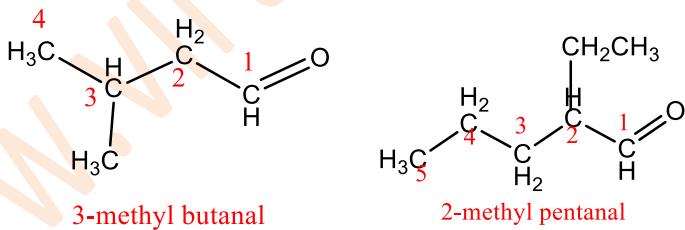


6.3.1 Nomenclature

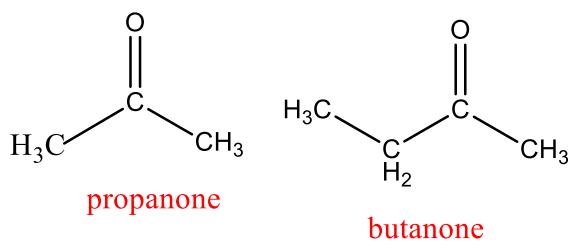
- The IUPAC system of nomenclature for aldehydes and ketones follows the familiar pattern of selecting the longest chain of carbon atoms that contains the functional group as the parent alkane.
- Aldehydes are named by changing the suffix **-e** of the parent alkane to **-al**. The suffix “**-al**” indicates the functional group **-CHO**.



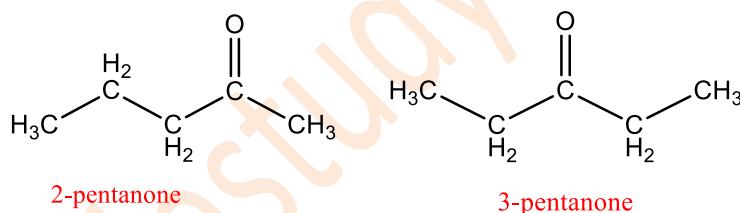
Because the carbonyl group of an aldehyde can appear only at the end of a parent chain and numbering must start with that group as carbon-1, its position is unambiguous; there is no need to use a number to locate it.



- The functional group of a ketone is a carbonyl group bonded to two carbon atoms.
- The IUPAC names of ketones are obtained by using the suffix **-one** to replace the terminal **-e** in the corresponding alkane name.
- The suffix ‘**-one**’ indicates the functional group **$\text{-RCOR}'$** .

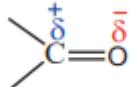


Unlike aldehydes, the position of the functional group must be indicated in the name of higher ketones. To do so, the longest chain containing the functional group is chosen as a parent structure and then the carbon atoms of the chain are numbered starting from the end closer to the carbonyl group.



6.3.2 Physical Properties Of Aldehydes and Ketones

- Oxygen is more electronegative than carbon; therefore, a carbon–oxygen double bond is polar, with oxygen bearing a partial negative charge and carbon bearing a partial positive charge:



Polarity of a carbonyl group

- Because of the polarity of the carbonyl group, aldehydes and ketones are polar compounds and interact in the liquid state by dipole–dipole interactions.
- As a result, aldehydes and ketones have higher boiling points than those of non-polar compounds with comparable molecular weight.
- For example, butanal and butanone both have a molecular mass (MM) of 72. The boiling point of butanal is 76 °C and of butanone is 80 °C , which is much higher than the boiling points of diethyl ether (MM) 74, 34 °C and pentane (MM) 72, 36 °C .
- Because the carbonyl groups of aldehydes and ketones interact with water molecules by hydrogen bonding, low-molecular-weight aldehydes and ketones are more soluble in water than are non-polar compounds of comparable molecular weight. **Table 6.2** lists the

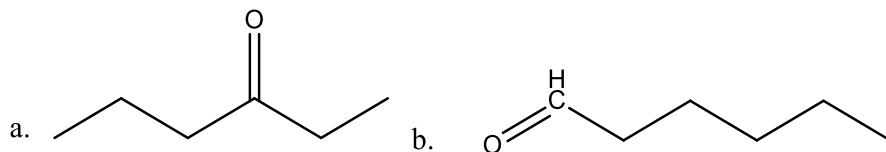
boiling points and solubility in water of several low-molecular-weight aldehydes and ketones.

Table 6.2: Physical properties of selected aldehydes and ketones

Name	Common Name	Structural Formula	Boiling Point (°C)	Solubility (g/100 g water)
Methanal	Formaldehyde	HCHO	-21	infinity
Ethanal	Acetaldehyde	CH ₃ CHO	20	infinity
Propanal	Propionaldehyde	CH ₃ CH ₂ CHO	49	16
Butanal	Butyraldehyde	CH ₃ CH ₂ CH ₂ CHO	76	7
Hexanal	Caproaldehyde	CH ₃ (CH ₂) ₄ CHO	129	slight
Propanone	Acetone	CH ₃ COCH ₃	56	infinity
2-Butanone	Methyl ethyl ketone	CH ₃ COCH ₂ CH ₃	80	26
3-pentanone	Diethyl ketone	CH ₃ CH ₂ COCH ₂ CH ₃	101	5

Exercise 6.6

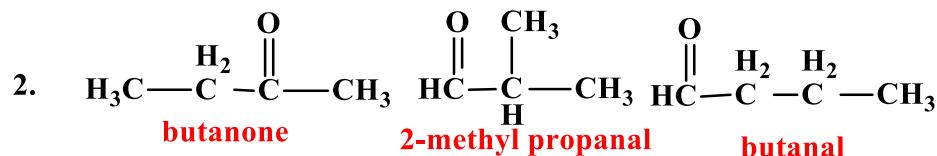
- Which of the following statements is false? Give your reason.
 - The carbonyl carbon in all aldehydes is bonded to a hydrogen and to an alkyl group.
 - Ketones are more soluble in water than alcohols of comparable molecular weight.
 - Any reaction that oxidizes an aldehyde to a carboxylic acid will also oxidize a ketone to a carboxylic acid.
- Draw a structural formula for the one ketone with molecular formula C₄H₈O and for the two aldehydes with molecular formula C₄H₈O.
- Draw structural formulas for these compounds:
 - 1-Chloro-2-propanone
 - 3-Hydroxybutanal
 - 4-Hydroxy-4-methyl-2-pentanone
- Give the IUPAC name of the following compounds:



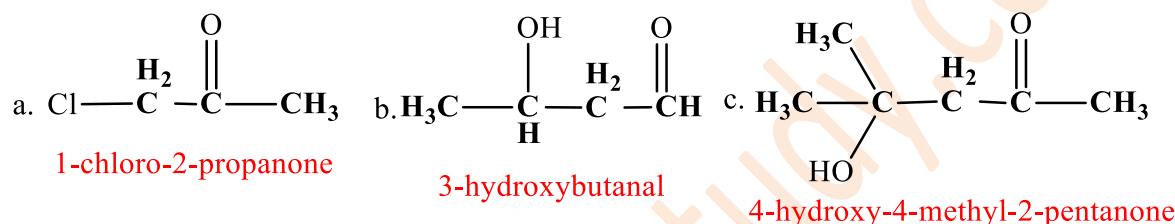
5. Formalin helps in the preservation of biological specimens. What is the main constituent of formalin?

Answers to Exercise 6.6

1. a. False b. False c. False



3.



4. a. hexan-3-one b. hexanal

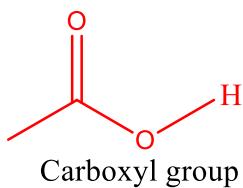
5. Formaldehyde (Ethanal)

6.4 Carboxylic Acids

6.4.1 Structure and Nomenclature of Carboxylic Acids

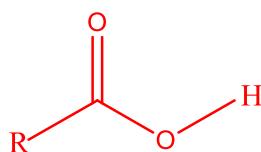
Structure of Carboxylic Acids

- Carboxylic acid is one of the class of organic compounds containing the **carbonyl functional group (C=O)**.
- A carboxyl group (COOH) is a functional group consisting of a **carbonyl group (C=O)** with a **hydroxyl group (O-H)** attached to the same carbon atom. It is usually written as –COOH or –CO₂H.



A. Saturated monocarboxylic acids

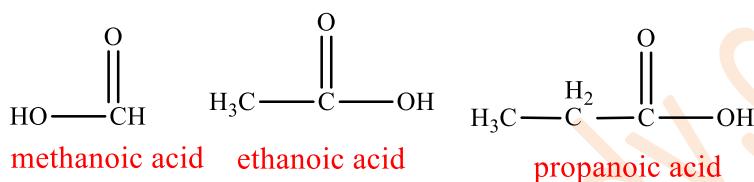
- The general formula for saturated monocarboxylic acids can be written as:



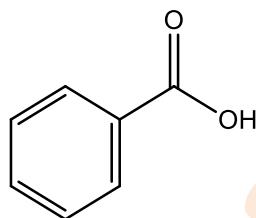
- Where R is either hydrogen or an alkyl group for aliphatic carboxylic acids. When R is phenyl (aryl) group, the structure represents aromatic carboxylic acids.

Example

1. The structure of the first three saturated monocarboxylic acids are written as follows:



2. The simplest aromatic acid is benzoic acid



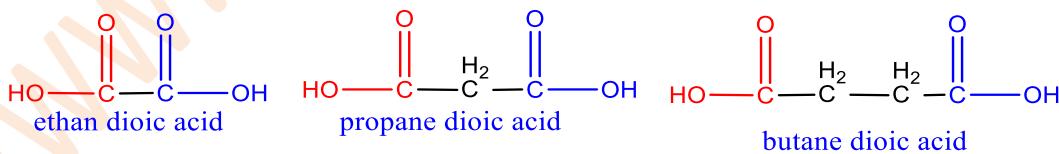
Benzoic acid (Benzene carboxylic acid)

B. Di- and tricarboxylic acids

- Carboxylic acids containing two carboxyl groups in their structure are called dicarboxylic acids.

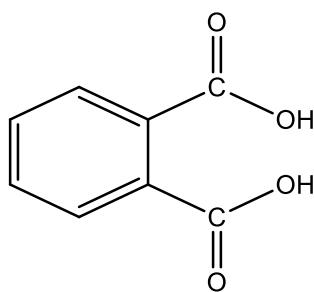
Example

1. The structure of the first three saturated dicarboxylic acids are shown below:



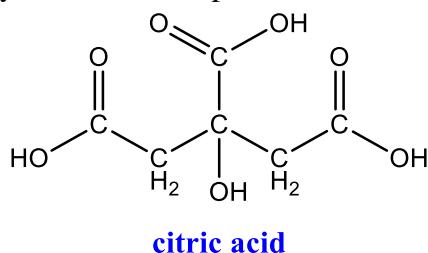
2. The simplest aromatic dicarboxylic acid occurs in three isomeric forms.

One of these is phthalic acid; its structure and IUPAC name are shown below.



1,2-Benzene dicarboxylic acid (Phthalic acid)

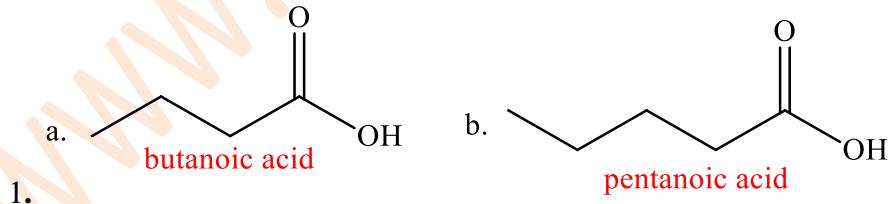
- Similarly, carboxylic acids that contain three carboxyl groups in their structure are called tricarboxylic acids. Example: citric acid is a typical tricarboxylic acid.

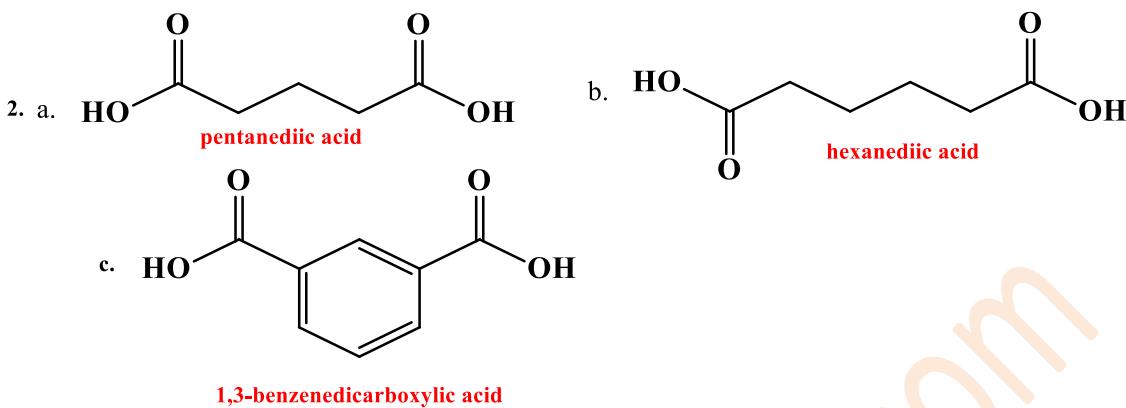


Exercise 6.7

1. Write the structure of the following monocarboxylic acids:
a. Butanoic acid b. Pentanoic acid
2. Write the structure of the following di-carboxylic acids:
a. Pentanedioic acid
b. Hexanedioic acid
c. 1,3-Benzenedicarboxylic acid
3. A great many carboxylic acids are encountered in nature. List some of them and their respective sources.

Answer to Exercise 6.7





3. A great many carboxylic acids are encountered in nature. List some of them and their respective sources.

- a. citric acid from lemons, orange,
- b. malic acid from bananas, apples,
- c. tartaric acid acids from avocados,
- d. citric and malic acids from salads, etc.

Nomenclature of Carboxylic Acids

i. Common names carboxylic acids

A. Straight chain monocarboxylic acids

- A large number of carboxylic acids have widely used common names which need to be learned.
- The common names of some basic carboxylic acids are derived from Latin names that indicate the first original natural source of the carboxylic acid.

Table 6.3 lists common names of some of the most important monocarboxylic acids.

Table 6.3: Common names of some monocarboxylic acids.

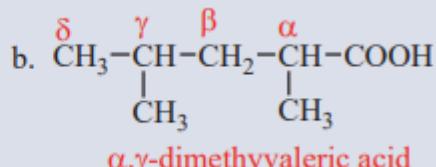
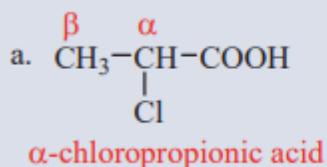
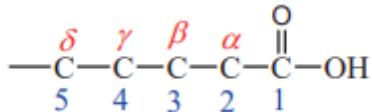
Structure of Acid	Natural Source	Common Name
HCOOH	Ants (Formica)	Formic acid
CH_3COOH	Vinegar (Acetum)	Acetic acid
$\text{CH}_3\text{CH}_2\text{COOH}$	Basic Fat (Propio)	Propionic acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	Rancid butter (Butyrum)	Butyric acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	Present in a Valerian herb	Valeric acid
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$	Goat (Caper)	Caproic acid

Note that the common name of carboxylic acids end with the suffix -ic acid.

B. Branched chain and substituted carboxylic acids

- In common naming system, the branched chain and substituted acids are named as derivatives of straight chain carboxylic acids. In this case, the

position of the side chain or substituents is indicated by Greek letters, α , β , γ , δ ... for designating the 1st, 2nd, 3rd,... position of carbon atoms as shown below:



Example

C. Dicarboxylic acids

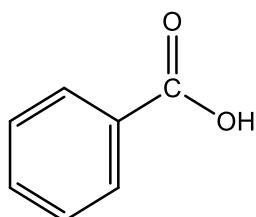
- Dicarboxylic acids also possess common names which are based on their sources.
-
- Table 6.4** lists common and IUPAC names of some of the most important dicarboxylic acids.

Table 6.4: Common and IUPAC names of some dicarboxylic acids.

Structure	Common Name	IUPAC Name
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC-CH₂-COOH	Malonic acid	Propanedioic acid
	Succinic acid	Butanedioic acid
HOOC-(CH₂)₃-COOH	Glutaric acid	Pentanedioic acid
HOOC-(CH₂)₄-COOH	Adipic acid	Hexanedioic acid
HOOC-(CH₂)₅-COOH	Pimelic acid	Heptanedioic acid

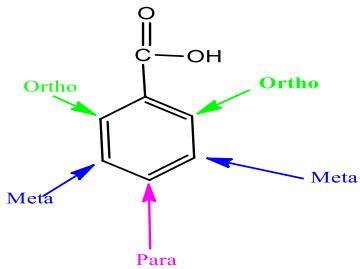
D. Aromatic carboxylic acids

- Aromatic carboxylic acids are compounds which have a carboxyl group directly attached to an aromatic ring. The common name of the simplest aromatic carboxylic acid is benzoic acid.

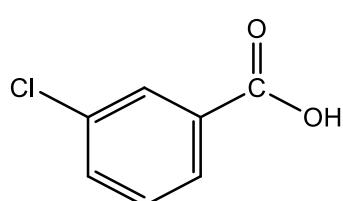


Benzoic acid

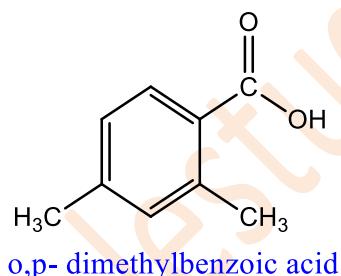
- In common naming system, the position of the substituent is indicated by the prefixes ortho (o-), meta (m-), para (p-) as it is shown in the structure below.



Example



m- chlorobenzoic acid



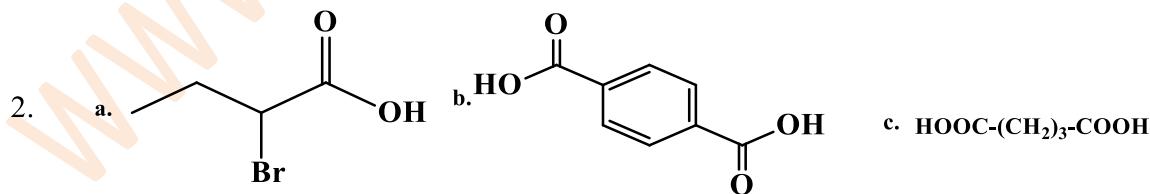
o,p- dimethylbenzoic acid

Exercise 6.8

1. Write the common names for the following carboxylic acids:
2. Write the structures of carboxylic acids for the given common names:

Answer to Exercise 6.8

1. a. γ -Bromo-Chlorovaleric acid b) Glutaric acid



ii. IUPAC names of carboxylic acids

A. Straight chain monocarboxylic acid

- In IPUAC system, monocarboxylic acids are named by replacing the terminal “-e” of the corresponding alkane name with “-oic acid.”
 - They are named as alkanoic acids
- Example

Write the IPUAC names for:



B. Branched chain and substituted monocarboxylic acids

- The IUPAC name of a branched carboxylic acid is derived from that of the longest carbon chain that contains the carboxyl group. The positions of the substitutes are indicated by Arabic numerals as 1, 2, 3.
- The numbering of the chain starts from the carboxyl carbon and it is always assigned C-1 position. Note that C-2 position in the IUPAC system corresponds to the α -position in the common naming system.



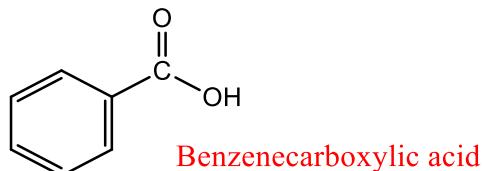
C. Dicarboxylic acids

- In the IUPAC system, dicarboxylic acids are named as alkanedioic acids. These names are obtained by replacing the suffix “-e” in the name of corresponding alkane by “-dioic acid”. **Table 6.4** above gives the common and IUPAC names of the first six dicarboxylic acids.

Example HOOC-(CH₂)₂-COOH (butandioic acid)

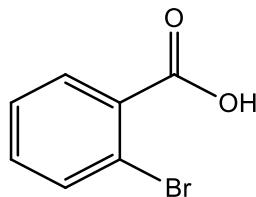
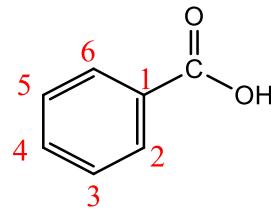
D. Aromatic carboxylic acids

- IUPAC name of the simplest aromatic carboxylic acid is benzenecarboxylic acids.



- Substituted aromatic acids with one carboxyl group are named as derivatives of benzenecarboxylic acids.

- The position of substituents is indicated using the Arabic numerals 2,3, etc according to their position on the benzene ring relative to the carboxyl group.
- The carbon on which the carboxyl group is attached is by convention C-1.

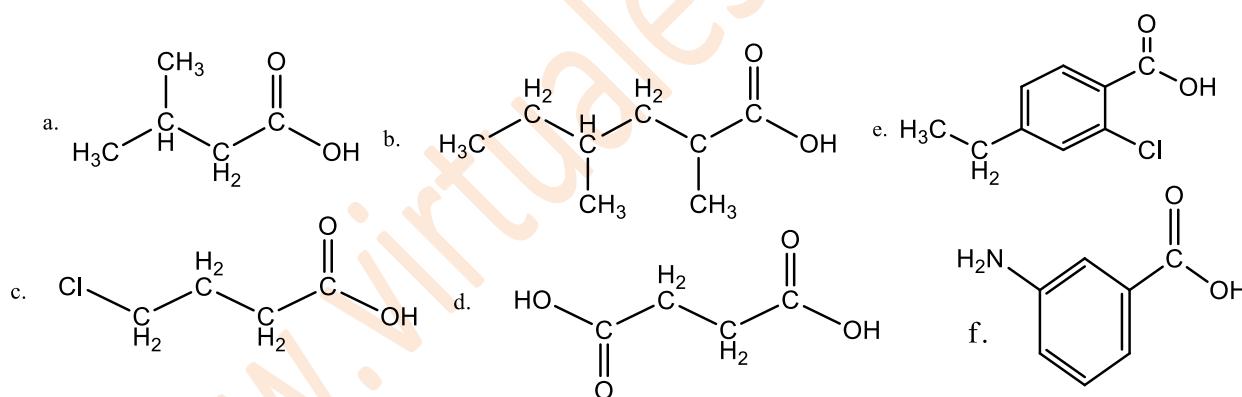


Example .

2-bromo benzenecarboxylic acid

Exercise 6.9

1. Write the IUPAC names for the following carboxylic acids:

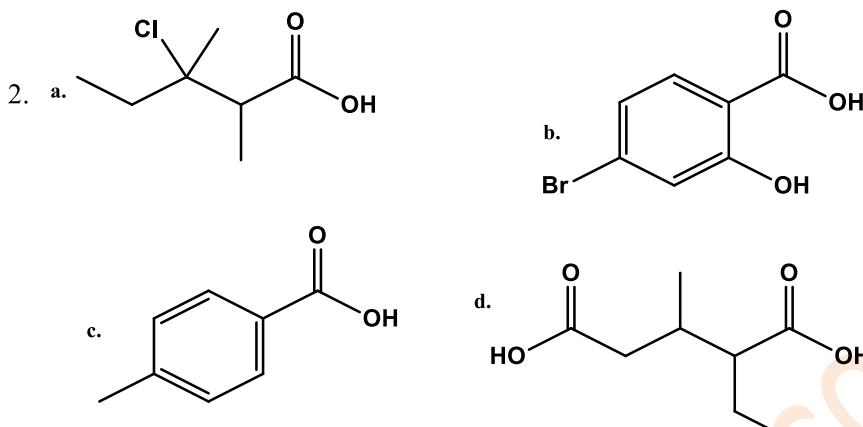


2. Draw the structures of the following carboxylic acids:

- a. 3-chloro-2,3-dimethylpentanoic acid
- b. 4-bromo-2-hydroxybenzoic acid
- c. *p*-Methylbenzoic acid
- d. 2-ethyl-3-methylpentanedioic acid.

Answer to Exercise 6.9

1. a. 2-methylbutanoic acid d. 4-hydroxybutanoic acid
- b. 2,4-dimethylhexanoic acid e. 2-chloro-5-ethylbenzoic acid
- c. 4-chlorobutanoic acid f. 3-aminobenzoic acid



6.4.2 Physical Properties of Carboxylic Acids

1. State

- The lower aliphatic acids containing up to 9 carbon atoms are liquids, whereas the higher members are colorless waxy solids. Benzoic acid and most of its derivatives are also colorless solids.

2.Odor

- The odors of the lower aliphatic acids progress from a sharp, irritating odor of methanoic acid and ethanoic acids to the distinctly unpleasant odor of the butanoic, pentanoic and hexanoic acids.

3.Melting and Boiling Points

- The melting points and boiling points of carboxylic acids are higher than those of hydrocarbons and oxygen-containing organic compounds of comparable size and shape and indicate strong intermolecular attractive forces. Figure 6.6 gives boiling point comparison of carboxylic acid with alkene, ketone, and alcohol.

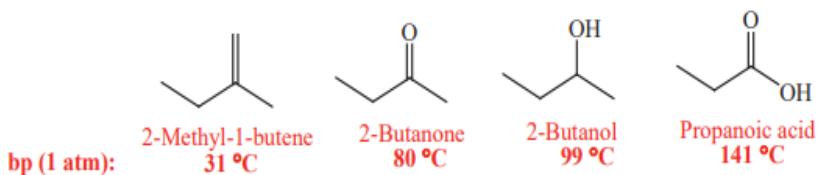


Figure 6.6: Boiling point comparison of carboxylic acid with alkene, ketone, and alcohol

- The hydroxyl group of one carboxylic acid molecule acts as a proton donor toward the carbonyl oxygen of a second. In a reciprocal fashion, the hydroxyl proton of the second carboxyl function interacts with the carbonyl oxygen of the first.

- The result is that the two carboxylic acid molecules are held together by two hydrogen bonds.

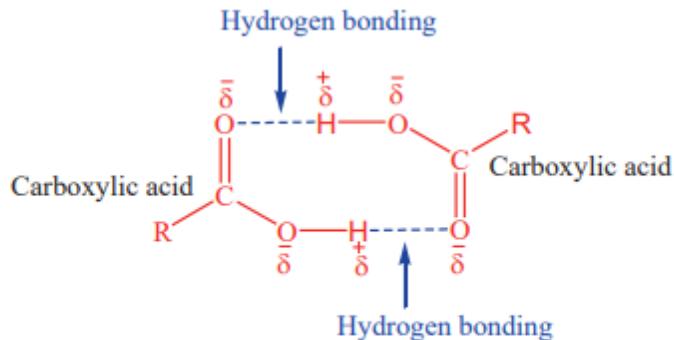


Figure 6.7: Carboxylic acid dimer

4.Solubility

- In aqueous solution intermolecular association between carboxylic acid molecules is replaced by hydrogen bonding to water. The solubility properties of carboxylic acids are similar to those of alcohols. Carboxylic acids of four carbon atoms or fewer are miscible with water in all proportions.

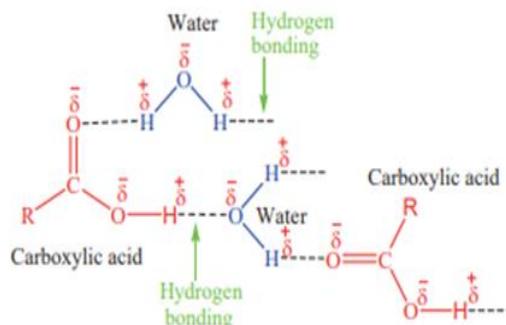


Figure 6.8: Formation of hydrogen bonding between carboxylic acids and water molecules

- The boiling points, melting points and solubility of some carboxylic acids are given in Table 6.5

Table 6.5: Physical constants of some carboxylic acids

Structure	IUPAC Name	Boiling point (°C)	Solubility (g/100 mL) H ₂ O at 25 °C
HCOOH	Methanoic acid	100.5	∞*
CH ₃ COOH	Ethanoic acid	118	∞*
CH ₃ CH ₂ COOH	Propanoic acid	141	∞*
CH ₃ (CH ₂) ₂ COOH	Butanoic acid	164	∞*
CH ₃ (CH ₂) ₃ COOH	Pentanoic acid	187	4.97
CH ₃ (CH ₂) ₄ COOH	Hexanoic acid	205	1.08

∞* means miscible in all proportions.

Exercise 6.10

- Arrange the following aliphatic carboxylic acids in the decreasing order of boiling point:
 a. butanoic acid c. octanoic acid
 b. decanoic acid d. propanoic acid
- Which of these aliphatic carboxylic acids has the lowest boiling point?
 a. pentanoic acid c. hexanoic acid
 b. methanoic acid d. propanoic acid
- Arrange the following compounds in increasing order of their boiling points:
 a. C₅H₁₂ c. C₄H₁₁OH
 b. C₂H₅COOH d. CH₃(CH₂)₄COOH

Answers to Exercise 6.10

- Decanoic acid > octanoic acid > butanoic acid > propanoic acid
- The aliphatic carboxylic acid, which has the lowest boiling point, is methanoic acid.

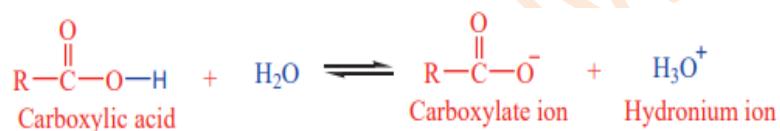


6.4.3 Chemical Properties of Carboxylic Acids

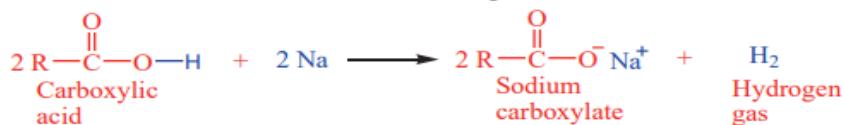
- The carboxylic acids show reactions due to the alkyl or aryl group and the carboxyl group.
- The carboxyl group is further considered to be made up of a carbonyl and a hydroxyl group. All these groups modify the properties of each other due to their interaction. Some of the common reactions of carboxylic acids are:

i. Reaction as an acid

- In aqueous solution, the cleavage of O–H bond occurs leading to the formation of carboxylate ion and hydronium ion. Carboxylic acids ionize partially and an equilibrium exists between the ionized and un-ionized forms.



- Carboxylic acids are weak acids and dissociates slightly. The following are examples of reactions of carboxylic acids as an acid
- a. **Reaction with metals:** Carboxylic acids react with active metals such as Na, K, Mg, Ca, etc. to give metal carboxylate salts, $\text{RCO}_2^- \text{M}^+$, and hydrogen gas.



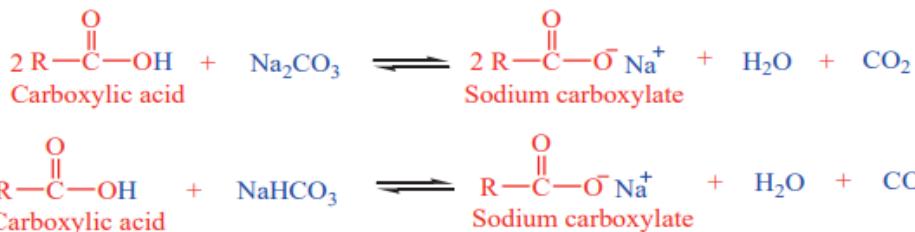
The salts of carboxylic acids are named by writing the name of the metal first, followed by the name of the acid replacing the ending -ic acid by -ate. For example, sodium reacts with ethanoic acid to form sodium ethanoate and hydrogen.



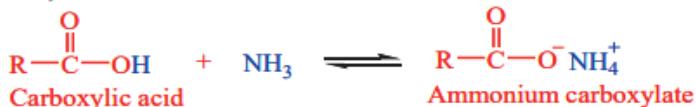
- b. **Reaction with Bases:** Carboxylic acids react with strong bases like sodium hydroxide or potassium hydroxide to form the corresponding metal carboxylate salts and water.



- Reaction with a base is a simple neutralization reaction. Carboxylic acids react with weak bases like carbonates or bicarbonates to form salt, water and carbon dioxide.

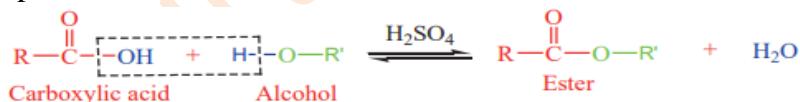


They also react with ammonia to form ammonium salts of carboxylic acids.



ii. Formation of Esters

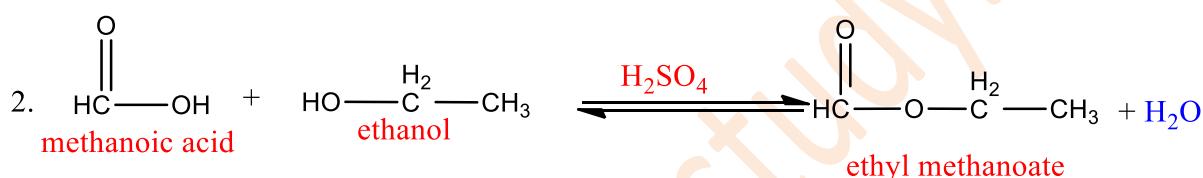
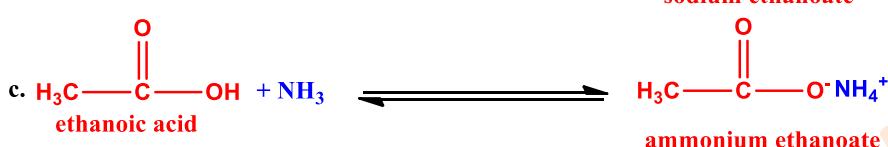
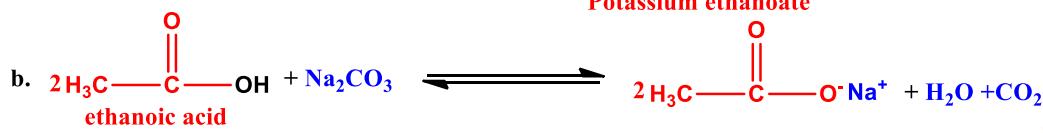
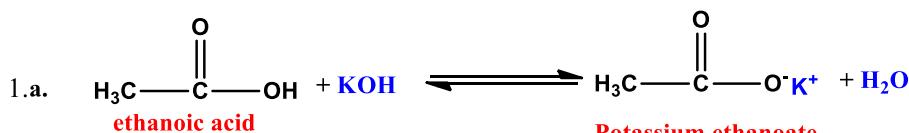
- One of the important reactions of carboxylic acids involves the replacement of –OH group by an alkoxy group to form esters as products. In this reaction, carboxylic acids are heated with alcohols in the presence of concentrated sulphuric acid. The reaction is called **esterification**.



Exercise 6.11

1. Write the chemical equations for the reaction between ethanoic acid and each of the following reagents and write the names of the products formed:
 - a. KOH b. Na₂CO₃ c. NH₃
2. Write the chemical equations for the reaction between methanoic acid and ethanol and write the name of the product.

Answers to Exercise 6.11

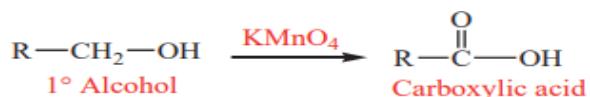


6.4.4 Preparation of Carboxylic Acids

One of the important methods for preparation of carboxylic acids is oxidation. Many saturated monocarboxylic acids are obtained by the oxidation of the corresponding primary alcohols, whereas aromatic acids are obtained from the corresponding alkyl benzenes.

i. Oxidation of Primary Alcohols

- The primary alcohols are readily oxidized to the corresponding carboxylic acids by their reaction with common oxidizing agents like $K_2Cr_2O_7$ or $KMnO_4$.



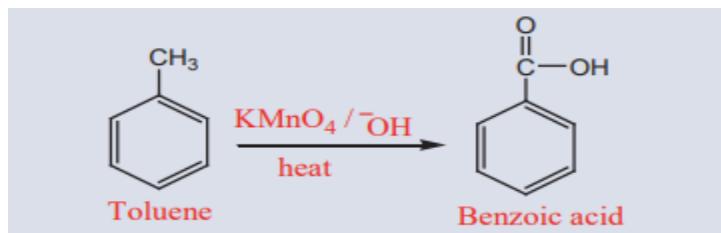
For example, oxidation of ethanol yields acetic acid (ethanoic acid).



ii. Oxidation of Alkyl benzenes

- Aromatic compounds containing alkyl group as substituent undergo oxidation to form aromatic acids. The reaction involves oxidation with KMnO_4 or K_2CrO_7 under vigorous conditions.

- The alkyl group is oxidized to carboxyl group irrespective of its size. For example, toluene and ethyl benzene, both give benzoic acid on refluxing with KMnO_4 in alkaline medium.



iii. Preparation of acetic acid (Ethanoic acid)

- Acetic acid is one of the important carboxylic acids which is used as food preservative. It can be prepared in laboratory by the oxidation of ethanol with potassium permanganate.
- Large quantities of acetic acid are obtained in industry from fermentation of ethanol.
- The process is known as Quick Vinegar Fermentation Process.
- In the process large wooden vats in figure 6. are used which have a perforated bottom.
- They are packed with wood shavings moistened with old vinegar.
- Ethanol solution is poured from the top and trickles down slowly to the perforated bottom.
- From the lower portion, air is pumped in the vat. The bacteria present in old vinegar, ferment the ethanol into acetic acid.
- The liquor obtained at the bottom is recirculated through the tower.
- The maximum concentration of acetic acid obtained by this process is about 10%, which can be fractionated to yield glacial acetic acid (anhydrous acetic acid).

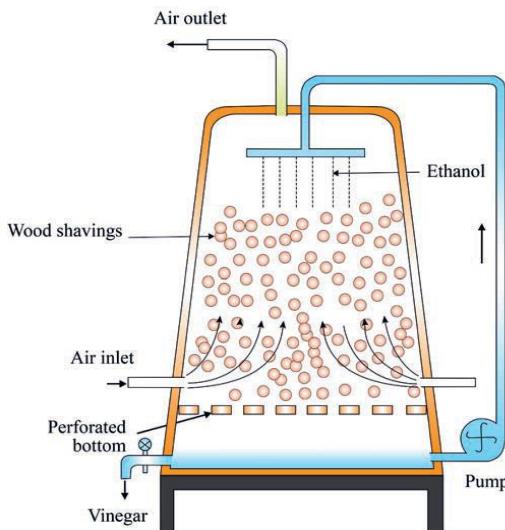


Figure 6.10 Industrial Preparation of Acetic Acid

6.4.5 Fatty Acids

- Fatty acids are carboxylic acids with long hydrocarbon chains. The fatty acids most frequently found in nature are shown in Table 6.6. Most naturally occurring fatty acids contain an even number of carbon atoms and are un-branched. Fatty acids can be classified as saturated or unsaturated.
- Double bonds in naturally occurring unsaturated fatty acids are never conjugated

Table 6.6: Some common naturally occurring fatty acids

Saturated			
12	Lauric acid	$\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	44
14	Myristic acid	$\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	58
16	Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	63
18	Stearic acid	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	69
20	Arachidic acid	$\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$	77
Unsaturated			
16	Palmitoleic acid	$\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	0
18	Oleic acid	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	13
18	Linoleic acid	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	-5
18	Linolenic acid	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	-11

- The physical properties of a fatty acid depend on the length of the hydrocarbon chain and the degree of unsaturation.
- The melting points of saturated fatty acids increase with increasing molecular weight because of increased van der Waals interactions between the molecules.
- The melting points of the unsaturated fatty acids decrease as the number of double bonds increases. For example, an 18-carbon fatty acid melts at 69 °C if it is saturated, at 13 °C if it has one double bond, at -5 °C if it has two double bonds, and at -11 °C if it has three double bonds (Table 6.6).

6.4.6 Uses of Carboxylic Acids

- Acetic acid is used as a solvent and as a starting material in the preparation of acetates, acetic anhydride, etc.
- It is also used to prepare the vinyl acetate polymer which is used in paints and adhesives.
- Vinegar contains about 8-10% acetic acid which is used in many food items.
- Perhaps one of the most important industrial applications of long chain carboxylic acid is for making soaps, detergents, and shampoos.

Exercise 6.12

1. Explain the difference in the melting points of the following fatty acids:
 - a. palmitic acid and stearic acid
 - b. palmitic acid and palmitoleic acid
 - c. oleic acid and linoleic acid
2. What are omega fatty acids? Give some examples of omega fatty acids.
3. What is the difference between omega-3-fatty acids and omega-6-fatty acids?
4. List some essential fatty acids. Why are they called ‘essential’?

Answers to Exercise 6.12

1.a. Stearic acid is a C18 fatty acid and palmitic acid is C16 fatty acid. Both are saturated fatty acids but stearic acid (C18) has more molecular weight than palmitic acid (C16) hence more melting point.

b. The presence of a cis-double bond significantly lowers the melting point of a compound. Thus, palmitoleic acid melts at lower temperature than palmitic acid.

c. The melting points of unsaturated fatty acids decreases with the increase in number of double bonds of comparable molecular weight. Linoleic acid has two double bonds whereas oleic acid has only one, so linoleic acid has a lower melting point.

2. “Omega-3” refers to the position of the final double bond in the chemical structure fatty acids, which is three carbon atoms from the “omega,” or tail end of the molecular chain. Omega-3 fatty acids are found in foods, such as fish and flaxseed, and in dietary supplements, such as fish oil.

3. ω -3 fatty acids (FAs) have in common a terminal carbon-carbon double bond in the omega three-position, the third bond from the methyl end of the acid, whereas, ω -6 acids have it in the omega six-position, the sixth bond from the methyl end of the fatty acid, respectively.

4. The term essential fatty acids (EFA) refers to those polyunsaturated fatty acids (PUFA) that must be provided by foods because these cannot be synthesized in the body yet are necessary for health. The human body is capable of producing all the fatty acids it needs, except for two: linoleic acid (LA) - an omega-6 fatty acid, and alpha-linolenic acid (ALA) - an omega-3 fatty acid. These have to be consumed from the diet and are termed “essential fatty acids”. Both of these fatty acids are needed for growth and repair but can also be used to make other fatty acids. For example, the omega-3 fatty acids, eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), can be synthesized from ALA. However, as conversion is limited, it is recommended that sources of these are also included in the diet. ALA and LA are found in plant and seed oils. Although the levels of LA are usually much higher than those of ALA, rapeseed oil and walnut oil are very good sources of the latter. EPA and DHA are found in oily fish (e.g., salmon, mackerel, herring).

6.5 Esters

6.5.1 Source of Esters

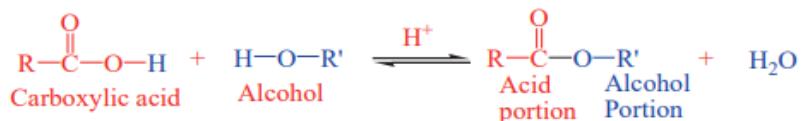
- Esters are among the most widely occurring compounds in nature. Many esters are pleasant smelling substances and are responsible for the flavor and fragrance of many fruits: for example, apples, pears, bananas, pineapples, strawberries, etc.
- Oils, fats and waxes of plants or animal origin are all esters. Many esters are found in flowers and form the part of essential oils obtained from flowers.

6.5.2 Nomenclature

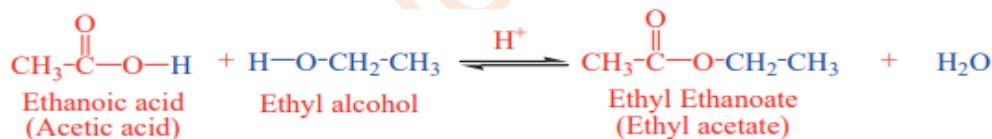
- Esters are derivatives of carboxylic acids in which the hydroxyl group (-OH) of a carboxylic acid is replaced by an alkoxy group (-OR).
- Esters can be formed by the reaction between acids and alcohols or phenols.
- In such cases, the hydroxyl group is replaced by an alkoxy group.
- Esters have the general formula **RCO₂R (or RCOOR')**, which can be represented by the general formula:

Where R = hydrogen, alkyl or an aryl group and R' = alkyl or an aryl group.

- Esters are named by the common system and IUPAC system. In both the cases, the name consists of two parts.
- The first part is named using the part from alcohol. The second part of the name is based on the acid. Therefore, we have to identify the parts coming from the alcohol and the carboxylic acid. The reaction below shows the part coming from the alcohol is attached to the oxygen as an alkyl group, and the acid part is attached to the oxygen through the carbonyl group.



The names of esters are derived from the names of the alcohol (with the ending -yl) and the acid (with the ending -ate or -oate). While writing their names the part of the name derived from the alcohol comes first. When we use the common name of carboxylic acid, the name of the ester is a common name, and when the IUPAC name of the acid is used, we get the IUPAC name for the ester. See the ester formed from ethyl alcohol and ethanoic acid:



The common name for this ester is ethyl acetate, and the IUPAC name is ethyl ethanoate. The formulas and names of some esters are listed in **Table 6.7**.

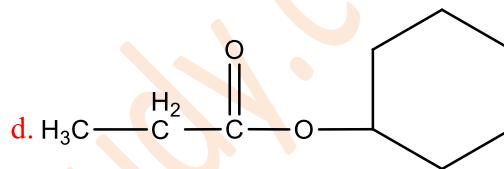
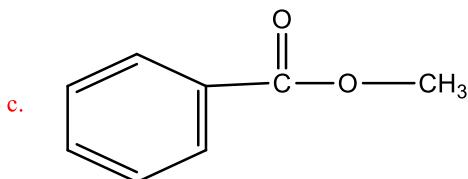
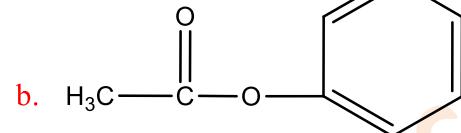
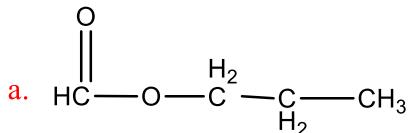
Table 6.7: Names and formulas of some common esters

Molecular Formula	Structure/Formula	Common Name	IUPAC Name
$\text{C}_2\text{O}_2\text{H}_4$	HCOOCH_3	Methyl formate	Methyl methanoate
$\text{C}_2\text{O}_2\text{H}_6$	$\text{CH}_3\text{COOCH}_3$	Methyl acetate	Methyl ethanoate
$\text{C}_2\text{O}_2\text{H}_6$	$\text{HCOOCH}_2\text{CH}_3$	Ethyl formate	Ethyl methanoate
$\text{C}_2\text{O}_2\text{H}_8$	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	Ethyl acetate	Ethyl ethanoate
$\text{C}_2\text{O}_2\text{H}_8$	$\text{HCOOCH}_2\text{CH}_2\text{CH}_3$	Propyl formate	Propyl methanoate
$\text{C}_2\text{O}_2\text{H}_{10}$	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$	Propyl acetate	Propyl ethanoate

Note that in the given **Table 6.7** molecular formulas can represent more than one structure. For example, methyl ethanoate and ethyl methanoate have the same molecular formula, $C_3O_2H_6$. Similarly, ethyl ethanoate and propyl methaoate have the same molecular formula ($C_4O_2H_8$).

Exercise 6.13

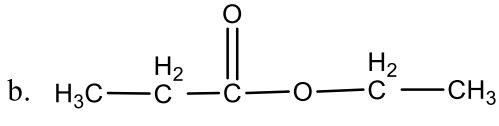
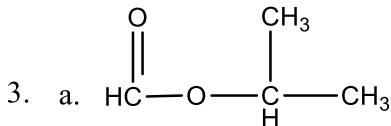
1. Name the following esters.



2. Identify the acid and alcohol (or phenol) portions of carboxylic esters give in question 1.
 3. Write the structure of the following esters:
 a. Isopropyl methanoate b. Ethyl propanoate

Answer to Exercise 6.13

1. a. propyl methanoate
 b. phenyl ethanoate
 c. methyl benzoate
 d. cyclohexyl propanoate
2. a. methanoic acid and n-propanol
 b. ethanoic acid and phenol
 c. benzoic acid and methanol
 d. propanoic acid and cyclohexanol



6.5.3 Physical Properties

i. Boiling points

- The boiling points of esters increase with increasing molecular mass. Branched chain esters have lower boiling points than their straight-chain isomers.
- Esters have lower boiling points than compounds of comparable molecular mass that are capable of forming hydrogen bonds such as carboxylic acids and alcohols.
- Ester molecules cannot form hydrogen bonds with each other.

ii. Solubility

- Esters of low molecular mass are fairly soluble in water. Esters have about the same solubility in water with that of the same molecular mass carboxylic acids. Because carboxylic esters can form hydrogen bonding with water, the solubility of esters in water decreases as their molecular mass increase.
- All esters are soluble in organic solvents.

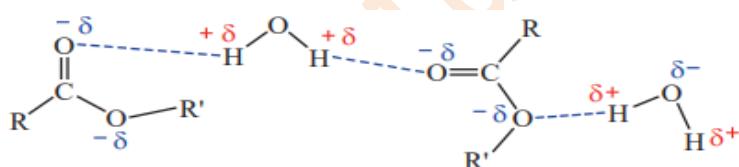


Figure 6.11: Hydrogen bonding between water and ester molecules

iii. Odor

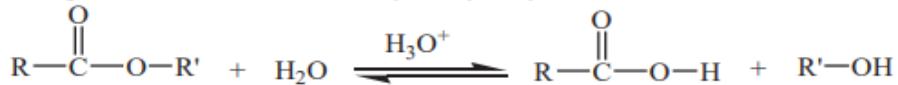
- In sharp contrast to the disagreeable odors of carboxylic acids, esters have pleasant odors. Many of the odors of fruits and flowers result from mixtures of carboxylic esters, and many of them are used in perfumes and food flavorings.

6.5.4 Chemical Properties

i. Hydrolysis

- The most important reaction of carboxylic esters is their hydrolysis, which may be catalyzed by either mineral acids or bases.
- The reaction yields the corresponding carboxylic acid and alcohol of the ester.

The general reaction for acid-catalyzed hydrolysis of esters can be written as:



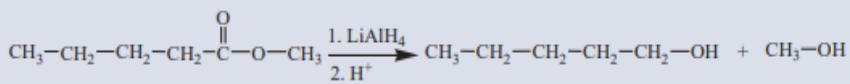
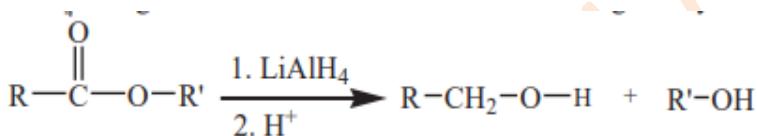
Example,



- In biological systems, many ester hydrolysis reactions take place, for example, in the digestion of fats. These reactions occur under very mild conditions, and in the presence of certain biological catalysts known as enzymes.

ii. Reduction

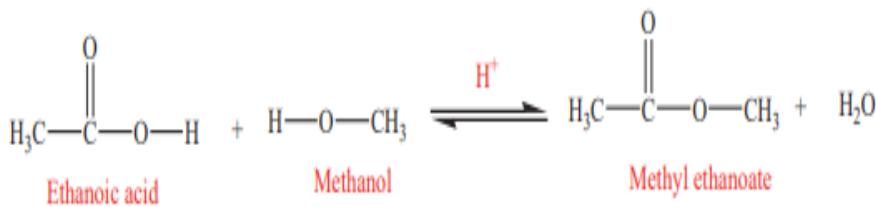
- Esters are reduced to primary alcohols by special reducing agents like lithium aluminum hydride, LiAlH₄.



Example ,

6.5.5. Preparations of Esters

- Esters can be synthesized by heating a mixture of a carboxylic acid and an alcohol in the presence of an acid (usually H₂SO₄) as catalyst. This reaction is called esterification and is a common method for the preparation of esters.
- In esterification, the -OH group from the carboxylic acid and the -H from the alcohol are removed and combine to form water molecule.



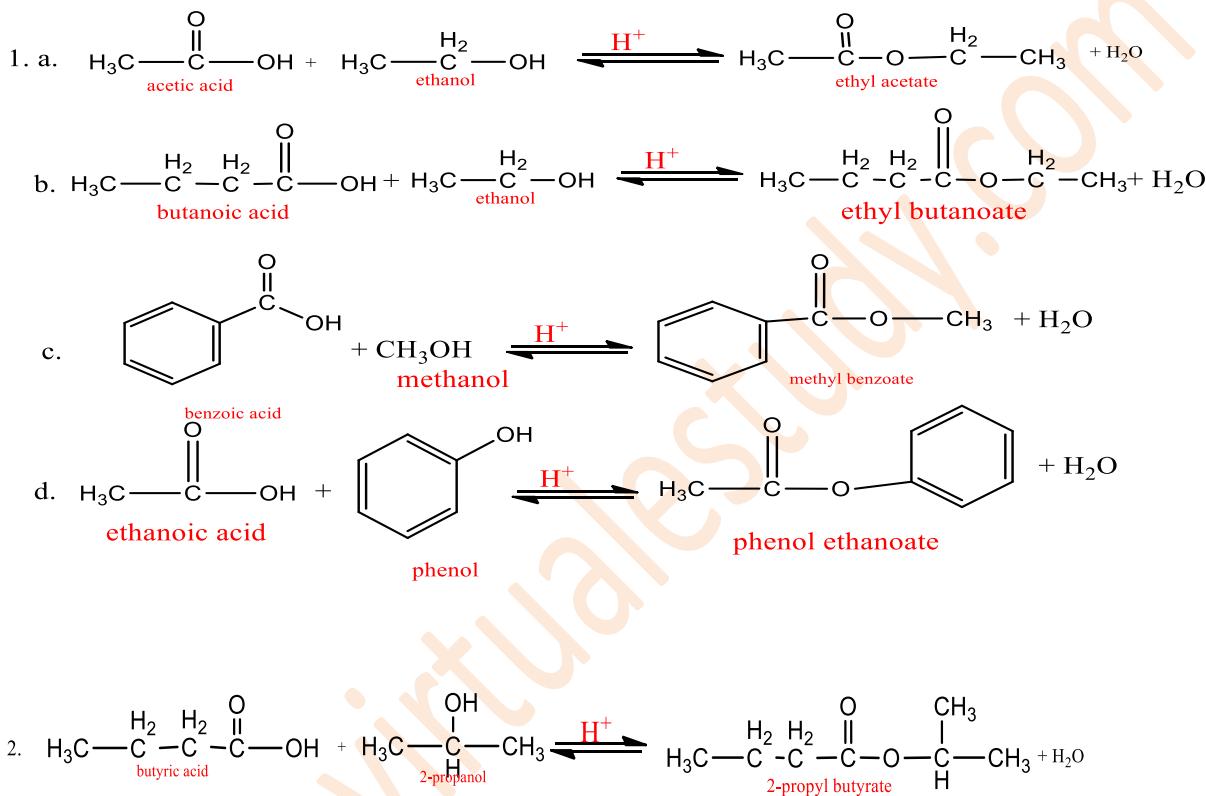
- In this condensation reaction, the hydroxyl group (-OH) from the acid and a hydrogen atom (-H) from the alcohol are eliminated in the form of water. In the same way, write the equation showing the preparation of acetylsalicylic acid, commonly known as aspirin from the salicylic acid and acetic acid.

Exercise 6.14

1. Write the reactions for the preparation of each of the following esters using appropriate acids and alcohols:

- a. ethyl acetate b. ethyl butanoate c. methyl benzoate d. phenyl ethanoate
 2. The esters formed from butyric acid are pleasant-smelling compounds found in fruits and used in perfumes. Draw the structural formula for the ester formed from the reaction of butyric acid with 2-propa nol.

Answer to Exercise 6.14



6.5.6 Uses of Esters

- Most simple esters are pleasant-smelling substances. They are responsible for the flavors and fragrances of most fruits.
- They are used in the manufacture of perfumes and as flavoring agents in the confectionery (cakes, candies, and ice cream) and soft drink industries.
- Esters of low molecular mass are non-toxic liquids and thus used as solvents.
- Esters are used as solvents for oils and fats, nail polishes, varnishes, paints, gums and resins; medicine (e.g. Aspirin); clothing, e.g. polyesters (Dacron); fragrance in perfumes; and plasticizers (e.g. octyl phthalate). Some common esters which are responsible for many pleasant fragrances in nature are presented in **Table 6.8**.

Table 6.8: Esters naturally available in fruits and responsible for their pleasant fragrances

Fruit	Formula	Ester present
Apple	$\text{C}_4\text{H}_9\text{COOC}_5\text{H}_{11}$	Isoamyl isovalerate
Pineapple	$\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$	Ethyl butyrate
Banana	$\text{CH}_3\text{COOC}_5\text{H}_{11}$	Isopentyl acetate
Orange	$\text{CH}_3\text{COOC}_8\text{H}_{17}$	Octyl acetate
Grape	$\text{C}_6\text{H}_4(\text{NH}_2)(\text{COOCH}_3)$	Methyl anthranilate
Pear	$\text{CH}_3\text{CO}_2(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$	Isopentyl acetate

6.6 Fats and Oils

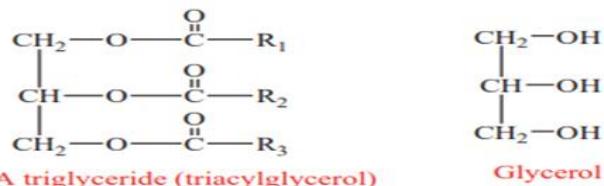
6.6.1 Sources of Fats and Oils

- Fats and oils are esters. They are triesters of glycerol which are collectively known as triglycerides or tri-acylglycerols.
- Glycerol contains three alcohol groups and therefore can form three ester groups.
- Fats and oils are widely found in nature especially in living things.
- They have long hydrocarbon tails which are derived from carboxylic acids, which make them hydrophobic.
- A triglyceride is called a fat if it is a solid or semi-solid at room temperature; it is called an oil if it is a liquid at that temperature.
- Triglycerides obtained from animals are usually solids, while those of plant origin are generally oils. Therefore, we commonly say animal fats and vegetable oils.
- Note that edible vegetable oils are entirely different from mineral oils such as petroleum.
- Mineral oils are long chain alkanes.

6.6.2 Structure of Fats and Oils

- Fats and oils are triesters.
- Variation in the structure of fats and oils occur in the fatty acid portion of the triglyceride (or triacylglycerol)

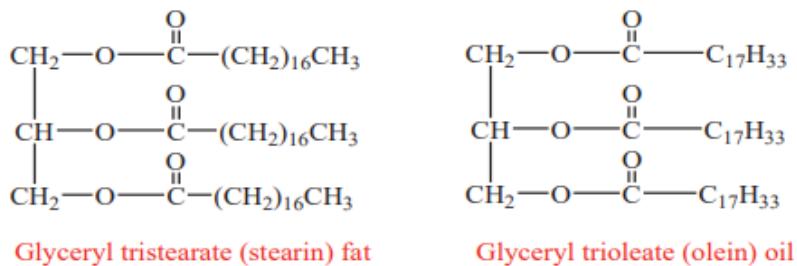
Fats and oils are represented by the following general structural formula:



Where R_1 , R_2 and R_3 may be the same or different hydrocarbon groups.

- Fats and oils are represented by the following general structural formula:
- Fats are esters of glycerol and mostly saturated fatty acids, whereas oils are liquid esters primarily derived from unsaturated fatty acids and glycerol. The acid part of fats and oils almost always contain an even number of carbon atoms.

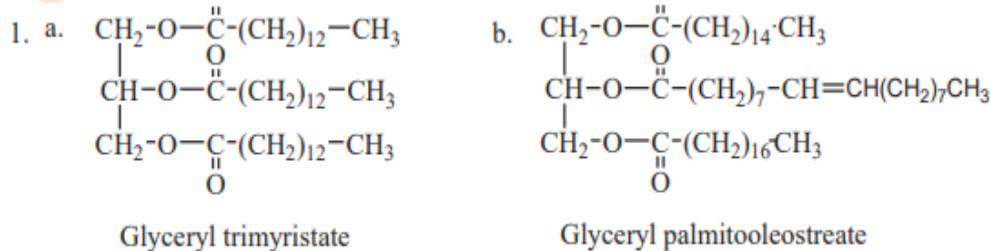
The structures of some common triglycerides are shown below:



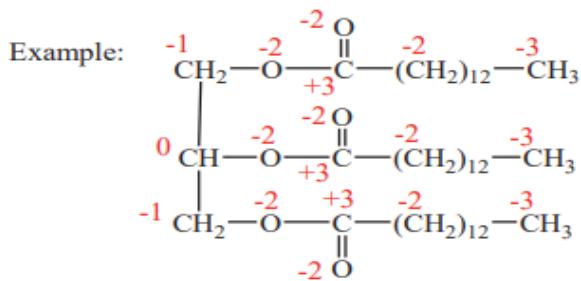
Exercise 6.15

1. Write the structure of the following compounds
 - a. Glyceryl trimyristate
 - b. Glyceryl palmitooleostrate
2. Calculate oxidation numbers of the various carbon atoms in both fats and oils and use oxidation number as an indicator of energy content; the lower the oxidation number the higher the energy content of the substance. Reference could also be made to the type of hybridization of the carbon atoms.

Answers to Exercise 6.15



2. Use the following steps to calculate the oxidation states of the various carbons in any fat and oil.
 - a. write the Lewis structure including lone-pair electrons
 - b. assign the electrons in a covalent bond between two atoms to the more electronegative partner
 - c. for a bond between two atoms of the same element, assign the electrons in the bond equally
 - d. count the number of electrons assigned to each atom and subtract that number from the number of valence electrons in the neutral atom; the result is the oxidation number.



6.6.3 Physical properties of fats and oils

- Fats and oils have common physical properties, including they are greasy to the touch, and have lubricating properties; they are not readily volatile; and may be burned without leaving any residue, that is, ash.
- Fats like butter, lard and tallow are solids at room temperature. On the other hand, oils which are mainly obtained from plants, e.g., corn oil, peanut oil, cotton seed oil, olive oil and soybean oil are liquids at room temperature.
- All oils and fats are colorless, odorless and neutral substances in their pure form.
- They are lighter than water and immiscible with it.
- They are soluble in organic solvents e.g. benzene, ether and chloroform etc.

6.6.4 Hardening of Oils

- Oils can be converted to fats by addition of hydrogen (hydrogenation) at high pressure in the presence of nickel or palladium as a catalyst.
- The process of converting oils to hard fats is known as hardening of oils.
- This reaction is used in the preparation of margarine.
- Hydrogenation of vegetable oils results in the formation of solid fat (eg. Sheno Lega) which is not different in composition from animal fat.

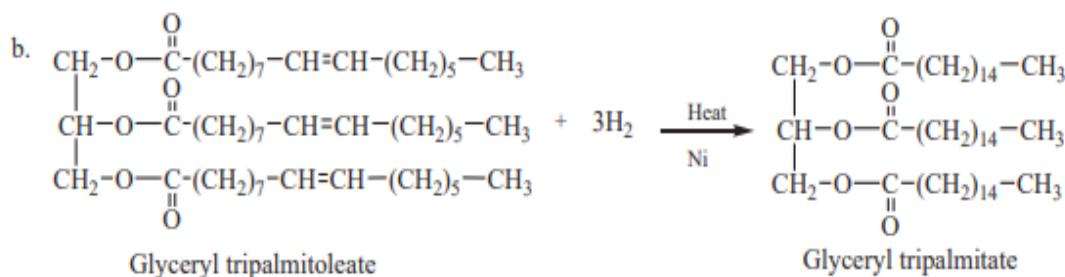
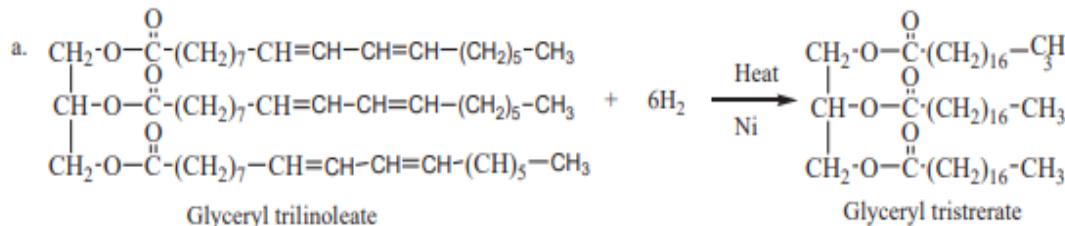
Exercise 6.16

Write the equation for the hydrogenation of:

- a. Glyceryl trilinoleate, and

b. Glyceryl tripalmitoleate

Answers to Exercise 6.16



- The various carbon atoms in fats and oils have different oxidation numbers, which are used as indicators of their energy contents.
- The lower the oxidation number the higher the energy content of the substance.
- In oils double bonded carbon atoms have sp^2 hybridization, while in fats all carbon atoms in the hydrocarbon tails have sp^3 hybridization.
- Vegetable oils differ from animal fats in possessing a higher degree of unsaturation, but could have double bonds.
- The number of fats also contain sites of unsaturation like vegetable oils. Unsaturation in fat tends to lower its melting point and thus tends to make it a liquid at room temperature.
- Saturated fat is found in many foods including:
 - Animal foods (like beef, chicken, lamb, pork, and veal)
 - Coconut, palm, and palm kernel oils
 - Dairy products (like butter, cheese, and whole milk) and lard.
- Unsaturated fats are found in two main types: mono or polyunsaturated fats (oils):
 - **Monounsaturated fats;** which can be found in avocados, nuts and seeds (like cashews, pecans, almonds, and peanuts), vegetable oils (like canola, olive, peanut, safflower, sesame, and sunflower).
 - **Polyunsaturated fat,** which can be found in fatty fish (like herring, mackerel, salmon, trout and smelt), fish oils, nuts and seeds (like cashews, pecans, almonds and peanuts), vegetable oils (like canola, corn, flaxseed, soybean and sunflower).

6.6.5 Rancidity

Fats and oils are quite reactive substances. When stored for any considerable length of time, especially when the temperature is high and the air has free access to them, they deteriorate and spoil. Among the various fats, spoilage takes the form of rancidity.

Fats and oils develop an unpleasant odor due to rancidity. It is caused mainly due to the hydrolysis of ester linkage and oxidation across the double bonds. In this respect, different fats differ markedly. Some spoil very much more rapidly than others.

The fat acquires a peculiarly disagreeable odor and flavor.

The rancidity of a given fat is not necessarily the result of long storage under unfavorable conditions. The fat may have been spoiled and rancid from the moment of its production. This will inevitably be true when the materials from which it was produced have undergone decomposition.

In other words, to obtain a sound and sweet fat, the raw material must be sound and sweet; it must be processed speedily before it gets time to decompose; and this must be done under clean and sanitary conditions.

The fat obtained must be stored under favorable conditions and its consumption should not be delayed.

UNIT SUMMARY

Alcohols are compounds containing the hydroxyl ($-OH$) group as their functional group and represented by the general formula $C_nH_{2n+1}OH$.

Alcohols are classified depending on the number of hydroxyl groups they contain as monohydric, dihydric and trihydric alcohols.

The names of alcohols contain the suffix ‘-ol’ which indicates the presence of $-OH$ group in the molecule.

Primary alcohols oxidize to give aldehydes and then carboxylic acids, and secondary alcohols yield ketones on oxidation.

The functional group of ether is an atom of oxygen bonded to two carbon atoms.

Ethers are used as solvents and in medicine as inhalation anesthetics.

Ethers are weakly polar compounds. Their boiling points are close to those of hydrocarbons with comparable molecular weight.

An aldehyde contains a carbonyl group bonded to a hydrogen atom and a carbon atom, whereas, a ketone contains a carbonyl group bonded to two carbons.

Aldehydes and ketones have higher boiling points and are more soluble in water than non-polar compounds of comparable molecular weight.

Carboxylic acids are compounds with a –COOH functional group.

Because of the –COOH functional group, carboxylic acids are polar compounds and can form hydrogen bonding with water and among themselves.

Esters are mildly polar compounds that are widely distributed in nature.

Fats are saturated fatty acids, whereas oils are unsaturated fatty acids.

The process of converting oils into hard fats is known as hardening of oils.

REVIEW EXERCISE

Part I: Multiple choice Type Questions

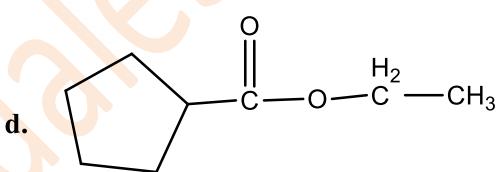
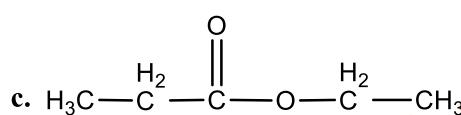
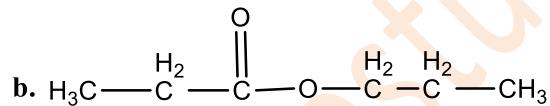
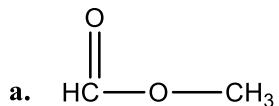
1. Which one is the least soluble in water?
a. methanol c. hexane
b. butanal d. hexanedioic acid
2. Which of the following compounds is ether?
a. $\text{CH}_3\text{CH}_2\text{COOCH}_3$ c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ d. $\text{CH}_3\text{CH}_2\text{OCH}_3$
3. The compounds CH_3OH and CH_3COOH react in the presence of an acid catalyst to form:
a. a carboxylic acid b. an aldehyde c. a ketone d. an ester
4. Alcohols that yield ketones on oxidation are classified as:
a. primary alcohols c. dihydric alcohols
b. secondary alcohols d. trihydric alcohols
5. What is the product of the reduction of 3-methyl-2-pentanone?
a. 3-methyl-2-pentanol c. 3-methyl-2-pentanal
b. 2-methyl-3-pentanol d. 3-methyl-2-pentene
6. Acetic acid is manufactured by the fermentation of:
a. ethanol b. methanol c. ethanal d. methanol
7. Fats and oils are:
a. acids b. alcohols c. esters d. hydrocarbons
8. Which pair of compounds can react to form a hemiacetal?
a. $\text{CH}_3\text{CH}_2\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{OH}$ c. CH_3COCH_3 and $\text{CH}_3\text{CH}_2\text{CHO}$
b. $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COOH d. CH_3COCH_3 and CH_3COOH

Part II: Answer the following questions:

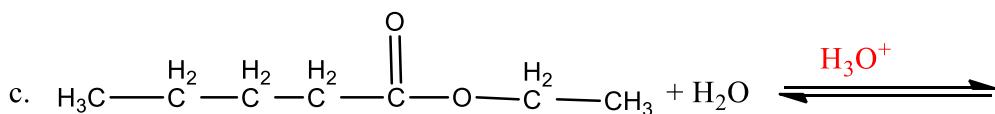
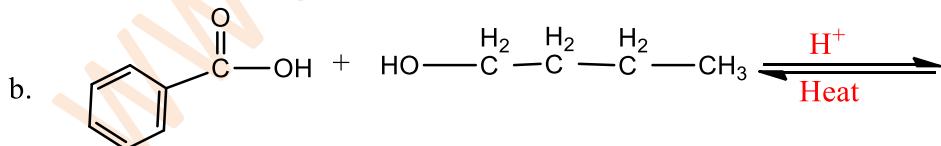
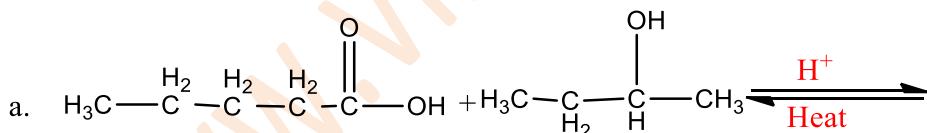
9. Why is there a large difference in the boiling points of butanal and 1-butanol?
10. Write a test to differentiate between 2-pentanone and pentanal.
11. Why are carboxylic acids more acidic than alcohols or phenols although all of them have hydrogen atom attached to an oxygen atom ($-\text{O}-\text{H}$)?
12. Draw the structural formula for the ester formed when each of the following reacts with methyl alcohol:

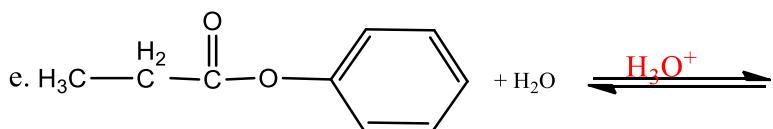
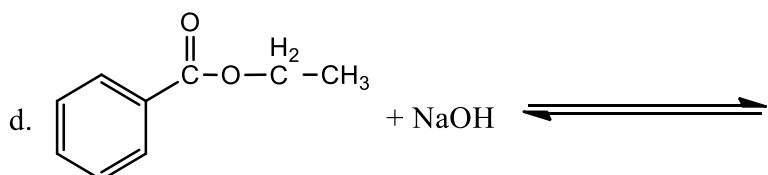
 - a. Acetic acid b. Benzoic acid c. formic acid d. Propionic acid

13. Give the IUPAC and common names, if any, for each of the following:



14. Draw the structural formula for each of the following reactions:





Answer to Review Exercise

Part I: Multiple choice Type Questions

1. C 2. D 3. D 4. B 5. A 6. A 7. C 8. A

Part II: Answer the following questions

9. Butan-1-ol contains an O-H group and hence undergoes intermolecular H-bonding. Therefore, its b.p. is much higher than that of butanal which does not contain an O-H group and hence does not undergo H-bonding.

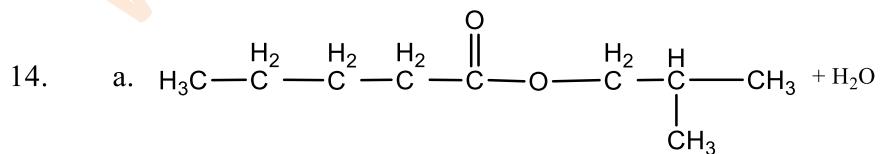
10. Pentanal and 2-pentanone can be distinguished by using Tollens' reagent. Pentanal is an aldehyde whereas 2-pentanone is ketone. Pentanal reacts with Tollens' reagent to give a silver mirror on glass surface.

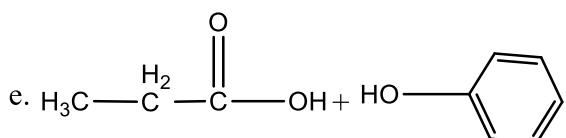
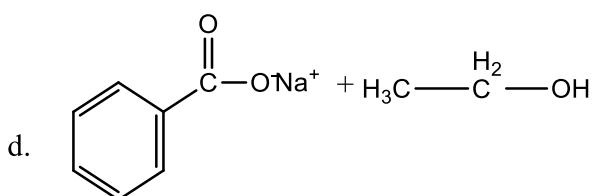
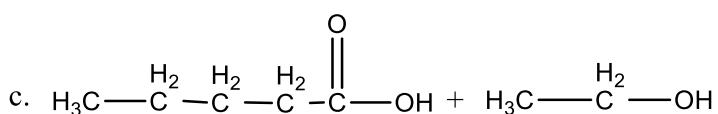
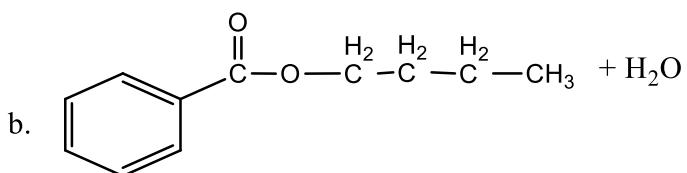
11. Carboxylic acids are more acidic than alcohols or phenols, although all of them have a hydrogen atom attached to an oxygen atom ($-\text{O}-\text{H}$) because the conjugate base of carboxylic acids or the carboxylate ion is stabilized by resonance. Thus, carboxylic acids can release proton easier than alcohols or phenols.

12. a. $\text{CH}_3\text{COOCH}_3$ b. $\text{C}_6\text{H}_5\text{COOCH}_3$ c. HCOOCH_3 d. $\text{CH}_3\text{CH}_2\text{COOCH}_3$

13. a. methyl methanoate b. propyl propanoate

c. ethyl propanoate d. ethyl cyclopentyl carboxylate





15. a. monounsaturated b. polyunsaturated c. Saturated